

Recent Advances in the Chemistry of Carborane Metal Complexes Incorporating d- and f-Block Elements

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I. Introduction

There is a large and growing field of transition metal cluster chemistry in which carborane ligands are involved. Several monographs and review articles that adequately cover the earlier work are available.¹⁻⁵ In a recent issue of *Chemical Reviews* Grimes discussed small clusters that contain carborane or organoboron ring ligands,^{3a} while Bregadze reviewed the chemistry of externally derivatized heterocarboranes in detail.^{3b} The latest developments in the general area of metallocarboranes have not been gathered into a single review article. Therefore, this review has a very different focus from the recently published articles and hence discusses the most promising research that has been published during the past 10 years or so on the d- and f-block metal complexes derived from various carborane ligand systems.

Carboranes constitute one of the most studied classes of polyhedral molecules with a variety of structural arrangements that are well understood and depicted using various electron counting rules.⁶ Most of the observed borane clusters can be grouped into three geometrically distinct classes: *closo*- $B_nH_n^{2-}$, *nido*- B_nH_{n+4} , and *arachno*- B_nH_{n+6} .⁷ The electron counting rules of Wade suggest that clusters with $(2n + 2)$ skeletal electrons adopt a *closo* structure, and those with $(2n + 4)$ and $(2n + 6)$ skeletal electrons possess *nido* and *arachno* geometries, respectively. Increasingly, however, exceptions to these rules are being observed. Therefore, these electron counting rules^{6,7} of Wade and Williams, although they predict accurate geometries of polyhedral boron hydrides, cannot be applied effectively in all cases of polyhedral complexes that incorporate heteroatoms.^{1,4}

Metallocarboranes are cluster compounds that incorporate metal atoms or units, and hydrides of carbon and boron in their polyhedral skeletons. A large number of metals have been incorporated as cluster vertices. Figure 1 shows the d- and f-block elements of the periodic table which have formed complexes with carborane ligands.

The chemistry of metallocarboranes originated with the assumption that the dicarbollide ion ($C_2B_9H_{11}^{2-}$) is very similar to the cyclopentadienyl ligand (Cp^-).^{8,9} For example, the dicarbollide ion has six delocalized electrons in π -type orbitals on the open C_2B_3 pentagonal face, as those found in the Cp^- ion. However, a number of important features of carborane dianions including the dinegative charge, the inward tilting of the frontier orbitals and the presence of heteroatoms on the bonding face, make them better ligands than Cp ligands. Consequently, a wide variety of metal complexes of the icosahedral and subicosahedral carborane ligand systems have been synthesized and characterized. The carborane ligands also seem to stabilize uncommon and high oxidation states of the metals, such as Cr(IV) and Sn(IV), more effectively than do their organic counterparts.^{10,11}

A large number of metallocarboranes that have been synthesized during the last decade display unusual structural and bonding features. The potential general applications of the boron cluster compounds have been reviewed recently by Plešek.¹² In general, metallocarboranes are found in an increasing number of applications in catalysis,¹³⁻¹⁸ boron neutron capture therapy (BNCT),^{19,20} siloxane-linked polymers,²¹ solvent extraction of radionuclides,¹² and ceramics.^{22,23} The transition metal complexes are also used to catalyze polyhedral borane reactions, e.g., syntheses of multicage compounds and alkenyl carboranes and ring closures.²⁴ The isolated and characterized transition metal carborane complexes also help in understanding the mechanisms of these reactions. With the continued progress of metallocarborane chemistry, the day is not far away when their practical applications will ultimately be developed.

II. Metallocarboranes of d-Block Elements

Our discussion is restricted to metallocarboranes in which the d-block element is incorporated as an integral part of the polyhedral framework. No attempt is made to cover those compounds where the metal atom bridges several carborane polyhedra or is involved solely as member of a substituent group. However, exception is made in one or two cases in which the metal atoms are



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in unusual coordinating sites. This restriction is dictated by the fact that the π -bonded metal atoms have unique properties that are not typical of their usual σ -bonding environment. A great deal of information on reactivity patterns and structures has recently become available on the metallocarboranes of d-block elements. Therefore, this section emphasizes

IIIB	IVB	VB	VIB	VIIb	VIII		IB	IIb	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Unq	Unp	Unh	Uns					

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
----	----	----	----	----	----	----	----	----	----	----	----	----	----

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
----	----	---	----	----	----	----	----	----	----	----	----	----	----

Figure 1. Periodic chart of the d- and f-block elements. (The asterisks denote the elements which have formed metallocarboranes.)

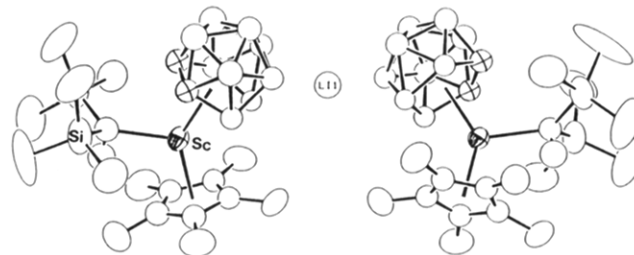


Figure 2. An ORTEP drawing of $[\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{-ScCH}(\text{SiMe}_3)_2]_2\text{Li}\cdot\text{Li}(\text{THF})_3$ showing the two anions with the bridging lithium atom. Reprinted from ref 26a. Copyright 1992 International Union of Crystallography.

as much the structural and bonding features of these complexes as their reaction chemistry. Earlier work is discussed only as background to current results or for purposes of comparison. Although the crystal structures of some of the complexes are discussed in the following subsections, the selected crystallographic parameters of most of the compounds published since 1982 are presented in Table I.

A. Early Transition Metal Complexes

Although the cyclopentadienyl π -complexes of scandium have been known for some time,²⁵ analogous carborane complexes were not known until recently. Bercaw et al. synthesized, in 1992, a novel permethylcyclopentadienyl dicarbollide scandium complex, $[\text{Li}(\text{THF})_3]\cdot\text{Li}[\text{Sc}(\text{C}_2\text{B}_9\text{H}_{11})(\text{Cp}^*)\text{CH}(\text{SiMe}_3)_2]_2$, whose structure was determined by X-ray crystallography.²⁶ A precursor to this complex, $\text{Cp}^*[\text{C}_2\text{B}_9\text{H}_{11}]\text{Sc}(\text{THF})_3$, can be synthesized either by the reaction of $[\text{Cp}^*\text{Sc}(\text{Me})_2]_x$ with the neutral *nido*-carborane $\text{C}_2\text{B}_9\text{H}_{13}$, followed by treatment with THF or by the reaction between $[\text{Cp}^*\text{ScCl}_2]_x$ and $\text{Na}_2[\text{C}_2\text{B}_9\text{H}_{11}]$, followed by addition of THF. Alkylation of the precursor with $\text{LiCH}(\text{SiMe}_3)_2$ in toluene followed by precipitation in petroleum ether yields the novel scandium complex $[\text{Li}(\text{THF})_3]\cdot[\text{Sc}(\text{C}_2\text{B}_9\text{H}_{11})(\text{Cp}^*)\text{CH}(\text{SiMe}_3)_2]_2$ that dimerizes upon diffusion of pentane in a concentrated toluene solution.²⁶ Figure 2 shows that each Sc atom is bonded to one Cp^* and one dicarbollide ligand in η^5 fashion, with one $(\text{SiMe}_3)_2\text{CH}$ unit in the plane between the two η^5 ligands. The centroid-Sc-centroid angle of 137.8° is identical to that found in the corresponding $(\text{Cp}^*)_2\text{Sc}$ analogue.²⁷ An interesting structural feature of the complex is that a Li atom bridges the two units by loosely bonding to three boron atoms of each dicarbollide ligand resulting in a dimeric monoanion, while the $\text{Li}^+(\text{THF})_3$ counterion resides outside the coordination sphere for charge balance.²⁶

The alkylated, mononuclear Sc complex can also be converted to the corresponding dimeric hydride $[\text{Li}(\text{THF})_n]_2[\text{ScH}(\text{C}_2\text{B}_9\text{H}_{11})(\text{Cp}^*)]_2$ by reacting with H_2 slowly. The crystal structure shows the presence of two Sc cores held together by a $2e^-$ dative bond between an electron-rich B-H unit and the Lewis acidic Sc center. Although the Sc-bound hydrogen has not been observed crystallographically, it could be detected by ^1H NMR spectroscopy (δ 5.23 broad).²⁶ The tremendous stability of the Sc-H bonds limits the utility of the Sc hydride species as olefin polymerization catalysts.

Although a mixed-ligand yttrium sandwich species is yet to be synthesized, the first carborane analogue of an ytrocene derivative $[\text{Li}(\text{THF})_4][\text{Y}(\text{Cl})(\text{THF})\{\eta^5-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4\}_2\text{Li}(\text{THF})]$ was reported very recently.²⁸ The complex was synthesized, in 83% yield, by treatment of the dilithium salt of the $[2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4]^{2-}$ dianion with anhydrous YCl_3 in a molar ratio of 2:1 in dry benzene, followed by extraction and crystallization of the product from anhydrous *n*-hexane and THF solution. The yttrium complex is composed of a dianionic $\{\text{Y}(\text{Cl})(\text{THF})\{\eta^5-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4\}_2\}^{2-}$ sandwich complexed with an exo polyhedral $\text{Li}(\text{THF})^+$ cation, and the negative charge is balanced by a discrete cationic $\text{Li}^+(\text{THF})_4$ unit outside the coordination sphere as found by X-ray structure analysis (see Figure 3).²⁸ The centroid-Y-centroid angle of 129.7° , Y-centroid distance of 2.38 Å, Y-Cl distance of 2.582 Å, Cl-Y-THF angle of about 90° , and the bent-sandwich geometry of this complex all resemble those of an ytrocene analogue. As in the Cp systems,²⁵ the average centroid-Y-THF and centroid-Y-Cl angles constitute a distorted-tetrahedral geometry of the Y metal. This work, together with the scandium complex described above, demonstrates that, by using a carborane ligand, a second metal atom such as lithium can be incorporated into the structure of bent-sandwich complexes as a counterion. One of the limitations of carborane ligands in metal chemistry is that, with two dianionic ligands and a $3+$ charge on the metal, there is little possibility of adding reactive anionic ligands such as alkyls without forming a highly charged species. The complexes described above offer a convenient solution to that problem. It is, therefore, expected that monomeric, bent, anionic, and mixed carborane-Cp-complexed Sc species such as $[\text{Cp}^*\text{Sc}(\text{R})\text{C}_2\text{B}_9\text{H}_{11}]^-$,²⁶ or a monomeric, anionic, and purely carborane-based Y bent-sandwich of the type $[\{\eta^5-(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4\}_2\text{Y}(\text{R})\text{Li}]^-$,²⁸ should support α -olefin polymerization or oligomerization catalytic activity as in the cases of analogous neutral group 4 complexes (discussed below).²⁹⁻³²

Until mid 1970s there were no known examples of metallocarboranes of early transition metals, but in 1975 Salentine and Hawthorne reported the first π -complexes of Ti, Zr, and V that were prepared from the $[1,2-\text{C}_2\text{B}_{10}\text{H}_{12}]^{2-}$ ion or its C,C' -dimethyl derivatives.³³ Subsequently, a number of metallocarboranes of early transition metals with the general formula $[\text{M}^{\text{II}}(\text{C}_2\text{B}_{10}\text{H}_{10}\text{R}_2)_2]^{2-}$ ($\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{R} = \text{H}$; $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{R} = \text{CH}_3$) as well as the mixed-ligand titanacarboranes of the formula $[\text{C}_x\text{H}_x\text{TiC}_2\text{B}_n\text{H}_{n+2}]^{m-}$ ($x = 5, n = 10, m = 1$; $x = 8, n = 9$ or $10, m = 0$ or 1) have been reported by the same authors.³⁴ The crystal structure of the titanium complex revealed that the titanium metal, in a formal oxidation state of $+2$, is

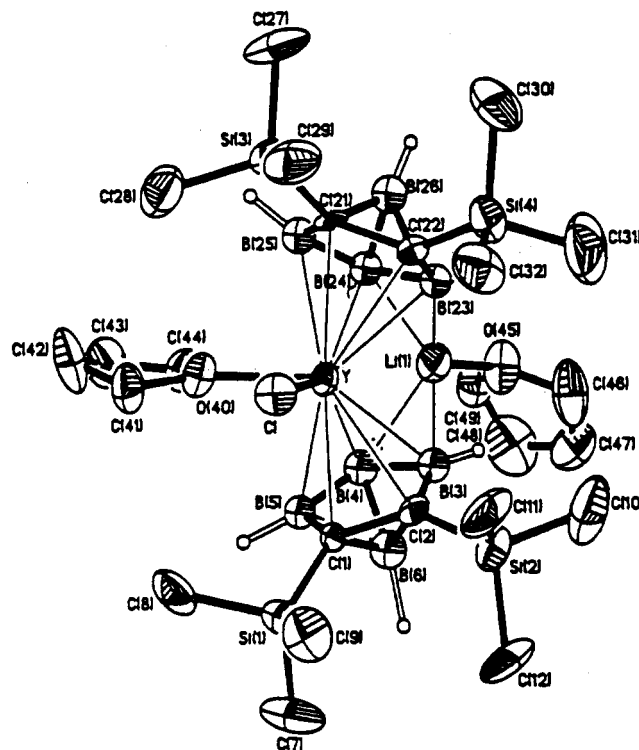
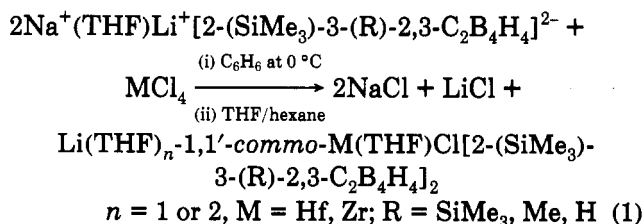


Figure 3. A perspective view of the yttracarborane $\{\text{Li}(\text{THF})-1,1'-\text{commo}-\text{Y}(\text{THF})\text{Cl}[2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4]_2\}-[\text{Li}(\text{THF})_4]$. Reprinted from ref 28. Copyright 1991 American Chemical Society.

sandwiched by two dinegative C_2B_{10} carborane cages, and hence the metal center represents a 14 interstitial electron system.³⁵ Apparently, the titanium, zirconium, and vanadium sandwich complexes are substantially more stable than the corresponding cyclopentadienyl analogues, which is consistent with the general trend of greater stability of the metallocarboranes compared to the corresponding metallocenes.³³⁻³⁵ However, both the C_2B_9 and C_2B_{10} carborane systems failed to produce the group 4 metal sandwich species in which the metal atoms are in their formal highest oxidation state of $+4$. The synthesis of the first "zwitterionic" zirconium(IV) sandwich complex was reported very recently.²⁹ This synthesis involved the reaction between ZrCl_4 and the C_2B_4 carborane double salt in a molar ratio of 1:2 in dry benzene and subsequent extraction of the product from a solvent mixture of THF and *n*-hexane. Similarly, a number of other Zr(IV) and Hf(IV) sandwich complexes of a C_2B_4 carborane system have been synthesized according to the general reaction pathway, shown in eq 1.²⁹⁻³¹



The crystal structure of a zirconium sandwich complex of a C_2B_4 carborane system is shown in Figure 4. The structure reveals that the zirconium atom is sandwiched by the two carborane cages with the metal to cage distances of 2.53–2.58 Å, which are comparable to the $\text{Zr}-\eta^5\text{-Cp}$ distance of 2.49 Å in the structure of

Table I. Selected Crystallographic Data of d- and f-Block Metal-Carborane Complexes^a

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
Early Transition Metal Complexes			
[Li(THF) ₃ ·Li]Sc(C ₂ B ₉ H ₁₁)(Cp*)CH(SiMe ₃) ₂] ₂	Sc-Cnt _{cage} (2.12)	Cnt _{Cp} -Sc-Cnt _{cage} (137.8)	26a
	Sc-C _{cage} (2.57)	C _{alkyl} -Sc-Cnt _{cage} (111.2)	
	Sc-B (2.55)	C _{alkyl} -Sc-Cnt _{Cp} (110.9)	
	Sc-Cnt _{Cp} (2.20)		
	Sc-C _{alkyl} (2.28)		
[Cp*(C ₂ B ₉ H ₁₁)ScH] ₂ [Li(THF) _n] ₂	Sc-Cnt _{cage} (2.08)	Cnt _{Cp} -Sc-Cnt _{cage} (136.2)	26b
	Sc-C _{cage} (2.51)	H-Sc-Cnt _{cage} (107.6)	
	Sc-B (2.52)	H-Sc-Cnt _{Cp} (105.6)	
	Sc-Cnt _{Cp} (2.20)		
	Sc-H (2.19)		
{Li(THF)-1,1'- <i>commo</i> -Y(THF)Cl[2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₂ }- [Li(THF) ₄]	Y-C _{cage} (2.71)	Cl-Y-O (89.5)	28
	Y-B (2.71)	Cnt _{cage} -Y-O (103.3)	
	Y-Cnt _{cage} (2.38)	Cnt _{cage} -Y-Cl (111)	
	Y-Cl (2.58)	Cnt _{cage} -Y-Cnt _{cage} (129.7)	
	Y-O (2.35)		
	Y...Li (3.34)		
	Li-B (2.27-2.41)		
(C ₈ H ₈)Ti[Et ₂ C ₂ B ₄ H ₄]	Ti-C _{cage} (2.30)	Ti-C _{cage} -C _{Et} (127.6)	43
	Ti-B (2.37)	Ti-C _{cage} -C _{Et} (134)	
	Ti-Cnt _{cage} (1.91)	Cnt _{cage} -Ti-Cnt _{arene} (177.2)	
	Ti-C _{arene} (2.29)		
	Ti-Cnt _{arene} (NR)		
Li(THF) ₂ -1,1'- <i>commo</i> -Zr(THF)Cl[2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₂	Zr-C _{cage} (2.57)	Cnt _{cage} -Zr-O (104.5)	29
	Zr-B (2.54)	Cnt _{cage} -Zr-Cl (104.1)	
	Zr-Cnt _{cage} (2.17)	Cnt _{cage} -Zr-Cnt _{cage} (130.4)	
	Zr-O (2.29)		
	Zr-Cl (2.46)		
Li(THF)-1,1'- <i>commo</i> -Zr(THF)Cl[2-(SiMe ₃)-3-(Me)- 2,3-C ₂ B ₄ H ₄] ₂	Li-B (2.41-2.60)		31
	Zr-C _{cage} (2.53)	Cnt _{cage} -Zr-O (105.2)	
	Zr-B (2.56)	Cnt _{cage} -Zr-Cl (106.7)	
	Zr-Cnt _{cage} (2.17)	Cnt _{cage} -Zr-Cnt _{cage} (133.6)	
	Zr-Cl (2.45)	Cl-Zr-O (91.2)	
Cp*(C ₂ B ₉ H ₁₁)Zr[C(Me)=CMe ₂]	Zr-O (2.24)		32
	Li-B (2.34)		
	Zr-Cnt _{cage} (2.04)	Cnt _{cage} -Zr-Cnt _{Cp} (141.3)	
	Zr-H (2.29)	Zr-C _{alkene} -C _{alkene} (147.8)	
	Zr-C _{alkene} (2.19)	Zr-C _{alkene} -C _{Me} (91.1)	
[(Cp*)(C ₂ B ₉ H ₁₁)Zr] ₂ (μ-CH ₂)	Zr-Cnt _{Cp} (2.19)		32
	Zr-B (NR)		
	Zr-C _{cage} (NR)		
	Zr-Cnt _{cage} (2.09)	Cnt _{cage} -Zr-Cnt _{Cp} (134.9)	
	Zr-H (2.09)		
Li(THF)-1,1'- <i>commo</i> -Hf(THF)Cl[2-(SiMe ₃)-3-(Me)- 2,3-C ₂ B ₄ H ₄] ₂	Zr-CH ₂ (2.18)		30
	Zr...B _{cage} (2.99)		
	Zr-Cnt _{Cp} (2.23)		
	Zr-B (NR)		
	Zr-C _{cage} (NR)		
Li(THF)-1,1'- <i>commo</i> -Hf(THF)Cl[2-(SiMe ₃)-3-(H)- 2,3-C ₂ B ₄ H ₄] ₂	Hf-C _{cage} (2.50)	Cnt _{cage} -Hf-Cnt _{cage} (134.1)	31
	Hf-B (2.54)	Cl-Hf-O (89.7)	
	Hf-Cnt _{cage} (2.15)	Cnt _{cage} -Hf-O (105.8)	
	Hf-Cl (2.43)	Cnt _{cage} -Hf-Cl (106.3)	
	Li-B (2.35)	Bi-Li-B (77.9-96.7)	
(C ₈ H ₈)V[Et ₂ C ₂ B ₄ H ₄]	Hf-O (2.19)		43
	Hf-C _{cage} (2.45)		
	Hf-B (2.57)		
	Hf-Cnt _{cage} (2.13)		
	Hf-Cl (2.45)		
(C ₂ B ₉ H ₁₁)TaCl ₃	Hf...Li (3.41)		38
	Li-B (2.29-2.42)		
	Hf-O (2.20)		
	V-C _{cage} (2.23)	V-C _{cage} -C _{Et} (130.5, 133.5)	
	V-B (2.30)	Cnt _{cage} -V-Cnt _{arene} (177.2)	
Cp'(C ₂ B ₉ H ₁₁)TaCl ₂	V-Cnt _{cage} (1.83)		38
	V-C _{arene} (2.28)		
	V-Cnt _{arene} (NR)		
	Ta-C _{cage} (2.41)	Cl-Ta-Cnt _{cage} (116.2, 124)	
	Ta-B (2.40)	Cl-Ta-Cl (97.7)	
(C ₇ H ₇)Cr[Et ₂ C ₂ B ₄ H ₄]	Ta-Cnt _{cage} (1.92)	Cl-Ta-B (116.3, 124)	43
	Ta-Cl (2.23)		
	Ta-C _{cage} (2.47)		
	Ta-B (2.47)		
	Ta-Cnt _{cage} (2.01)		

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
1,1'- <i>commo</i> -Cr[2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₂	Cr-B (2.25)	Cnt _{cage} -Cr-Cnt _{arene} (177.2)	10
	Cr-C _{arene} (2.18)		
	Cr-Cnt _{arene} (NR)		
	Cr-Cnt _{cage} (NR)		
	Cr-C _{cage} (2.18)	Cnt _{cage} -Cr-Cnt _{cage} (180)	
Li(THF) ₄ {1,1'- <i>commo</i> -Cr[2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₂ }	Cr-B (2.27-2.38)		42
	Cr-Cnt _{cage} (1.80)		
	Cr-C _{cage} (2.18)	Cnt _{cage} -Cr-Cnt _{cage} (180)	
	Cr-B (2.26)	O-Li-O (108.5)	
Li(TMEDA) ₂ {1,1'- <i>commo</i> -Cr[2-(SiMe ₃)-2,3-C ₂ B ₄ H ₅] ₂ }	Cr-Cnt _{cage} (1.77)		42
	Li-O (1.97)		
	Cr-C _{cage} (2.18)	Cnt _{cage} -Cr-Cnt _{cage} (175.3)	
	Cr-B (2.21)	N-Li-N (121.2)	
[Mo ₂ Cu ₂ (μ-CO) ₄ (CO) ₂ (μ-H) ₂ (C ₂ B ₉ H ₁₀) ₂] ²⁻	Cr-Cnt _{cage} (1.77)		46
	Li-N (2.11)		
	Mo-Cu (2.65, 2.83)	Cu-Mo-Cu (51.7)	
	Cu...B (2.18)	Cu-H-B (97)	
	Mo-C _{cage} (2.35)		
	Mo-B (2.45)		
	Cu-Cu (2.40)		
	Mo-C _{CO} (1.94)		
	Cu-C _{CO} (2.24)		
	Cu-H (1.69)		
	Mo-Cnt _{cage} (NR)		
[W ₂ (μ-CC ₆ H ₄ Me-4)(CO) ₃ (η ⁵ -C ₂ B ₉ H ₉ Me ₂)(η ⁵ -Cp)]	W-B (2.33)	B-W-W (51.7)	51
	W-C _{cage} (2.40)	W-W-H (83)	
	W-W (2.65)	W-H-B (94)	
	W-C _{CO} (1.99)	W-C _{bridge} -W (82.9)	
	W-Cnt _{cage} (NR)		
	W-Cnt _{Cp} (NR)		
	W-H _{bridge} (2.05)		
	W-C _{bridge} (1.97, 2.05)		
	B-H _{bridge} (1.27)		
	W-C _{cage} (2.38)	W-W-B (52.2)	
	W-B (2.25, 2.41)	W-H-B (100)	
[W ₂ (μ-CMe)(CO) ₃ (η ⁵ -C ₂ B ₉ H ₈ (CH ₂ C ₆ H ₄ Me-4)Me ₂)-(η ⁵ -Cp)]	W-W (2.65)	W-W-B (53.3)	51
	W-C _{CO} (1.98)		
	W-C _{bridge} (1.95, 2.03)		
	W-H _{bridge} (1.85)		
	W-Cnt _{cage} (NR)		
	W-Cnt _{Cp} (NR)		
	B-H _{bridge} (1.30)		
	B-C _{aryl} (1.58)		
	Mo-B (2.44)	B-Mo-W (53.9)	
	W-B (2.45)	Mo-H _{bridge} -B (96)	
	W-C _{cage} (2.22, 2.52)	W-C _{bridge} -Mo (84.0)	
[MoW(μ-CC ₆ H ₄ Me-4)(CO) ₂ (PMe ₃)(η ⁶ -C ₂ B ₁₀ H ₁₀ Me ₂)-(η ⁵ -Cp)]	W-Mo (2.70)		51
	W-C _{CO} (2.00)		
	Mo-P (2.49)		
	Mo-C _{Cp} (2.32)		
	W-C _{bridge} (2.10)		
	Mo-C _{bridge} (1.94)		
	Mo-H _{bridge} (1.80)		
	B-H _{bridge} (1.50)		
	W-C _{cage} (2.51)	P-W-P (128)	
	W-B (2.41)	W-C _{cage} -C _{Me} (111)	
	W-P (2.57)	W-B-C _{aryl} (109.6)	
[W(CO) ₂ (PPh ₃) ₂ (η ⁵ -C ₂ B ₉ H ₈ (CH ₂ C ₆ H ₄ Me-4)Me ₂)]	W-C _{CO} (1.97)		52
	W-C _{cage} (2.40)		
	W-B (2.39)		
	W-P (2.57)		
	W-C _{CO} (1.99)		
[W(CO) ₃ (PPh ₃)(η ⁵ -C ₂ B ₉ H ₈ (CH ₂ C ₆ H ₄ OMe-2)Me ₂)]	W-B (2.38)	C _{cage} -W-C _{cage} (40.6)	53
	W-C _{cage} (2.46)	B-W-B (44.4)	
	W-W (2.79)	P-W-C _{CO} (73.2-119.8)	
	W-C _{CO} (1.96)	W-B-C _{aryl} (114)	
	W-C _{cage} (2.39)	W-W-B (125.8-157.2)	
[W ₂ (μ-CC ₆ H ₄ Me-4)(CO) ₃ (PMe ₃)(η ⁵ -Cp){η ⁵ -2,8-C ₂ B ₉ H ₈ -10-(CH ₂ C ₆ H ₄ Me-4)-2,8-Me ₂ }]	W-B (2.38)	W-C _{bridge} -W (87.1)	54
	W-C _{cage} (2.46)	W-B-C _{aryl} (115.1)	
	W-W (2.79)		
	W-C _{CO} (1.96)		
	W-C _{cage} (2.39)		
[W{CH(C ₆ H ₄ Me-4)PPh ₂ CH ₂ PPh ₂ }(CO) ₂ (η ⁵ -C ₂ B ₉ H ₉ Me ₂)]	W-B (2.40)	P-W-C _{CO} (77.2, 121.8)	55
	W-P (2.48)	P-W-C _{phos} (72.2)	
	W-C _{CO} (1.96)		
	W-C _{phos} (2.34)		
	W-C _{cage} (2.39)		
[NEt ₄][<i>closio</i> -1,8-Me ₂ -11-(CH ₂ C ₆ H ₄ Me-4)-2-Cl-2,2,2-(CO) ₃ -2,1,8-WC ₂ B ₉ H ₉]	W-Cl (2.54)	Cl-W-C _{CO} (75.1-134)	56
	W-C _{CO} (1.99)	W-B-C _{aryl} (113.5)	
	W-B (NR)		

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
[<i>closo</i> -1,8-Me ₂ -11-(CH ₂ C ₆ H ₄ Me-4)-2,2-(CO) ₂ -2-(η -PhCCMe)-2,1,8-WC ₂ B ₉ H ₈]	W-C _{cage} (2.41) W-B (2.37) W-C _{CO} (1.99) W-C _{aryl} (2.06)	W-B-C _{aryl} (114.7)	56
[N(PPh ₃) ₂][<i>closo</i> -1,7-Me ₂ -2-I-2,2,2-(CO) ₃ -2,1,7-WC ₂ B ₉ H ₉]	W-C _{cage} (2.43) W-I (2.89) W-B (2.37) W-C _{CO} (1.97)	I-W-C _{CO} (74.7-131.2) W-C _{cage} -C _{Me} (108.5) I-W-C _{cage} (108.3)	56
[WPt(μ -CC ₆ H ₄ Me-4)(μ - σ : η^5 -C ₂ B ₉ H ₈ Me ₂)(CO) ₂ (PMe ₂ Ph) ₂]	W-B (2.21-2.37) W-C _{cage} (2.50) Pt-B (2.17) W-Pt (2.72) W-C _{bridge} (1.89) Pt-C _{bridge} (2.14) Pt-P (2.27, 2.37) W-C _{CO} (1.99)	W-Pt-P (120.1, 142.1) W-Pt-C _{bridge} (43.9)	60
[WPt(μ -CC ₆ H ₄ Me-4)(μ - σ : η^6 -C ₂ B ₁₀ H ₉ Me ₂)(CO) ₂ (PMe ₂ Ph) ₂]	W-C _{cage} (2.34) W-B (2.23-2.55) Pt-B (2.15) W-Pt (2.73) W-C _{bridge} (1.92) Pt-C _{bridge} (2.14) Pt-P (2.28, 2.36) W-C _{CO} (2.01)	W-Pt-P (121.4, 139.4) W-Pt-C _{bridge} (44.3)	60
[<i>exo-nido</i> -9,11-(CH ₂ C ₆ H ₄ Me-4)-5,10-{W(CO) ₂ (η -Cp)}-5,10-(μ -H) ₂ -7,8-C ₂ B ₉ H ₈]	W-B (2.38, 2.50) W-C _{Cp} (2.31) W-C _{CO} (1.98) W-H _{bridge} (1.95, 2.16)	B-W-B (39.6) W-B-B (101, 153) B-W-B (39.6) C _{CO} -W-B (90.8-117.5)	50
[<i>exo-nido</i> -9,10-{W(CO) ₂ (η -Cp*)}-5,10-(μ -H) ₂ -7,8-C ₂ B ₉ H ₈ -7,8-Me ₂]	W-B (2.38, 2.50) W-C _{CO} (1.94) W-H (1.95, 2.16) W-C _{Cp} (2.28-2.41)	B-W-H (63, 71) W-H-B (98)	50
[W ₂ Au ₂ (μ -CR) ₂ (μ -PPh ₂ (CH ₂) ₄ PPh ₂)(CO) ₄ (η^5 -C ₂ B ₉ H ₉ Me ₂) ₂]	W-C _{cage} (2.43) W-B (2.39) W-Cnt _{cage} (1.91) W-Au (2.79) W-C _{bridge} (1.87)	W-Au-P (161.1) W-C _{bridge} -Au (86.6)	61
[<i>closo</i> -3,3,3-(CO) ₃ -3-SnPh ₃ -3,1,2-WC ₂ B ₉ H ₁₁]-	W-Sn (2.85) W-C _{cage} (2.33) W-B (2.40) W-C _{CO} (1.95)	Sn-W-Cnt _{cage} (116.4) W-Sn-C _{Ph} (114.5)	47
[Li ⁺ (THF)][Li ⁺ (TMEDA)] ₂ [<i>commo</i> -Mn ₃ [2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₄] ³⁻	Mn-Mn (2.68) Mn-C _{cage} (2.16) Mn-B (2.19) Mn-Cnt _{cage} (1.70) Li...B (2.23-2.46)	Cnt _{cage} -Mn-Cnt _{cage} (177.6) Mn-Mn-Cnt _{cage} (90.5, 177.6)	64
[Mn(TMEDA)][<i>commo</i> -1,1'-Mn[2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₂]	Mn-C _{cage} (2.16) Mn-B (2.24) Mn-Cnt _{cage} (1.71) Mn-Mn (2.66) Mn...B (2.32-2.48)	Cnt _{cage} -Mn-Cnt _{cage} (175.7)	67
[(B ₉ C ₂ H ₁₁)ReCO] ₃ Cs	Re-C _{CO} (1.89) Re-C _{cage} (2.31) Re-B (2.34)	C _{CO} -Re-C _{CO} (41) C _{cage} -Re-B (43) B-Re-B (44.5)	68b
Middle and Late Transition Metal Complexes			
{[(Et ₂ C ₂ B ₄ H ₄)FeH(C ₅ Me ₄)] ₂ C ₆ H ₄ }	Fe-C _{cage} (2.06) Fe-B (2.20) B-H _{bridge} (1.45) Fe-H _{bridge} (1.62) Fe-C _{Cp} (2.06)	B-H-Fe (93.1) B-H-B (75) B-H-Fe (93.1)	145
[Me ₂ C ₂ B ₄ H ₄] ₂ Fe ₂ (OMe) ₂ C ₂ H ₄	Fe-Fe (2.41) Fe-C _{cage} (2.06) Fe-B (2.13) Fe-O (2.08-2.23) Fe...B (2.23-2.44) Fe-Cnt _{cage} (1.64)	C _{cage} -Fe-C _{cage} (43.5) C _{cage} -Fe-B (42.4) B-Fe-B (45.1) Fe-Fe-B (53.7)	75
(η^5 -C ₉ H ₇)Fe(Et ₂ C ₂ B ₄ H ₄)NiCp*	Fe...Ni (3.37) Ni-B (2.02) Ni-C _{cp} (2.10) Fe-C _{cage} (1.99) Fe-B (1.91, 2.16) Fe-C _{arene} (2.03-2.18)	Fe-B-Ni (104, 122) B-B-B (86.4)	143
[<i>closo</i> -3-(η^6 -C ₆ H ₆)3,1,2-FeC ₂ B ₉ H ₁₁]	Fe-C _{cage} (2.03) Fe-B (2.12) Fe-Cnt _{cage} (1.48)	C _{cage} -Fe-C _{cage} (46.3) C _{cage} -Fe-B (48.9-83.1) B-Fe-B (49.6-86.1)	77

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
$\text{Fe}(\text{Cp})(\text{CO})_2(\text{CB}_{11}\text{H}_{12})$	Fe-Cnt _{arene} (1.57)		
	Fe-C _{arene} (2.10)		
	Fe...B (2.59)	Fe-H-B (141.1)	160
	Fe-H (1.56)	Cnt _{cage} -Fe-H (114.3)	
	Fe-Cnt _{cage} (1.70)		
$\text{Fe}(\text{TPP})(\text{B}_{11}\text{CH}_{12})$	Fe-C _{Cp} (2.08)		
	Fe-H (1.82)	Fe-H-B (NR)	162
	Fe...B (NR)		
$3,1,2-(\eta^6-1,3,5-\text{Me}_3\text{C}_6\text{H}_3)\text{FeC}_2\text{B}_9\text{H}_{11}$	Fe-C _{cage} (2.06)	C _{cage} -Fe-C _{cage} (47.0)	148
	Fe-B (2.12)	B-Fe-B (50.9)	
	Fe-Cnt _{cage} (1.48)	C _{cage} -Fe-B (47.5)	
	Fe-Cnt _{arene} (1.60)	Cnt _{cage} -Fe-Cnt _{arene} (NR)	
	Fe-C _{arene}		
$1-(\eta\text{-Cp})\text{Fe-2-Me-2,3,4-C}_3\text{B}_7\text{H}_9$	Fe-C _{cage} (1.95, 2.26)	Cnt _{cage} -Fe-Cnt _{Cp} (NR)	168
	Fe-B (2.24)		
	Fe-Cnt _{Cp} (1.68)		
$1-(\eta\text{-Cp})\text{Fe-4-Me-2,3,4-C}_3\text{B}_7\text{H}_9$	Fe-C _{cage} (1.94, 2.28)	Cnt _{cage} -Fe-Cnt _{Cp} (NR)	168
	Fe-B (2.23)		
	Fe-Cnt _{Cp} (1.68)		
<i>commo</i> -Fe-(1-Fe-2-Me-2,3,5-C ₃ B ₇ H ₉) ₂	Fe-C _{cage} (1.98, 2.43)	Cnt _{cage} -Fe-Cnt _{cage} (NR)	169
	Fe-B (2.27)		
	Fe-Cnt _{cage} (NR)		
<i>commo</i> -Fe-(1-Fe-5-Me-2,3,5-C ₃ B ₇ H ₉) ₂	Fe-C _{cage} (1.96, 2.44)	Cnt _{cage} -Fe-Cnt _{cage} (NR)	169
	Fe-B (2.28)		
	Fe-Cnt _{cage} (NR)		
<i>commo</i> -Fe-(1-Fe-5-Me-2,3,5-C ₃ B ₇ H ₉)(1-Fe-4-Me-2,3,4-C ₃ B ₇ H ₉)	Fe-C _{cage} (1.96, 2.46)	Cnt _{cage} -Fe-Cnt _{cage} (NR)	169
	Fe-B (2.27)		
	Fe-Cnt _{cage} (NR)		
<i>commo</i> -Fe-(1-Fe-10-Me-2,3,10-C ₃ B ₇ H ₉) ₂	Fe-C _{cage} (1.99)	Cnt _{cage} -Fe-Cnt _{cage} (NR)	169
	Fe-B (2.24-2.36)		
	Fe-Cnt _{cage} (NR)		
$(\eta^6\text{-C}_9\text{H}_8)\text{Fe}^{\text{II}}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$	Fe-C _{cage} (2.05)	Cnt _{cage} -Fe-Cnt _{arene} (177.2)	143
	Fe-B (2.12)		
	Fe-C _{arene} (2.04-2.12)		
	Fe-Cnt _{cage} (NR)		
	Fe-Cnt _{arene} (NR)		
$(\eta^6\text{-C}_6\text{H}_6)\text{Fe}[\text{Et}_2\text{C}_2\text{B}_4\text{H}_4]$	Fe-C _{cage} (2.02)	Cnt _{cage} -Fe-Cnt _{arene} (177.9)	201
	Fe-B (2.13)		
	Fe-C _{arene} (2.04)		
	Fe-Cnt _{arene} (1.54)		
	Fe-Cnt _{cage} (1.61)		
$(\eta^6\text{-C}_6\text{Me}_3\text{H}_3)\text{Fe}[\text{Et}_2\text{C}_2\text{B}_4\text{H}_4]$	Fe-C _{cage} (1.93, 2.06)	Cnt _{cage} -Fe-Cnt _{arene} (177.1)	201
	Fe-B (2.12)		
	Fe-C _{arene} (2.08)		
	Fe-Cnt _{cage} (1.58)		
	Fe-Cnt _{arene} (1.58)		
$(\eta^6\text{-C}_6\text{Me}_6)\text{Fe}[\text{Et}_2\text{C}_2\text{B}_4\text{H}_4]$	Fe-C _{cage} (2.06)	Cnt _{cage} -Fe-Cnt _{arene} (177.9)	201
	Fe-B (2.13)		
	Fe-C _{arene} (2.09)		
	Fe-Cnt _{arene} (1.55)		
	Fe-Cnt _{cage} (1.62)		
$(\eta^6\text{-C}_8\text{H}_{10})\text{Fe}[\text{Me}_2\text{C}_2\text{B}_4\text{H}_4]$	Fe-C _{cage} (2.09)	Cnt _{cage} -Fe-Cnt _{arene} (168)	202
	Fe-B (2.15)		
	Fe-Cnt _{cage} (1.64)		
	Fe-Cnt _{arene} (NR)		
	Fe-C _{arene} (2.05-2.16)		
$[\text{NEt}_4][\text{FeW}\{\mu\text{-CH}(\text{C}_6\text{H}_4\text{Me-4})\}(\mu\text{-}\sigma'\text{-}\eta^5\text{-C}_2\text{B}_9\text{H}_8\text{Me}_2)\text{-}(\mu\text{-CO})(\text{CO})_5]$	Fe-B (2.13)	W-Fe-B (53.7)	203
	W-B (2.19)	Fe-W-B (51.7)	
	Fe-W (2.62)	W-Fe-C _{bridge} (53)	
	W-C _{bridge} (2.17)	W-Fe-C _{CO bridge} (53.9)	
	Fe-C _{bridge} (2.15)		
	Fe-C _{CO bridge} (2.02)		
	W-C _{CO bridge} (2.17)		
	Fe-B (2.13)	W-B-Fe (75.6)	203
	W-B (2.17)	Fe-W-Fe (58.3)	
	Fe-W (2.64)	W-Fe-C _{bridge} (49.2)	
$[\text{NEt}_4][\text{Fe}_2\text{W}(\mu\text{-3-CPh})(\mu\text{-}\sigma'\text{-}\eta^5\text{-C}_2\text{B}_9\text{H}_7\text{Me}_2)(\text{CO})_5]$	Fe-Fe (2.57)	W-Fe-Fe (60.8)	
	W-C _{bridge} (2.02)	Fe-Fe-C _{bridge} (51.5)	
	Fe-C _{bridge} (2.06)		
	Fe-C _{CO} (1.77)		
	Fe-C _{cage} (2.06)	C _{cage} -Fe-C _{cage} (41)	204
	Fe-B (2.14)	B-Fe-B (46.3)	
	Co-B (2.05)	Co-B(cap)-Fe (78)	
$[\text{CoFe}(\text{Me}_4\text{C}_4\text{B}_8\text{H}_8)(\text{PET}_3)_2]$	Fe-Co (2.53)	Cnt _{cage} -Fe-Cnt _{cage} (173.1)	
	Co-P (2.24)		
	Fe-Cnt _{cage} (1.63)		

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
$[closo-3,3-(CO)_2-3-[Sn(C_6H_5)_3]-3,1,2-FeC_2B_9H_{11}]^-$	Fe-Sn (2.55) Fe-B (2.17) Fe-C _{cage} (2.09) Fe-Cnt _{cage} (1.55) Fe-C _{CO} (1.73)	Sn-Fe-C _{cage} (83, 143.6) C _{CO} -Fe-C _{cage} (91.4, 167.0) B-Fe-B (49.4, 84.4)	79
$[closo-3-(CO)-3-(\eta^3-C_3H_5)-3,1,2-FeC_2B_9H_{11}]^-$	Fe-C _{cage} (2.08) Fe-B (2.15) Fe-Cnt _{cage} (1.53) Fe-C _{CO} (1.72) Fe-C _{allyl} (2.03, 2.14)	C _{cage} -Fe-C _{CO} (151.2) B-Fe-B (49, 82.2) C _{cage} -Fe-C _{allyl} (90.5, 120.0)	79
$[closo-3-(CO)-3-COCH_3-3-P(CH_3)_3-3,1,2-FeC_2B_9H_{11}]^-$	Fe-C (2.10) Fe-B (2.18) Fe-Cnt _{cage} (1.57) Fe-P (2.18) Fe-C _{CO} (1.75) Fe-C _{acyl} (1.97) Fe-C _{cage} (2.05) Fe-B (2.10)	C _{cage} -Fe-C _{cage} (45.8) B-Fe-B (46.9, 81.7) P-Fe-C _{acyl} (85.0)	79
$(\eta^6-C_{10}H_8)Fe(Et_2C_2B_4H_4)$	Fe-C _{cage} (2.05) Fe-B (2.10) Fe-Cnt _{cage} (1.60) Fe-Cnt _{arene} (1.55) Fe-C _{arene} (2.02-2.14)	Cnt _{cage} -Fe-Cnt _{arene} (176.4)	205
$(\eta^6-C_{14}H_{10})Fe(Et_2C_2B_4H_4)$	Fe-C _{cage} (2.05) Fe-B (2.17-2.33) Fe-Cnt _{cage} (1.73) Fe-C _{arene} (1.47) Fe-C _{arene} (1.92-2.14)	Cnt _{cage} -Fe-Cnt _{arene} (173.1)	205
$[7,7'-\mu-1,4-C_4H_8-7,8-C_2B_9H_{10}]_2Fe^-$	Fe-Cnt _{cage} (1.54) Fe-C _{cage} (2.12) Fe-B (2.13) Fe-C _{cage} (2.15) Fe-B (2.14) Fe-Cl (2.27) Fe-P (2.25) Fe-Cnt _{cage} (NR) Fe-C _{cage} (2.04) Fe-B (2.14) Fe-C _{arene} (2.05) Fe-Cnt _{cage} (NR) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.01)	C _{cage} -Fe-C' _{cage} (108.5) Fe-C _{cage} -C _{bridge} (115.1)	102a
1,1-(PPh ₂ CH ₂) ₂ -1-Cl-1,2,3-Fe(Et ₂ C ₂ B ₄ H ₄)	Fe-C _{cage} (2.15) Fe-B (2.14) Fe-Cl (2.27) Fe-P (2.25) Fe-Cnt _{cage} (NR) Fe-C _{cage} (2.04) Fe-B (2.14) Fe-C _{arene} (2.05) Fe-Cnt _{cage} (NR) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.01)	Cl-Fe-C _{cage} (92.5) Cl-Fe-B (119-164.3) Cl-Fe-P (91.0)	92
$[(\eta^6-C_6H_6)Fe(Et_2C_2B_4H_3)]_2CH(CH_3)CH_2$	Fe-C _{cage} (2.04) Fe-B (2.14) Fe-C _{arene} (2.05) Fe-Cnt _{cage} (NR) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.01)	Cnt _{cage} -Fe-Cnt _{arene} (NR)	206
$[\eta^6-C_6H_5(\overline{CH_2})_3]Fe(C_2B_4H_5)$	Fe-B (2.13) Fe-Cnt _{cage} (1.60) Fe-Cnt _{arene} (1.53) Fe-C _{arene} (2.07) Fe-C _{cage} (2.05) Fe-B (2.12) Fe-Cnt _{cage} (1.61) Fe-Cnt _{aryl} (1.54) Fe-C _{aryl} (2.08) Fe-C _{cage} (2.06) Fe-B (2.04-2.21) Fe-C _{arene} (2.11) Fe-Cnt _{cage} (1.58) Fe-Cnt _{arene} (1.58) Fe-C _{cage} (2.02) Fe-B (2.09) Fe-C _{arene} (2.00-2.12) Fe-Cnt _{cage} (1.52) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	Cnt _{cage} -Fe-Cnt _{arene} (172.5)	138
$[\eta^6-(C_6H_5)_2Fe(Et_2C_2B_4H_4)]$	Fe-C _{cage} (2.05) Fe-B (2.12) Fe-Cnt _{cage} (1.61) Fe-Cnt _{aryl} (1.54) Fe-C _{aryl} (2.08) Fe-C _{cage} (2.06) Fe-B (2.04-2.21) Fe-C _{arene} (2.11) Fe-Cnt _{cage} (1.58) Fe-Cnt _{arene} (1.58) Fe-C _{cage} (2.02) Fe-B (2.09) Fe-C _{arene} (2.00-2.12) Fe-Cnt _{cage} (1.52) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	Cnt _{cage} -Fe-Cnt _{aryl} (160.7)	206
1- $[\eta^6-C_6(CH_3)_6]Fe-4,5,7,8-Me_4C_4B_3H_3$	Fe-C _{cage} (2.06) Fe-B (2.04-2.21) Fe-C _{arene} (2.11) Fe-Cnt _{cage} (1.58) Fe-Cnt _{arene} (1.58) Fe-C _{cage} (2.02) Fe-B (2.09) Fe-C _{arene} (2.00-2.12) Fe-Cnt _{cage} (1.52) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	C _{cage} -Fe-C _{cage} (39.4) B-Fe-B (51.6) C _{cage} -Fe-B (42.6) Cnt _{cage} -Fe-Cnt _{arene} (174.1)	172
2- $[\eta^6-CH_3C_6H_5]Fe-6,7,9,10-Me_4C_4B_5H_5$	Fe-C _{cage} (2.02) Fe-B (2.09) Fe-C _{arene} (2.00-2.12) Fe-Cnt _{cage} (1.52) Fe-Cnt _{arene} (NR) Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	C _{cage} -Fe-C _{cage} (41.6) B-Fe-B (51.3) C _{cage} -Fe-B (41.7-81.7) Cnt _{cage} -Fe-Cnt _{arene} (NR)	172
$[commo-3,3'-Fe\{8-N(Et)_3\}-3,1,2-FeC_2B_9H_{10}]_2$	Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	C _{cage} -Fe-C _{cage} (48) B-Fe-B (49.5, 80) Cnt _{cage} -Fe-Cnt _{cage} (166)	90
$[commo-3,3'-Fe\{3,1,2-FeC_2B_9H_{11}\}_2][NMe_4]_2$	Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	C _{cage} -Fe-C _{cage} (46.9) B-Fe-B (50.2, 86.2) Cnt _{cage} -Fe-Cnt _{cage} (180) Fe-C _{cage} -B (74.9, 120.9) Cnt _{cage} -Fe-Cnt _{arene} (NR)	90
2- $[\eta^6-Me_3C_6H_3]Fe-1,6-C_2B_7H_9$	Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) B-N (1.63) Fe-C _{cage} (2.03) Fe-B (2.03) Fe-Cnt _{cage} (1.48) Fe-C _{cage} (1.93, 2.09) Fe-B (2.12) Fe-C _{arene} (2.09) Fe-Cnt _{arene} (1.564) Fe-Cnt _{cage} (NR) Fe-B (2.12) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	Fe-C _{cage} -B (74.9, 120.9) Cnt _{cage} -Fe-Cnt _{arene} (NR)	96
6- $[\eta^6-Me_3C_6H_3]Fe(9,10-C_2B_7H_{11})$	Fe-C _{cage} (2.05) Fe-B (2.20) Fe-Cnt _{cage} (1.53) Fe-Cnt _{arene} (1.56) Fe-C _{arene} (2.10)	B-Fe-B (50, 83.8) Cnt _{cage} -Fe-Cnt _{arene} (178.4)	96

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
<i>dl</i> -3,3'- <i>commo</i> -Fe{[(C ₂ B ₉ H ₉)N] ₂ (CH ₂) ₃ }	Fe-C _{cage} (2.08-2.15) Fe-B (2.05-2.12) Fe-Cnt _{cage} (1.52) B-N (1.51)	Cnt _{cage} -Fe-Cnt _{cage} (170.4) B-Fe-B' (173.5)	216
3,3'- <i>commo</i> -Co{[(C ₂ B ₉ H ₉)N] ₂ (CH ₂) ₃ }	Co-C _{cage} (2.07) Co-B (2.04-2.09) Co-Cnt _{cage} (1.48) B-N (1.52)	Cnt _{cage} -Co-Cnt _{cage} (173.4) B-Co-B' (175.4)	216
(PC ₄ Me ₄)Co(Et ₂ C ₂ B ₃ H ₃)Co(NC ₄ Me ₄)	Co-C _{cage} (2.08) Co-B (2.08) Co-P (2.31) Co-N (2.09) Co-C _{pyrrolyl} (2.05) Co-C _{phospholyl} (2.08) Co-Cnt _{cage} (1.61) Co-Cnt _{pyrrolyl} (1.70) Co-Cnt _{phospholyl} (1.70)	Cnt _{cage} -Co-Cnt _{pyrrolyl} (178.9) Cnt _{cage} -Co-Cnt _{phospholyl} (178)	207
CH ₂ [<i>clos</i> o-1-(η -C ₅ H ₄)Co(2,3-Et ₂ C ₂ B ₄ H ₄)] ₂	Co-C _{cage} (2.01) Co-B (2.07) Co-C _{Cp} (2.05) Co-Cnt _{cage} (NR) Co-Cnt _{Cp} (NR)	Cnt _{cage} -Co-Cnt _{Cp} (NR)	144a
<i>commo</i> -Co(1-Co-2-Me-2,3,5-C ₃ B ₇ H ₉)(1-Co-5-Me-2,3,5-C ₃ B ₇ H ₉)	Co-C _{cage} (2.01, 2.60) Co-B (2.24, 2.44) Co-Cnt _{cage} (NR)	Cnt _{cage} -Co-Cnt _{cage} (NR)	169
<i>commo</i> -Co(1-Co-2-Me-2,3,5-C ₃ B ₇ H ₉) ₂	Co-C _{cage} (2.03, 2.65) Co-B (2.28, 2.54) Co-Cnt _{cage} (NR)	Cnt _{cage} -Co-Cnt _{cage} (NR)	169
[(Et ₂ C ₂ B ₄ H ₄)Co(C ₅ H ₄)] ₂	Co-C _{cage} (2.01) Co-B (2.09) Co-Cnt _{cage} (1.56) Co-Cnt _{Cp} (1.65) Co-C _{Cp} (2.03)	Cnt _{cage} -Co-Cnt _{Cp} (176.8)	142
[(Et ₂ C ₂ B ₃ H ₅)Co(C ₅ Me ₄)] ₂ C ₆ H ₄	Co-B (1.96, 2.05) Co-C _{cage} (2.08) Co-C _{Cp} (2.05) Co-Cnt _{cage} (NR) Co-Cnt _{Cp} (NR)	Cnt _{cage} -Co-Cnt _{Cp} (NR)	142
[(Et) ₄ C ₄ B ₈ H ₇] ₂ [OC(CH ₃) ₂] ₂ CoH	Co-C _{cage} (2.07) Co-B (2.08) Co-H (NR) Co-Cnt _{cage} (NR)	B-Co-B' (67.6-98.1) Co-B-O (95.9) B-O-B (100)	174
[(Et) ₂ C ₂ B ₄ H ₄]Co[(Et) ₄ C ₄ B ₈ H ₇ OC ₄ H ₈]	Co-B (2.17) Co-C _{cage} (2.23) Co-Cnt _{cage} (1.66)	B-Co-B' (89-129.6) C _{cage} -Co-C' (98, 115.8) Cnt _{cage} -Co-Cnt _{cage} (169.1)	173
{Cp*Co(Et ₂ C ₂ B ₃ H ₂)-5-C(O)Me} ₂ Ni	Co-C _{cage} (2.09) Ni-B (2.07-2.15) Ni-C _{cage} (2.09-2.19) Co-B (2.09) Co-Cnt _{cage} (NR) Co-Cnt _{Cp} (NR) Co-C _{Cp} (NR)	Cnt _{cage} -Ni-Cnt _{cage} (NR) Cnt _{cage} -Co-Cnt _{Cp} (NR)	208
(CpCoC ₄ Ph ₄ BH)	Co-C _{cage} (2.04) Co-B (2.14) Co-C _{Cp} (2.04)	Cnt _{cage} -Co-Cnt _{Cp} (176.7)	176
(C ₅ Me ₅)Co[2,3-Et ₂ C ₂ B ₃ H ₄ -5-C(=CH ₂)OC(O)Me]	Co-C _{cage} (2.06) Co-B (2.04) Co-Cnt _{cage} (NR) Co-Cnt _{Cp} (NR) Co-C _{Cp} (2.06)	Cnt _{cage} -Co-Cnt _{Cp} (NR) C _{ester} -O-C _{ester} (117.7)	98
(η^5 -C ₅ H ₅)Fe(μ -Et ₂ C ₃ B ₂ H ₃)Co(η^5 -C ₅ H ₅)	Co-Cnt _{cage} (1.58) Fe-Cnt _{cage} (1.62) Fe-C _{cage} (2.07) Fe-B _{cage} (2.11) Co-C _{cage} (2.02) Co-B _{cage} (2.09) Co-Cnt _{Cp} (1.65) Fe-Cnt _{Cp} (1.65) Co-C _{Cp} (2.02) Fe-C _{Cp} (2.03)	Cnt _{cage} -Fe-Cnt _{Cp} (NR) Cnt _{cage} -Co-Cnt _{Cp} (NR)	209
2-(η^6 -C ₆ H ₅ Me)-1-[(Me ₃ Si) ₂ CH]-2,1-CoCB ₁₀ H ₁₀	Co-C _{arene} (2.14) Co-B (2.07) Co-C _{cage} (2.14) Co-Cnt _{cage} (NR) Co-Cnt _{arene} (NR)	Cnt _{cage} -Co-Cnt _{arene} (NR)	157
5:1',2'-[1-(η -Cp)Co-2,3-(Me ₃ Si) ₂ C ₂ B ₄ H ₃][B ₂ H ₅]	Co-C _{cage} (2.01)	Cnt _{cage} -Co-Cnt _{Cp} (NR)	95

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
3,3'- <i>commo</i> -Co{[(C ₂ B ₉ H ₉)N(CH) ₂ C(O)OH]}	Co-B (2.11)		
	Co-C _{Cp} (2.00)		
	Co-Cnt _{cage} (NR)		
	Co-Cnt _{Cp} (NR)		
	Co-C _{cage} (2.07)	Cnt _{cage} -Co-Cnt _{cage} (NR)	101
	Co-B (2.06)		
[7,7'-μ-1,3-C ₃ H ₆ -7,8-C ₂ B ₉ H ₁₀) ₂ Co] ⁻	Co-Cnt _{cage} (NR)		
	B-N (1.53)		
	Co-C _{cage} (2.09)	C _{cage} -Co-C' _{cage} (101.9)	102a
	Co-B (2.14)	Co-C _{cage} -C _{bridge} (109.8)	
	C _{cage} -C _{bridge} (1.57)	Cnt _{cage} -Co-Cnt _{cage} (NR)	
	Co-Cnt _{cage} (1.50)		
[7,7'-μ-1,4-C ₄ H ₈ -7,8-C ₂ B ₉ H ₁₀) ₂ Co] ⁻	Co-C _{cage} (2.10)	C _{cage} -Co-C' _{cage} (108)	102a
	Co-B (2.11)	Co-C _{cage} -C _{bridge} (115.9)	
	Co-Cnt _{cage} (1.51)	Cnt _{cage} -Co-Cnt _{cage} (NR)	
	C _{cage} -C _{bridge} (1.56)		
	Co-C _{cage} (2.07)		
	Co-Cnt _{cage} (1.54)	Cnt _{cage} -Co-Cnt _{Cp} (177.3)	146
Cp*Co[(Me ₂ C ₂ B ₃ Me ₃)(μ-H) ₂]	Co-B (2.05)		
	Co-C _{Cp} (2.06)		
	Co-Cnt _{Cp} (1.68)		
	Ni-C _{cage} (2.12)	C _{cage} -Ni-C' _{cage} (102.9)	102a
	Ni-B (2.09)	Cnt _{cage} -Co-Cnt _{cage} (NR)	
	C _{cage} -C _{bridge} (1.51)		
1,1'- <i>commo</i> -Ni[2,4-(SiMe ₃) ₂ -2,4-C ₂ B ₄ H ₄] ₂	Ni-Cnt _{cage} (1.48)		
	Ni-Cnt _{cage} (1.59)	Cnt _{cage} -Ni-Cnt _{cage} (174.4)	104
	Ni-B (2.09)		
	Ni-C _{cage} (2.09)		
	Ni-B (2.17, 2.38)	B-Ni-B (49.8)	96
	Ni-C _{cage} (1.94, 2.52)	B-Ni-C _{cage} (42.2)	
5,7,8-Me ₃ -11,7,8,10-[η ³ -C ₄ Me ₄ H]NiC ₃ B ₇ H ₇	Ni-Cnt _{allylic} (1.78)	C _{cage} -Ni-C _{cage} (103.9)	
	Ni-Cnt _{cage} (NR)	Cnt _{cage} -Ni-Cnt _{allylic} (NR)	
	Ni-C _{cage} (2.07)	Cnt _{cage} -Ni-Cnt _{borolyl} (NR)	210
	Ni-B (2.15)		
	Ni-Cnt _{cage} (1.68)		
	Ni-Cnt _{borolyl} (1.64)		
[(1,4,6-Me ₃ -2,3-Et ₂ -2,3,5-C ₃ B ₃ H)Ni(COD)] ⁺ [BF ₄] ⁻	Ni-C _{cage} (2.11)	Cnt _{cage} -Ni-Cnt _{COD} (NR)	210
	Ni-B (2.12)		
	Ni-Cnt _{cage} (NR)		
	Ni-Cnt _{COD} (NR)		
	Ni-C _{COD} (2.10)		
	Ni-C _{cage} (2.04, 2.26)	N-Ni-N (91.9)	105
[closo-3-(η ² -Ph ₂ B(pz) ₂)-3,1,2-NiC ₂ B ₉ H ₁₁] ⁻	Ni-B (2.11)	Ni-N-N (123.1)	
	Ni...B _{pyrazolyl} (3.20)	N-B-N (107.0)	
	Ni-N (1.92)		
	Ni-Cnt _{cage} (NR)		
	Ni-C _{cage} (2.12)	Br-Ni-C _{cage} (102, 136)	92
	Ni-B (2.14)	Br-Ni-B (93-167.9)	
1-Br-1,5-(PPh ₃) ₂ -1,2,3-Ni(Et ₂ C ₂ B ₄ H ₃)	Ni-Br (2.33)	P-Ni-Br (92.7)	
	Ni-P (2.17)		
	Ni-Cnt _{cage} (NR)		
	B-P (1.88)		
	Ni-Cnt _{cage} (1.69, 1.72)	Cnt _{cage} -Ni-Cnt _{Cp} (NR)	209
	Ni-Cnt _{Cp} (1.74, 1.77)		
(η ⁵ -C ₅ H ₅)Ni(μ-Et ₂ C ₃ B ₂ H ₃)Ni(η ⁵ -C ₅ H ₅)	Ni-B (2.17)		
	Ni-C _{cage} (2.13)		
	Ni-Cnt _{cage} (1.72)	Cnt _{cage} -Ni-Cnt _{Cp} (NR)	209
	Co-Cnt _{cage} (1.60)	Cnt _{cage} -Co-Cnt _{Cp} (NR)	
	Ni-Cnt _{Cp} (1.77)		
	Co-Cnt _{Cp} (1.66)		
(η ⁵ -C ₅ H ₅)Ni(μ-Et ₂ C ₃ B ₂ H ₃)Co(η ⁵ -C ₅ H ₅)	Ni-B (2.14)		
	Ni-C _{cage} (2.12-2.22)		
	Co-B (2.14)		
	Co-C _{cage} (2.02)		
	Ni-C _{cage} (2.11)	Cnt _{cage} -Ni-Cnt _{Cp} (170.5)	157
	Ni-B (2.05)		
2-(η-Cp)-1-[(Me ₃ Si) ₂ CH]-2,1-NiCB ₁₀ H ₁₀	Ni-Cnt _{cage} (NR)		
	Ni-C _{Cp} (2.06)		
	Ni-C _{cage} (2.15)	Cnt _{cage} -Co-Cnt _{cage} (172)	216
	Ni-B (2.07-2.18)	B-Ni-B' (173.7)	
	Ni-Cnt _{cage} (1.56)		
	B-N (1.50)		
<i>dl</i> -3,3'- <i>commo</i> -Ni{[(C ₂ B ₉ H ₉)N] ₂ (CH ₂) ₃ }	Ni-C _{cage} (2.18)	Cnt _{cage} -Co-Cnt _{cage} (169.6)	216
	Ni-B (2.09-2.14)	B-Ni-B' (171.9)	
	Ni-Cnt _{cage} (1.57)		
	B-N (1.50)		
	Ni-C _{cage} (2.18)		
	Ni-B (2.09-2.14)		
<i>meso</i> -3,3'- <i>commo</i> -Ni{[(C ₂ B ₉ H ₉)N] ₂ (CH ₂) ₃ }	Ni-Cnt _{cage} (1.57)		
	B-N (1.50)		
	Ni-C _{cage} (2.18)		
	Ni-B (2.09-2.14)		
	Ni-Cnt _{cage} (1.57)		
	B-N (1.50)		

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
[2-(η^6 -C ₆ Me ₆)- <i>closo</i> -2,1,6-RuC ₂ B ₇ H ₉]	Ru-C _{cage} (2.05, 2.19) Ru-B (2.23) Ru-Cnt _{cage} (NR) Ru-Cnt _{arene} (NR) Ru-C _{arene} (NR)	Cnt _{cage} -Ru-Cnt _{arene} (NR)	151
(MeC ₆ H ₄ CHMe ₂) ₂ Ru ₂ (Et ₂ C ₂ B ₃ H ₃)	Ru...Ru (3.47) Ru-C _{cage} (2.32) Ru-B (2.21) Ru-Cnt _{cage} (NR) Ru-Cnt _{arene} (NR) Ru-C _{arene} (2.15-2.25)	Ru-C _{cage} -Ru (102.8) Ru-B-Ru (103.5) Cnt _{cage} -Ru-Cnt _{arene} (174.8)	141
(MeC ₆ H ₄ CHMe ₂) ₂ Ru(Et ₂ C ₂ B ₃ H ₃)CoCp	Ru...Co (3.29) Ru-C _{cage} (2.21) Ru-B (2.21) Co-C _{cage} (2.04) Co-B (2.08) Ru-C _{arene} (2.14-2.25) Co-C _{Cp} (2.00-2.09) Co-Cnt _{cage} (NR) Co-Cnt _{Cp} (NR)	Co-C _{cage} -Ru (101.3) Co-B-Ru (100.1) Cnt _{cage} -Co-Cnt _{arene} (173.8) Cnt _{cage} -Ru-Cnt _{arene} (NR)	141
2,5,6-(η -C ₆ H ₆)RuC ₂ B ₇ H ₁₁	Ru-C _{cage} (2.15) Ru-B (2.19) Ru-C _{arene} (2.22) Ru-Cnt _{cage} (NR) Ru-Cnt _{arene} (NR)	C _{cage} -Ru-C _{cage} (39.8) B-Ru-B (48.9) Cnt _{cage} -Ru-Cnt _{arene} (NR)	149
[(η^6 -MeC ₆ H ₄ CHMe ₂)Ru(Et ₂ C ₂ B ₃ H ₃)Co(η^5 -Me ₄ C ₅)] ₂ -C ₆ H ₄ -2CH ₂ Cl ₂	Ru-C _{cage} (2.24) Ru-B (2.21) Ru-C _{arene} (2.09-2.26) Ru-Cnt _{arene} (NR) Ru-Cnt _{cage} (NR) Co-B (2.08) Co-C _{cage} (2.07) Co-C _{Cp'} (2.01-2.10) Co-Cnt _{cage} (NR) Co-Cnt _{Cp'} (NR)	Cnt _{cage} -Ru-Cnt _{arene} (NR) Cnt _{cage} -Co-Cnt _{Cp} (NR)	142
[1-(η^6 -MeC ₆ H ₄ - <i>i</i> -Pr)-2,4-Me ₂ -1,2,4-RuC ₂ B ₈ H ₈]	Ru-C _{cage} (2.12, 2.68) Ru-B (2.06-2.36) Ru-Cnt _{cage} (NR) C _{cage} -C _{cage} (1.48) Ru-C _{arene} (NR) Ru-Cnt _{arene} (NR)	Cnt _{cage} -Ru-Cnt _{arene} (172.6)	111
[5-(η^6 -C ₆ Me ₆)-7-(OMe)- <i>arachno</i> -5-RuN(Me)C(H)B ₉ H ₁₁]	Ru-B (2.22-2.35) Ru-C _{arene} (2.18-2.25) B-N (1.48) Ru-Cnt _{cage} (NR) Ru-Cnt _{arene} (NR)	B-N-B (104.4) B-C _{cage} -B (59) Cnt _{cage} -Ru-Cnt _{arene} (NR)	159
[1-(η^5 -C ₅ Me ₅)-2-(NH ₂ Et)-7-(CNEt)- <i>closo</i> -1,2-RhCB ₉ H ₈]	Rh-C _{cage} (2.16) Rh-B (2.12-2.46) Rh-C _{Cp} (2.17-2.28) Rh-Cnt _{cage} (NR) Rh-Cnt _{Cp} (NR)	C _{cage} -N-C _{cage} (117.5, 177.2) Cnt _{cage} -Rh-Cnt _{Cp} (NR)	159
[1-(η^5 -C ₅ Me ₅)-2-Me- <i>closo</i> -1,2,3-RhC ₂ B ₈ H ₉]	Rh-C _{cage} (2.10) Rh-B (2.37) Rh-C _{Cp} (2.19) Rh-Cnt _{cage} (NR) Rh-Cnt _{Cp} (NR)	Cnt _{cage} -Rh-Cnt _{Cp} (NR)	159
(Cp*)Rh(Et ₂ C ₂ B ₃ H ₃)Co(Et ₂ MeC ₃ B ₂ Et ₂)CoCp	Rh...Co (3.32) Rh-C _{cage} (2.20) Rh-B (2.18) Rh-C _{Cp} (2.14-2.22) Rh-Cnt _{cage} (NR) Rh-Cnt _{Cp} (NR) Co...Co (3.23) Co-B (2.09) Co-C _{cage} (2.12) Co-C _{Cp} (2.05) Co-Cnt _{cage} (NR) Co-Cnt _{Cp} (NR)	Co-Co'-Rh (175) Cnt _{cage} -Rh-Cnt _{Cp} (NR) Cnt _{cage} -Co-Cnt _{Cp} (NR) Cnt _{cage} -Co-Cnt _{cage} (NR)	212
(Et ₂ C ₂ B ₄ H ₄)Rh(Et ₂ MeC ₃ B ₂ Et ₂)CoCp	Rh-C _{cage} (2.22) Rh-B (2.24) Co-B (2.05) Co-C _{cage} (2.01) Rh-Cnt _{cage} (1.76, 1.80) Rh-Cnt _{borolyl} (NR) Co-C _{Cp} (2.03)	Cnt _{cage} -Rh-Cnt _{borolyl} (171.4) Cnt _{borolyl} -Co-Cnt _{Cp} (178.1)	213

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
1,2-Ph ₂ -3-(η -C ₅ Me ₅)-3,1,2-pseudo-closo-RhC ₂ B ₉ H ₉	Co-Cnt _{borolyl} (NR)	Cnt _{cage} -Rh-Cnt _{Cp} (NR)	214
	Co-Cnt _{Cp} (NR)		
	Rh-C _{cage} (2.17)		
	Rh-B (2.05-2.23)		
	Rh-C _{Cp} (2.18-2.27)		
[closo-1,2- μ -(1',2'-CH ₂ C ₆ H ₄ CH ₂)-3,3-(PPh ₃) ₂ -3-H-3,1,2-RhC ₂ B ₉ H ₉]	Rh-Cnt _{cage} (NR)	C _{cage} -Rh-C _{aryl} (40.5) B-Rh-B (45.5, 77.8) H-Rh-B (168) P-Rh-P (98.7)	59
	Rh-Cnt _{Cp} (NR)		
	Rh-C _{cage} (2.30)		
	Rh-B (2.26)		
	Rh-P (2.33)		
[exo-nido-6,10-(PPh ₃)(PCy ₃)Rh]-6,10- μ -(H) ₂ -7,8- μ -(1',2'-CH ₂ -C ₆ H ₄ CH ₂)-10,11- μ -(H)-7,8-C ₂ B ₉ H ₇]	Rh-H (1.56)	B-Rh-B (42.4) B-Rh-H _{bridge} (28.2, 70.3) P-Rh-P (99.3)	59
	Rh-Cnt _{cage} (NR)		
	Rh-B (2.36)		
	Rh-H _{bridge} (1.83)		
	Rh-P (2.25)		
[closo-1-Me-2,2-(PEt ₃) ₂ -2-H-8-Ph-2,1,8-RhC ₂ B ₉ H ₉]	Rh-Cnt _{cage} (NR)	B-Rh-B (43.0) B-Rh-H _{bridge} (24, 64) P-Rh-P (95.6)	59
	Rh-B (2.38)		
	Rh-H _{bridge} (1.92)		
	Rh-P (2.23)		
	Rh-Cnt _{cage} (NR)		
[(PPh ₃) ₃ Rh] ⁺ nido-7-R-7,8-C ₂ B ₉ H ₁₁]	Rh-B (2.19)	B-Rh-B (48.2, 82.7) P-Rh-P (102.4) P-Rh-H (19.1) Cnt _{cage} -Rh-P (124) Cnt _{cage} -Rh-O (124) Cnt _{cage} -Rh-C _{acrylate} (118)	59
	Rh-H (1.53)		
	Rh-P (2.35)		
	Rh-C _{cage} (2.25)		
	Rh-B (2.21)		
[closo-1-Me-3,3-(CH ₂ CH ₂ C(O)OBu)-3-PPh ₃ -3,1,2-RhC ₂ B ₉ H ₁₀]	Rh-C _{acrylate} (2.10)	P-Rh-B (96.3-128.5) P-Rh-C _{cage} (96.7, 175.2) P-Rh-Cl (88.0) Cnt _{cage} -Rh-P (NR) Cnt _{cage} -Rh-Cl (NR) Cnt _{cage} -Rh-Cnt _{arene} (NR)	193
	Rh-O (2.18)		
	Rh-P (2.32)		
	Rh-C _{cage} (2.18)		
	Rh-B (2.13)		
[closo-2-PPh ₃ -2-Cl-2,1,7-RhC ₂ B ₉ H ₁₀ -C ₆ H ₆]	Rh-Cl (2.29)		
	Rh-P (2.32)		
	Rh-Cnt _{cage} (NR)		
	Rh-C _{cage} (2.26)		
	Rh-B (2.19)		
[closo-3,3-(η^2 , η^3 -C ₇ H ₇ CH ₂)-1,2-Me ₂ -3,1,2-Rh(C ₂ B ₉ H ₉)]	Rh-C _{allyl} (2.13-2.35)	C-Rh-C (44.3) B-Rh-B (49.3, 83.3) C _{cage} -Rh-B (46.3-80.3) Cnt _{cage} -Rh-Cnt _{Cp} (172.9)	152
	Rh-Cnt _{cage} (NR)		
	Rh-C _{cage} (2.17)		
	Rh-B (2.18)		
	Rh-C _{Cp} (2.15-2.23)		
[3-(η^5 -Cp*)-closo-3,1,2-RhC ₂ B ₉ H ₁₁]	Rh-Cnt _{cage} (NR)	Rh-Pt-P (138.6) Pt-H _{bridge} -Rh (102) Cnt _{cage} -Rh-P (NR) Cnt _{cage} -Rh-Pt (NR)	116
	Rh-Cnt _{Cp} (NR)		
	Rh-C _{cage} (2.31)		
	Rh-B (2.26)		
	Rh-Pt (2.73)		
[RhPt(μ -H)(μ -CO)(PEt ₃) ₂ (PPh ₃)(η^5 -C ₂ B ₉ H ₁₁)]	Rh-H _{bridge} (1.70)	Pt-B-Rh (74.9) Pt-H _{bridge} -B (93) B-Pt-Rh (51.8) Cnt _{cage} -Rh-Pt (NR)	116
	Rh-P (2.33)		
	Rh-CO bridge (1.99)		
	Rh-Cnt _{cage} (NR)		
	Pt-H _{bridge} (1.80)		
[RhPt(σ -C(C ₆ H ₄ Me-4)=C(C ₆ H ₄ Me-4)H)(CO)(PEt ₃) ₂ (PPh ₃)(η^5 -C ₂ B ₉ H ₁₁)]	Pt-CO bridge (1.99)	Cnt _{cage} -Rh-C _{aryl} (125.7) Cnt _{cage} -Rh-P (130.1)	123
	Pt-P (2.33)		
	Rh-B (2.25)		
	Rh-C _{cage} (2.34)		
	Rh-Pt (2.76)		
[closo-3-PPh ₃ -3,3-{C(Ph)C(PPh ₃)C(H)C(Ph)}-3,1,2-RhC ₂ B ₉ H ₁₁]	Rh-P (2.29)	CN _{bridge} -Rh-CN _{bridge} (173.9) P-Rh-CN (85.9-95.9)	123
	Rh-CO (1.84)		
	Rh-Cnt _{cage} (NR)		
	Pt-B (2.29)		
	Pt-P (2.22)		
[closo-3-PPh ₃ -3(μ -CN)-3,1,2-RhC ₂ B ₉ H ₁₁]	Pt-C _{aryl} (2.03)	N-Rh-N (84.6)	105
	Rh-C _{cage} (2.28)		
	Rh-B (2.28)		
	Rh-C _{aryl} (2.06)		
	Rh-P (2.33)		
[closo-3-PPh ₃ -3(μ -CN)-3,1,2-RhC ₂ B ₉ H ₁₁]	Rh-Cnt _{cage} (NR)		
	Rh-C _{cage} (2.21)		
	Rh-B (2.21)		
	Rh-P (2.30)		
	Rh-CN _{bridge} (2.03)		
closo-3-(η^3 -HB(pz) ₃)-3,1,2-RhC ₂ B ₉ H ₁₁	Rh-Cnt _{cage} (NR)		
	Rh-C _{cage} (2.13)		
	Rh-B (2.19)		
	Rh-N (2.13)		
	Rh-Cnt _{cage} (NR)		

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
<i>closo</i> -2-(η^3 -HB(pz) ₃)-2,1,7-RhC ₂ B ₉ H ₁₁	Rh-C _{cage} (2.16) Rh-B (2.14) Rh-N (2.10) Rh-Cnt _{cage} (NR)	N-Rh-N (83.8)	105
[PPN][<i>closo</i> -2-(PPh ₃)-2-{ η^2 -C(<i>m</i> -FC ₆ H ₄)NOC(=O)}-2,1,7-RhC ₂ B ₉ H ₁₁]	Rh-C _{cage} (2.30) Rh-B (2.24) Rh-P (2.26) Rh-C _{aryl} (2.27) Rh-Cnt _{cage} (NR)	P-Rh-B (90.9, 152.6) P-Rh-C _{cage} (112) C _{aryl} -Rh-C _{aryl} (77.8)	122
[Rh ₂ (μ - σ : η^5 -C ₂ B ₉ H ₉ Me ₂)(CO) ₃ (η^5 -C ₂ B ₉ H ₉ Me ₂)] ⁻	Rh-C _{cage} (2.21-2.44) Rh-B (2.05-2.27) Rh-Rh (2.87) Rh-C _{CO} (1.88) Rh-Cnt _{cage} (NR)	Rh-Rh-B (45.3, 48.2)	117
[RhPt(μ -H)(μ -CO)(PEt ₃) ₂ (PPh ₃)(η^5 -7,9-C ₂ B ₉ H ₁₁)]	Rh-C _{cage} (2.33) Rh-B (2.24) Rh-Pt (2.74) Rh-C _{CO} bridge (2.35) Rh-H _{bridge} (1.47) Rh-Cnt _{cage} (NR) Pt-P (2.30) Pt-H _{bridge} (1.75) Pt-C _{CO} bridge (2.01)	Rh-Pt-P (119.9, 135.3) P-Pt-H _{bridge} (91.2) Pt-H _{bridge} -Rh (116.1) P-Rh-H _{bridge} (95.0) Rh-C _{CO} bridge-Pt (87.0)	118
[ReRh{ μ - σ , η^5 -C ₂ B ₉ H ₇ (CH ₂ C ₆ H ₄ Me-4)Me ₂ }(CO) ₄ -(η -C ₅ H ₄ Me)]	Rh-B (2.22) Rh-C _{cage} (2.25) Re-B (2.17) Rh-Re (2.88) Rh-C _{CO} (1.93) Re-C _{CO} (1.92) Re-C _{Cp'} (NR) Rh-Cnt _{cage} (NR) Re-Cnt _{Cp'} (NR)	Rh-Re-B (48.2) Rh-B-Re (83.4)	119
8,8-(PPh ₃) ₂ -8-H-8,7,9-RhCSB ₈ H ₁₀	Rh-C _{cage} (2.17) Rh-B (2.21) Rh-S (2.44) Rh-P (2.33)	Cnt _{cage} -Rh-P (NR)	165
1,1-(PPh ₃) ₂ -1,1-RhCSB ₈ H ₉	Rh-C _{cage} (2.11) Rh-B (2.32-2.46) Rh-S (2.34) Rh-P (2.33)	Cnt _{cage} -Rh-P (NR)	165
[(dppe)PdC ₂ B ₁₀ H ₁₂]	Pd-C _{cage} (2.18, 2.60) Pd-B (2.25-2.45) Pd-P (2.28) Pd-Cnt _{cage} (NR)	B-Pd-P (97.4-165.1)	125
<i>nido</i> -[2-(η^6 -C ₆ Me ₆)-8,10-Me ₂ -2,8,10-OsC ₂ B ₈ H ₈]	Os-B (2.17) Os-C _{cage} (2.26) Os-C _{arene} (2.26) Os-Cnt _{cage} (NR) Os-Cnt _{arene} (NR)	Cnt _{cage} -Os-Cnt _{arene} (NR)	153
[3-(η^5 -Cp*)- <i>closo</i> -3,1,2-IrC ₂ B ₉ H ₁₁]	Ir-C _{cage} (2.16) Ir-B (2.17) Ir-C _{Cp*} (2.15-2.23) Ir-Cnt _{Cp*} (NR) Ir-Cnt _{cage} (NR)	C _{cage} -Ir-C _{cage} (44.0) B-Ir-B (47.8-85.1) C _{cage} -Ir-B (47.1-81.7) Cnt _{cage} -Ir-Cnt _{Cp*} (NR)	115
[1,1-(PPh ₃) ₂ -1-H-1,2,4-IrC ₂ B ₈ H ₁₀]	Ir-C _{cage} (2.19) Ir...C _{cage} (2.77) Ir-B (2.08, 2.34) Ir-P (2.35) Ir-H (1.62) Ir-Cnt _{cage} (NR)	B-Ir-C _{cage} (69.1) Cnt _{cage} -Ir-P (NR)	215
[(PPh ₃)HIrC ₂ B ₁₀ H ₁₁ (OMe)]	Ir-C _{cage} (2.23-2.36) Ir-B (2.30-2.52) Ir-P (2.32) Ir-Cnt _{cage} (NR) Ir-H (NR)	B-Ir-P (79.5-164.3) Cnt _{cage} -Ir-P (NR)	125
[(dppe)PtC ₂ B ₉ H ₁₁]	Pt-C _{cage} (2.50) Pt-B (2.26) Pt-P (2.26) Pt-Cnt _{cage} (NR)	B-Pt-P (97.1-171.6) Cnt _{cage} -Ir-P (NR)	125
[1,1-(PMe ₂ Ph) ₂ -2-Me-1,2,3-PtC ₂ B ₈ H ₉]	Pt-C _{cage} (2.18) Pt-B (2.38) Pt-P (2.28) Pt-Cnt _{cage} (NR)	C _{cage} -Pt-C _{cage} (107.2) Cnt _{cage} -Pt-P (NR)	114
[1,1-(PMe ₂ Ph) ₂ -1,2,3-PtC ₂ B ₈ H ₁₀]	Pt-C _{cage} (2.15) Pt-B (2.43, 2.57) Pt-P (2.26) Pt-Cnt _{cage} (NR)	C _{cage} -Pt-C _{cage} (98.1) Cnt _{cage} -Pt-P (NR)	114

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
[<i>closo</i> -3-(PPh ₃)-3,1,2-CuC ₂ B ₉ H ₁₁] ⁻	Cu-C _{cage} (2.31) Cu-B (2.13) Cu-P (2.14)	C _{cage} -Cu-C _{cage} (40) B-Cu-B (48.6, 80.2) B-Cu-P (127-155.5)	89
[<i>closo</i> -3-(PPh ₃)-4-{4-(C ₅ H ₄ N)CO ₂ CH ₃ }-3,1,2-CuC ₂ B ₉ H ₁₀]	Cu-Cnt _{cage} (1.67) Cu-C _{cage} (2.38, 2.48) Cu-B (2.11, 2.25) Cu-P (2.16) Cu-Cnt _{cage} (1.72) B-N (NR)	Cnt _{cage} -Cu-P (NR) C _{cage} -Cu-C _{cage} (37.4) B-Cu-B (49.5, 80.3) B-Cu-P (127.7-153.3) Cnt _{cage} -Cu-P (NR)	89
[Cu ₃ (μ-H) ₃ {C ₂ B ₉ H ₉ (4-(C ₅ H ₄ N)CO ₂ CH ₃) ₃ }]·n-C ₇ H ₁₆	Cu-Cu' (2.51) Cu-C _{cage} (2.63) Cu-B (2.11-2.30) Cu-H _{bridge} (1.60) Cu-Cnt _{cage} (1.84) B-N (1.55)	Cu-Cu'-Cu'' (60) H _{bridge} -Cu-B (111.8-156.6) B-Cu-B (47/8, 74.3) Cu-H-B (96.4)	89
<i>meso</i> -3,3'- <i>commo</i> -Cu[(C ₂ B ₉ H ₉ N) ₂ (CH ₂) ₃]	Cu-C _{cage} (2.22-2.35) Cu-B (2.15) Cu-Cnt _{cage} (1.67) B-N (1.51)	Cnt _{cage} -Cu-Cnt _{cage} (165.9) B-Cu-B' (167.4)	216
AgB ₁₁ CH ₁₂ ·2C ₆ H ₆	Ag-H (1.97) Ag...B (2.58-2.95) Ag-C _{arene} (2.40)		164
IrCl(CO)(PPh ₃) ₂ ·Ag(B ₁₁ CH ₁₂)	Ag-H (1.06) Ag...B (2.52) Ag-Ir (2.68)		161
Li[(HgC ₂ B ₁₀ H ₁₀) ₄ Cl]	Hg-C _{cage} (2.09) Hg-Cl (2.94)	C _{cage} -Hg-C' (162) Hg-C _{cage} -C _{cage} (125.7)	128
f-Block Metal Complexes			
[3,3-(THF) ₂ - <i>commo</i> -3,3'-Sm(3,1,2-SmC ₂ B ₉ H ₁₁) ₂]-[PPN] ⁺	Sm-C _{cage} (2.72) Sm-B (2.72) Sm-Cnt _{cage} (2.33) Sm-O (NR)	Cnt _{cage} -Sm-O (104-111) Cnt _{cage} -Sm-Cnt _{cage} (131.9)	179
{[η ⁵ -1-Sm-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₃ {(μ ₂ -1-Li-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄) ₃ (μ ₃ -OMe)}[μ ₂ -Li(C ₄ H ₈ O)] ₃ (μ ₃ -O)}	Sm-Cnt _{cage} (2.40) Sm-O (2.21) Li-Cnt _{cage} (1.85) Li-O (1.83) Sm-C _{cage} (2.74) Sm-B (2.69-2.86) Li-B (2.29-2.54) Li-C _{cage} (2.16)	Cnt _{cage} -Sm-O (115.9) Sm-O-Sm (119.2) Li-O-Li (107.8) Li-O-C _{OMe} (107.4-114.1)	67
[1,1,1-(t-C ₄ H ₉ OH) ₃ -2,3-(SiMe ₃) ₂ -4,5-{Li(C ₄ H ₈ O)Cl}- <i>closo</i> -η ⁵ -1-Sm-2,3-C ₂ B ₄ H ₄]-C ₄ H ₈ O	Sm-Cnt _{cage} (2.44) Sm-O (2.10-2.31) Sm-C _{cage} (2.73) Sm-B (2.77-2.90) Li-B (2.52) Li-Cl (2.60) Li-O (1.98)	O-Sm-Cnt _{cage} (113.3) O-Sm-O (77, 113.4) Sm-O-Li (100.1) Sm-B-Li (75.3) O-Li-O (136.6) B-Li-O (92.7-106.5)	67
[<i>closo</i> -1,1,1-(MeCN) ₃ -1,2,4-EuC ₂ B ₁₀ H ₁₂] _n	Eu-C _{cage} (2.96, 3.12) Eu-B (2.83, 3.05) Eu-N (2.66-2.76) Eu-Cnt _{cage} (NR)	Cnt _{cage} -Eu-N (NR)	183
[1,1-(THF) ₂ - <i>commo</i> -1,1'-Eu(C ₂ B ₁₀ H ₁₂) ₂] ²⁻	Eu-O (2.63) Eu-B (2.98-3.09) Eu-C _{cage} (2.89, 3.20) Eu-Cnt _{cage} (NR)	B-Eu-B (127.4) O-Eu-O (74.8) B-Eu-O (110.7) Cnt _{cage} -Eu-Cnt _{cage} (NR)	183
{[η ⁵ -1-Gd-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₃ {(μ ₂ -1-Li-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄) ₃ (μ ₃ -OMe)}[μ ₂ -Li(C ₄ H ₈ O)] ₃ (μ ₃ -O)}	Gd-Cnt _{cage} (2.37) Gd-O (2.19) Gd-C _{cage} (2.70) Gd-B (2.69) Li-Cnt _{cage} (1.82-1.89) Li-C _{cage} (2.17) Li-B (2.24-2.40) Li-O (1.85)	Cnt _{cage} -Gd-O (115.9) Gd-O-Gd (119.1) Cnt _{cage} -Li-O (170) Li-O-Li (106) Li-O-C _{OMe} (113)	66
{[η ⁵ -1-Tb-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₃ {(μ ₂ -1-Li-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄) ₃ (μ ₃ -OMe)}[μ ₂ -Li(C ₄ H ₈ O)] ₃ (μ ₃ -O)}	Tb-C _{cage} (2.71) Tb-B (2.72) Tb-O (2.18) Tb-Cnt _{cage} (2.36) Li-B (2.30-2.41) Li-O (1.88) Li-Cnt _{cage} (NR) Li-C _{cage} (2.13)	C _{cage} -Tb-C _{cage} (32.8) B-Tb-B (34.7) Cnt _{cage} -Tb-O (NR) Tb-O-Tb (119.0) Li-O-Li (106) Li-O-C _{OMe} (113.4)	67
{[η ⁵ -1-Dy-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄] ₃ {(μ ₂ -1-Li-2,3-(SiMe ₃) ₂ -2,3-C ₂ B ₄ H ₄) ₃ (μ ₃ -OMe)}[μ ₂ -Li(C ₄ H ₈ O)] ₃ (μ ₃ -O)}	Dy-C _{cage} (2.69) Dy-B (2.68) Dy-O (2.18) Dy-Cnt _{cage} (2.32)	C _{cage} -Dy-C _{cage} (32.5) B-Dy-B (34.8) Cnt _{cage} -Dy-O (NR) Dy-O-Dy (120.1)	67

Table I. (Continued)

compound	M-X (length, Å)	X-Y-X' (angle, deg)	ref
[$\{\eta^5\text{-1-Ho-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4\}\{\mu_2\text{-1-Li-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4\}_3(\mu_3\text{-OMe})\{\mu_2\text{-Li-C}_4\text{H}_8\text{O}\}_3(\mu_3\text{-O})\}$]	Li-B (2.23–2.42)	Li-O-Li (105.3)	67
	Li-O (1.88–1.95)	Li-O-COMe (113.1)	
	Li-Cnt _{cage} (NR)		
	Li-C _{cage} (2.19)		
	Ho-Cnt _{cage} (2.33)	Cnt _{cage} -Ho-O (117.4)	
	Ho-C _{cage} (2.70)	Ho-O-Ho (118.8)	
	Ho-B (2.69)	Li-O-Li (104.1)	
	Ho-O (2.15)	Li-O-COMe (109.2–117.9)	
	Li-B (2.26–2.46)		
	Li-C _{cage} (2.14)		
	Li-Cnt _{cage} (1.86)		
	Li-O (1.82–1.95)		
Yb(C ₂ B ₉ H ₁₁)(DMF) ₄	Yb-B/C _{cage} (2.74)	O-Yb-O (90)	179
[U(C ₂ B ₉ H ₁₁) ₂ Cl ₂][Li(OC ₄ H ₈) ₄] ₂	Yb-O (2.37)		190
	U-B (2.64–2.86)	Cl-U-Cl (90.3)	
	U-Cl (2.59)	Cnt _{cage} -U-Cnt _{cage} (137)	
	Li-O (1.92)	Cnt _{cage} -U-Cl (NR)	
	U-C _{cage} (2.73)		
	U-Cnt _{cage} (NR)		

^a Mean values are given for bond angles and bond lengths. Cnt denotes the centroid of the bonding face. NR means not reported.

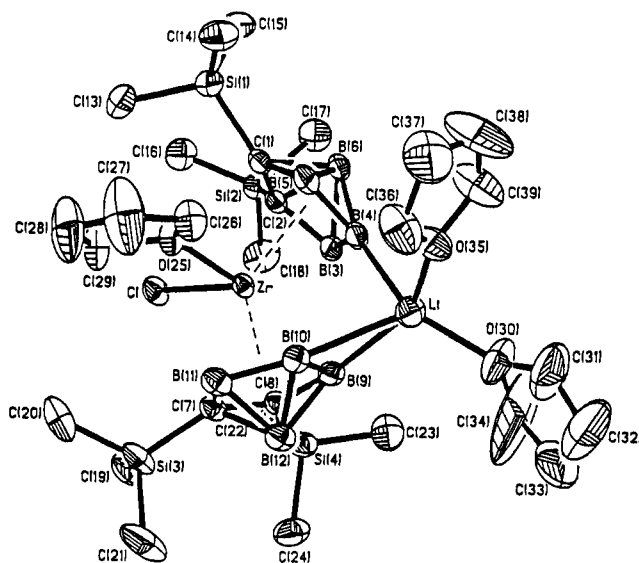


Figure 4. An ORTEP drawing of a zwitterionic zircona-carborane sandwich complex. Reprinted from ref 29. Copyright 1990 American Chemical Society.

[$\eta^5\text{-(C}_5\text{H}_5)_2$] ZrCl_2 .³⁶ The coordination geometry of the zirconium metal was described as a distorted tetrahedron whose vertices are occupied by a Cl atom, a THF molecule, and two C₂B₄ cages. Since the Zr metal is bonded to a chlorine atom as well as the carborane cages, for charge compensation an additional Li⁺(THF)₂ moiety is bound to the unique boron and one other boron of the carborane faces within the coordination sphere so as to form a formal "zwitterion" consisting of an anionic {Zr(Cl)(THF)[$\eta^5\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4$]₂}⁻ sandwich that is complexed with an exo-polyhedral [Li(THF)₂]⁺ cation. The bent-sandwich geometry of the complex has been rationalized on the basis of the location of the THF molecule and the Cl atom on the metal with the average Cl-Zr-THF angle of 90°, thus resembling those of the metallocene derivatives. With the exception of the number of Li⁺-bound THF's, all of the zirconium- and hafnium-sandwiched metalla-carboranes are isostructural as determined by X-ray crystallography.^{29–31} For comparison, the crystal structure of a hafnacarborane of a similar ligand system, 4',5',6-Li(THF)-1,1'-*commo*-Hf(THF)Cl[2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₄]₂, is shown in Figure 5.

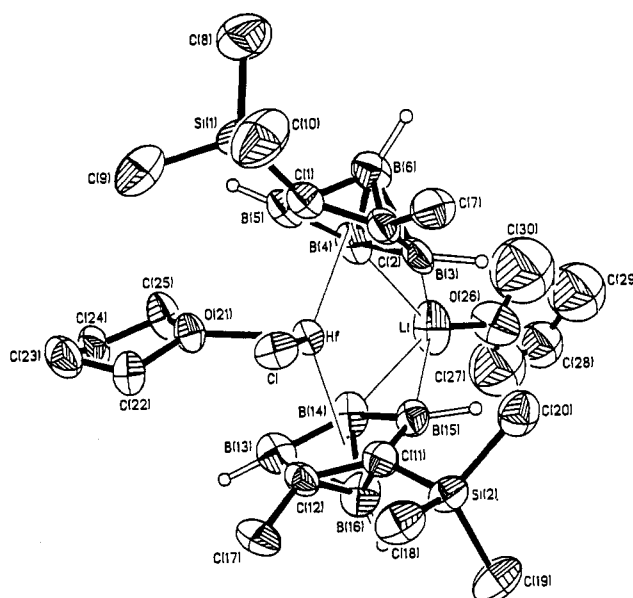


Figure 5. Crystal structure of 1-Cl-1-(THF)-2,2'-(SiMe₃)₂-3,3'-Me₂-4',5,5',6'-Li(THF)[1,1'-*commo*-Hf(C₂B₄H₄)₂]. Reprinted from ref 30. Copyright 1993 International Union of Crystallography.

The presence of a Cl atom and THF molecules on the metals provides a new dimension to the chemistry of these complexes as these could be converted to a neutral, THF-free and alkyl-substituted derivative of the type R'M[(R₂C₂B₄H₄)₂Li] (M = Zr, Hf) that does not possess a counterion outside the coordination sphere. Since 14-electron, d⁰, alkyl-substituted and solvent-free bent metallocene [(C₅R₅)₂M(R')]⁺ with the selective counteranion such as methylaluminoxane has proven to be an effective catalyst in the Ziegler-Natta olefin polymerization, the bent-sandwich carborane complexes, described above, could be developed as better catalysts than the corresponding Cp analogues.³⁷ Such neutral, isoelectronic, carborane-based complexes could obviate the severe problems of devising an innocent, noncoordinating counteranion which have complicated the metallocene systems. In fact, it was demonstrated most recently by Jordan et al. that a new class of neutral, d⁰, group 4 metal bent-metallocene-carborane complexes of the general formula [(Cp*)M(R)(C₂B₉H₁₁)] (M = Zr,

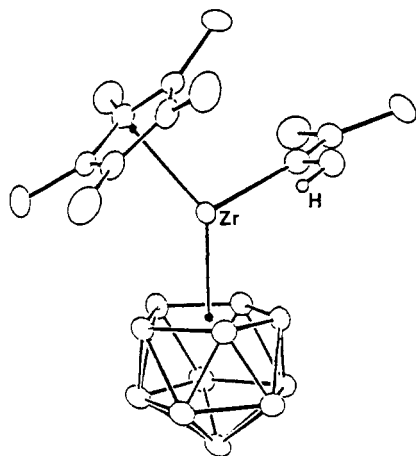


Figure 6. X-ray structure of $\text{Cp}^*(\text{C}_2\text{B}_9\text{H}_{11})\text{Zr}[\text{C}(\text{Me})=\text{CMe}_2]$. Reprinted from ref 32. Copyright 1991 American Chemical Society.

Hf) can be synthesized and structurally characterized.³² The synthesis and reactivity of this novel class of compounds are summarized in Scheme I.

As can be seen from Scheme I, both Zr and Hf sandwich complexes react with 2-butyne via single insertion to yield the monomeric alkenyl complexes $(\text{Cp}^*)(\text{C}_2\text{B}_9\text{H}_{11})\text{M}[\text{C}(\text{Me})=\text{C}(\text{Me})_2]$. The crystal structure of the Zr complex (see Figure 6)³² unambiguously shows its bent-sandwich geometry at the metal center similar to those described above.²⁹⁻³¹ The alkenyl group lies in the plane between the two η^5 ligands and is distorted by an agostic interaction involving one of the β -Me hydrogens. The neutral complexes, $[(\text{Cp}^*)\text{M}(\text{R})(\text{C}_2\text{B}_9\text{H}_{11})]$ ($\text{M} = \text{Zr}, \text{Hf}$), are found to be moderately active catalysts in ethylene polymerization as evidenced by the room temperature oligomerization of propylene to 2-methylpentene predominantly (see Scheme I). Thermolysis of the Zr complex in toluene- d_8 at 45 °C quantitatively yields the novel methyldene-bridged complex, while the hafnium complex undergoes a slower CH_4 elimination, even at 75 °C, to yield the analogous CH_2 -bridged dimeric complex. The crystal

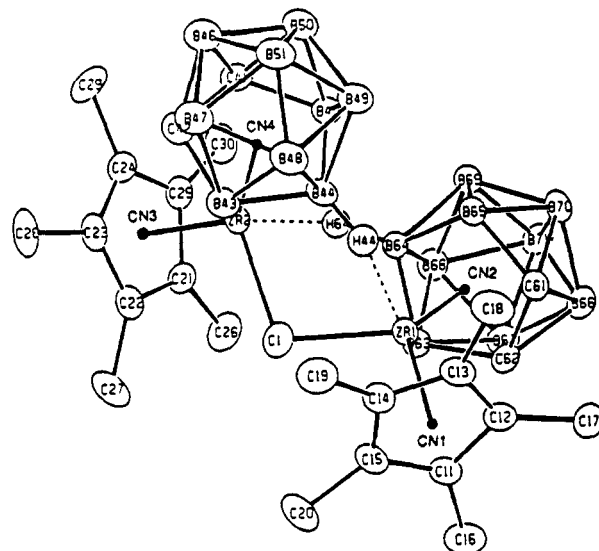
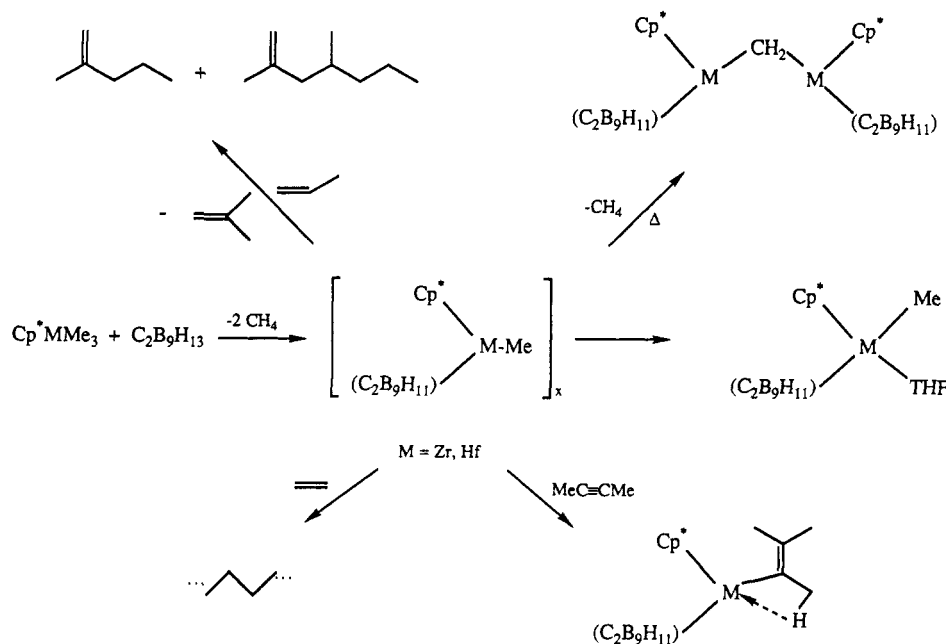


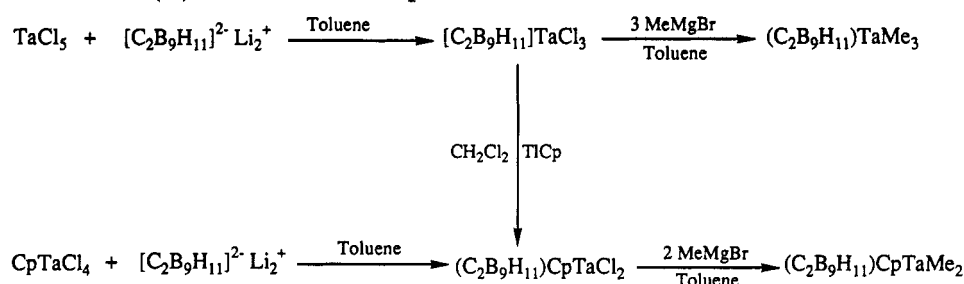
Figure 7. X-ray structure of $[(\text{Cp}^*)(\text{C}_2\text{B}_9\text{H}_{11})\text{Zr}]_2(\mu\text{-CH}_2)$. Reprinted from ref 32. Copyright 1991 American Chemical Society.

structure of the methyldene-bridged Zr complex $[(\text{Cp}^*)(\text{C}_2\text{B}_9\text{H}_{11})\text{Zr}]_2(\mu\text{-CH}_2)$, shown in Figure 7, exhibits two bent-metalocene-carborane Zr centers bridged by a CH_2 group.³² The centroid-Zr-centroid angle is 134.9° and the Zr-centroid distances are 2.234 Å (Zr-Cp*) and 2.091 Å (Zr-C₂B₉H₁₁). There are close B-H...Zr contacts involving a B-H bond of each dicarbollide ligand and the Zr (Zr...H = 2.09 Å). The bond distances and angles are consistent with the increased steric crowding in the complex. Thus, the work of Jordan et al.³² suggests that 14-electron, d^0 , mixed-ligand bent-metalocene complexes are highly electrophilic as evidenced by the high olefin and acetylene insertion reactivity and by the facile reactions leading to CH_2 -bridged dimeric complexes. These promising results have led Jordan et al. to synthesize a number of high-valent tantalum complexes as precursors to cationic, d^0 , and mixed-ligand Ta-alkyl derivatives such as $[(\text{Cp})$ -

Scheme I. Synthesis and Reactivity of Bent-Metalocene-Carborane Complexes of Group 4 Metals (Reprinted from ref 32. Copyright 1991 American Chemical Society)



Scheme II. Syntheses of Ta(V) Dicarbollide Complexes



$(\text{C}_2\text{B}_9\text{H}_{11})\text{Ta}(\text{R})(\text{L})]^+$.³⁸ Since this complex is isoelectronic and isostructural with group 4 alkyl of the type $[(\text{C}_5\text{R}_5)_2\text{M}(\text{R}')^+]$,²⁷ a rich insertion, olefin polymerization, and C–H activation chemistry with the mixed-ligand bent-sandwiched tantalum(V) complexes could also be expected. Scheme II represents the systematic synthetic approach to these novel bent-metalocene-carborane complexes.³⁸ The crystal structure of one of the precursors, $(\text{C}_2\text{B}_9\text{H}_{11})\text{TaCl}_3$, shows that the complex consists of a monomeric, three-legged piano-stool geometry with the dicarbollide ligand symmetrically bonded to the apical TaCl_3 unit (see Figure 8), thus resembling the structure of CpTiCl_3 .³⁹ As described in Scheme II, this complex reacts further with 1 equiv of TICp' in CH_2Cl_2 to produce a mixed-ligand bent-metalocene-carborane complex, $\text{Cp}'(\text{C}_2\text{B}_9\text{H}_{11})\text{TaCl}_2$, which could also be prepared directly from the reaction of dicarbollide dianion with $\text{Cp}'\text{TaCl}_4$ in toluene.³⁸ The structure of this mixed-ligand Ta precursor was also determined by X-ray crystallography. As can be seen in Figure 9, the compound adopts a monomeric bent-metalocene-type structure with the $(\text{C}_2\text{B}_3 \text{ centroid})\text{--Ta--}(\text{Cp}' \text{ centroid})$ angle of 133.5° and Cl--Ta--Cl angle of about 92° , which are similar to those observed for $d^0 \text{Cp}_2\text{MX}_2$ complexes.³⁶ The Ta–dicarbollide distances are almost identical to those found in the previous Ta complex with Ta–B and Ta–C distances ranging from 2.45 to 2.50 Å. However, the shorter Ta– $(\text{C}_2\text{B}_3 \text{ centroid})$ distance (2.011 Å), 0.1 Å less than the Ta– $(\text{Cp}' \text{ centroid})$ distance, is in line with the general trend of stronger donor ability of the carborane ligands versus a Cp ligand.

It is clear from the recent results, described above in the area of sandwiched metallacarborane-metalocene derivatives containing Sc, Y, Zr, and Hf metals, that a fascinating and potentially useful research is emerging.^{26,28–32,38}

The first anionic chromium sandwich complex, $[3,3'\text{-Cr}\{1,2\text{-(Me)}_2\text{-}1,2\text{-C}_2\text{B}_9\text{H}_9\}_2]^-$, and the corresponding mixed Cp-carborane analogue, $(\eta^5\text{-Cp})\text{Cr}(\text{C}_2\text{B}_9\text{H}_{11})$, were synthesized nearly 25 years ago by Hawthorne and co-workers.⁴⁰ The crystal structure of the sandwich complex consisted of two icosahedral cages fused at the formal Cr(III) metal ion.⁴¹ Unlike the chromicinium analogue and the mixed ligand complex, the *commo*-chromacarborane is stable to hydrolysis and is not affected even by hot concentrated sulfuric acid. In addition, the complex could not be reduced to the corresponding Cr(II) species when treated with sodium amalgam or oxidized to Cr(IV) species with strong oxidizing reagents, without cluster demolition.⁴⁰ However, the first anionic, formal Cr(III) sandwich complex of a C_2B_4 carborane system, that could be oxidized to the corresponding neutral Cr(IV) complex, was reported only recently.^{10,42} The anionic sandwich complex of the type $[1,1'\text{-commo-Cr}\{2\text{-(SiMe}_3\text{)}\text{-}3\text{-(R)}\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4\}_2]^-$

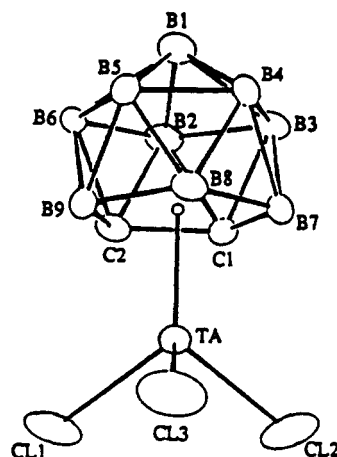


Figure 8. Structure of $(\text{C}_2\text{B}_9\text{H}_{11})\text{TaCl}_3$. Reprinted from ref 38. Copyright 1992 American Chemical Society.

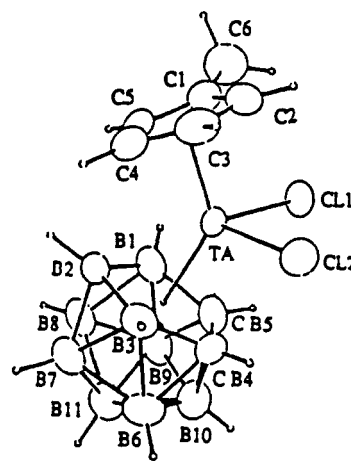


Figure 9. Structure of $\text{Cp}'(\text{C}_2\text{B}_9\text{H}_{11})\text{TaCl}_2$. Reprinted from ref 38. Copyright 1992 American Chemical Society.

($\text{R} = \text{SiMe}_3, \text{Me}, \text{H}$), with the counterion $\text{Li}(\text{THF})_4$ or $\text{Li}(\text{TMEDA})_2$, was synthesized from the reaction between CrCl_3 and the corresponding THF-solvated lithium sodium double salt in a molar ratio of 1:2 in benzene, followed by extraction and crystallization of the product from a solution of benzene and THF or TMEDA as shown in Scheme III.⁴² The structures of these complexes were determined by X-ray crystallography. The structures reveal that the chromacarborane complexes are all ionic species in which the Cr metal is parallel sandwiched by the two carborane ligands with the slight slippage of the metal toward the cage carbons (av $\text{Cr--C} = 2.17 \text{ Å}$, av $\text{Cr--B} = 2.25 \text{ Å}$) giving rise to a C_{2h} symmetry for the $\text{Cr}(\text{C}_2\text{B}_4)_2$ cage framework.⁴² A representative structure of the complex, when $\text{R} = \text{SiMe}_3$, is shown in Figure 10.

The Cr–C(cage) bond distances are shorter than those (2.26 and 2.27 Å) found in the corresponding icosahedral

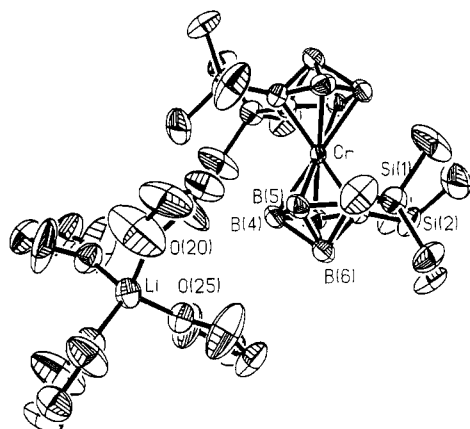
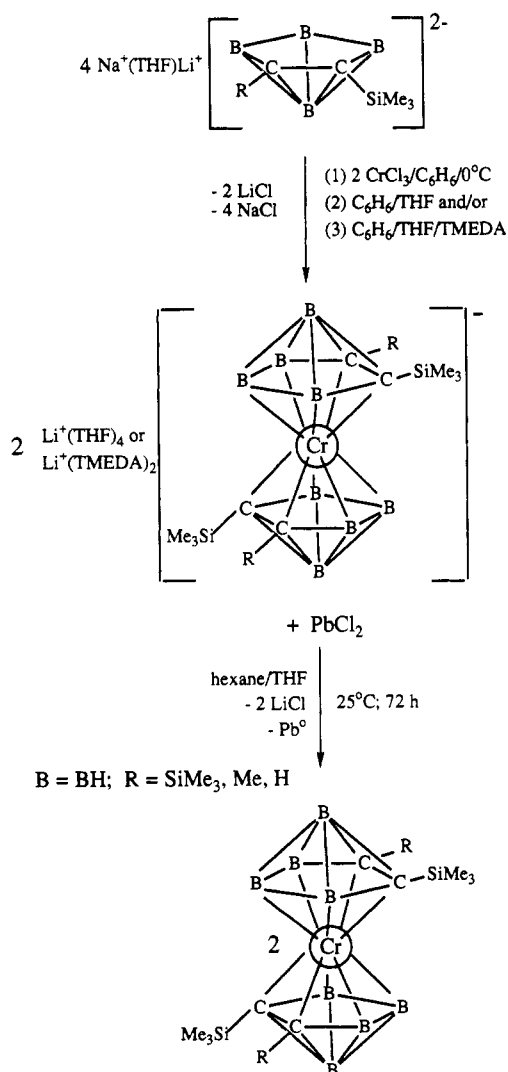


Figure 10. Molecular structure of $\text{Li(THF)}_4\{1,1'\text{-commo-Cr[2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4\}_2\}$. Reprinted from ref 42. Copyright 1992 American Chemical Society.

Scheme III. Syntheses of Cr(III) and Cr(IV) Complexes (Reprinted from ref 42. Copyright 1992 American Chemical Society)



analogue⁴¹ and about the same as those in the mixed-ligand complex, $1\text{-Cr}(\eta^7\text{-C}_7\text{H}_7)\text{-2,3-(Et)}_2\text{-2,3-C}_2\text{B}_4\text{H}_4$,⁴³ and in chromocene.⁴⁴ The ESR spectrum of the anionic Cr complex, $\{[(\text{SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]_2\text{Cr}\}^-$, exhibits an unresolved ESR signal at $g = 1.989$ with a peak to peak line width of 2.2 mT. The observed signal is too broad for detection of ⁵³Cr isotope splitting which is typically in the order of 1.5 mT. However, the solid-state low-

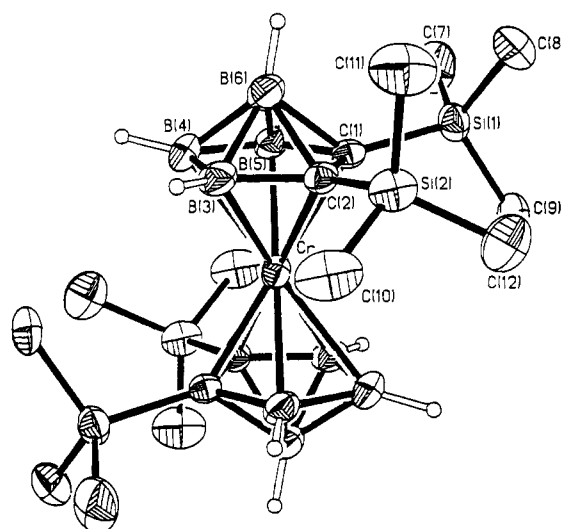


Figure 11. Perspective view of the neutral Cr(IV) complex. Reprinted from ref 10. Copyright 1992 American Chemical Society.

temperature ESR spectrum exhibits the characteristic features of Cr(III) (d^3) centers with large zero-field splitting D . The effective magnetic moment of $3.93 \mu_B$ at room temperature is consistent with an $S = 3/2$ paramagnetic system that follows the Curie law with a Curie constant of 1.933 and a g value of 2.03.⁴²

The chemical oxidation of the anionic Cr(III) sandwich species with PbCl_2 produced the novel, diamagnetic, and neutral Cr(IV) sandwich complexes as dark-red, air-sensitive, and crystalline solids in 63% yields (see Scheme III). The structure of the oxidized species, when $\text{R} = \text{SiMe}_3$, was determined by X-ray diffraction and is shown in Figure 11.^{10,42} The structure shows that the Cr^{IV} metal is not symmetrically bonded to the C_2B_3 faces, but is slightly dislocated toward the cage carbons. This slippage produces Cr-C distances that are about 0.14 Å shorter than the average Cr-B distances. Although the experimental deviations tend to mask any differences in the analogous bond lengths in the Cr(III) precursor, the bond distances suggest a similar slip distortion is occurring in all complexes regardless of the difference in formal charges of the metal atoms.^{10,42} The effective magnetic moment of $0.99 \mu_B$ at 25°C indicates the presence of some paramagnetic impurities, such as unoxidized Cr^{III} precursor or products of the reaction of Cr^{IV} complex with the sample holder. Nonetheless, the singlet state of the complex is consistent with the observation that its well-resolved ¹H, ¹¹B, and ¹³C NMR spectra could be obtained.^{10,42}

Fenske-Hall MO calculations on the model compounds, $[1,1'\text{-commo-Cr}\{2,3\text{-C}_2\text{B}_4\text{H}_6\}_2]^-$ and $1,1'\text{-commo-Cr}\{2,3\text{-C}_2\text{B}_4\text{H}_6\}_2$, revealed that the Cr bonds to the carborane cages mainly with its d_{xz} and d_{yz} orbitals, and the d^3 electrons of the metal are distributed in MO's $29a_g$, $30b_g$, and $31a_g$ (see Figure 12).⁴² Despite the structural similarity, as one goes from the Cr(III) sandwich to the corresponding Cr(IV) species, there is an increase in the energy difference between MO's $29a_g$ and $30b_g$. However, in view of the calculated orbital energy separations in the paramagnetic Cr(III) species including the icosahedral analogue and chromocene, it is difficult to rationalize how depopulation of MO $31a_g$ could induce spin pairing in the two lower energy orbitals. X α -scattered wave SCF MO calculations on

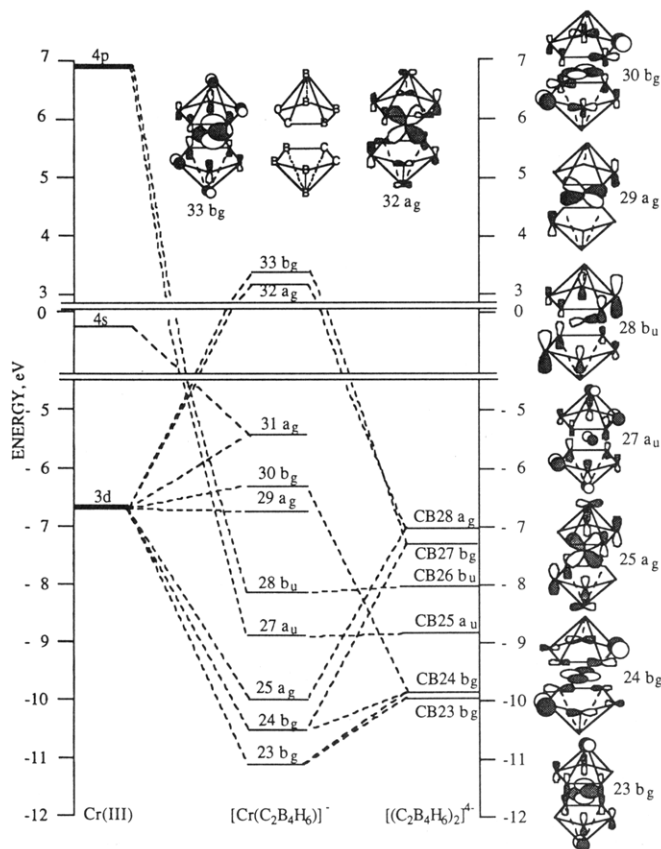
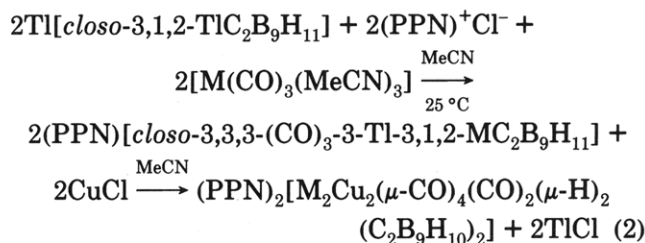


Figure 12. Molecular orbital correlation diagram for $\{1,1'\text{-commo-Cr}[2,3\text{-C}_2\text{B}_4\text{H}_6]_2\}^-$. Reprinted from ref 42. Copyright 1992 American Chemical Society.

both species showed essentially the same results as did the Fenske–Hall calculations, that the metal d electrons are distributed in a set of three closely spaced metal centered MO's very similar to those described above (see Figure 12).⁴² One other possibility is that of a singlet... $(29a_g)^1(30b_g)^1$ configuration that could arise from unusually large zero-field splitting in the triplet state, or by some other interaction. Such a configuration would be more consistent with the MO analysis. However, it is not apparent how such interaction could

arise. Since the unit cell of the structure of Cr(IV) sandwich complex consists of four molecules that are well separated with the shortest Cr–Cr distance of 9.851 Å, it seems unlikely that intermolecular interactions could be an important factor for spin pairing in the complex to yield a diamagnetic species.

The syntheses and structures of polynuclear metal clusters, so-called “clustered clusters”, have dominated the chemistry of d-block elements in recent years. In addition to several interesting papers by Hawthorne and co-workers, Stone's research group has contributed significantly to this area of research.⁴⁵ The first in the series of heterotetranuclear metallacarboranes has been $[\text{M}_2\text{Cu}_2(\mu\text{-CO})_4(\text{CO})_2(\mu\text{-H})_2(\text{C}_2\text{B}_9\text{H}_{10})_2]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$), whose $(\text{PPN})_2$ salt was synthesized, in yields of 18–61%, as shown in eq 2.⁴⁶



The structure of the Mo complex was determined by X-ray diffraction which displays well-separated PPN^+ cations and cluster anion consisting of a planar MoCu_2Mo rhomb that is incorporated into two 12-vertex molybdacarboranes with C_{2h} symmetry (Figure 13). Two uneven MoCu_2 triangles share the Cu–Cu edge to form a heteronuclear “raft”. The shorter of the two Mo–Cu distances, the first known bonds (2.656 and 2.834 Å) between Mo^0 and Cu^{I} metals, is also associated with two CO groups that bridge the metal atoms.⁴⁶

An interesting bimetallic cluster $(\text{PPN})[\text{closo-3,3,3-(CO)}_3\text{-3-(SnPh}_3\text{)-3,1,2-M(C}_2\text{B}_9\text{H}_{11})]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), that incorporates both transition and main group metals, has been synthesized in an analogous reaction, described in eq 2.⁴⁷ The crystal structure of the tungstacarborane derivative, shown in Figure 14, consists of a discrete anion of metallacarborane fragment

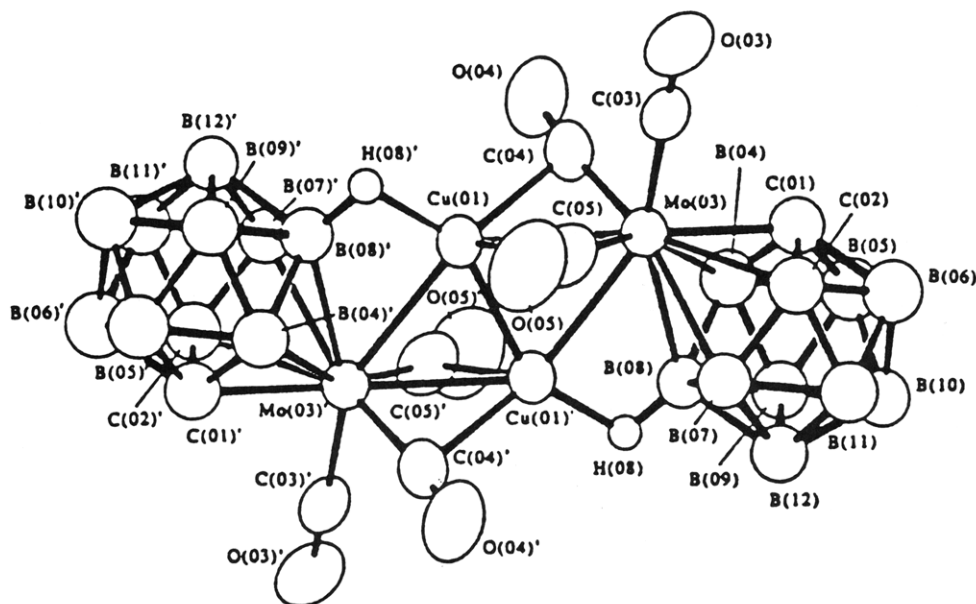


Figure 13. Structure of $[\text{Mo}_2\text{Cu}_2(\mu\text{-CO})_4(\text{CO})_2(\mu\text{-H})_2(\text{C}_2\text{B}_9\text{H}_{10})_2]^{2-}$. Reprinted from ref 46. Copyright 1987 American Chemical Society.

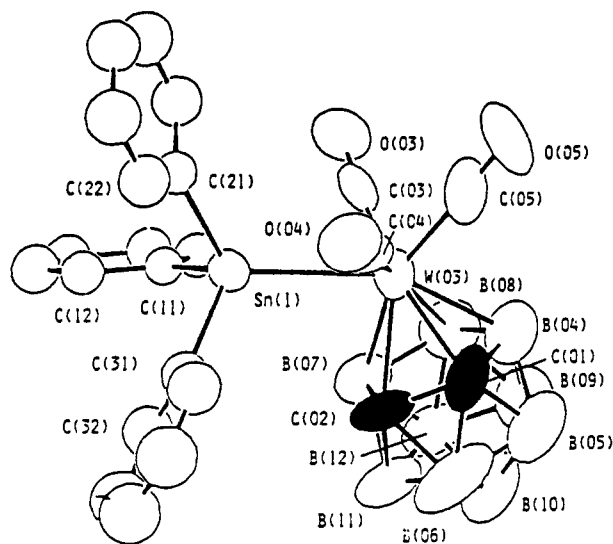


Figure 14. A view of the molecular structure of [closo-3,3,3-(CO)₃-3-SnPh₃-3,1,2-WC₂B₉H₁₁]⁻. Reprinted from ref 47. Copyright 1991 Elsevier Sequoia.

and the PPN⁺ cation (not shown). The transition metal unit, while bonding to SnPh₃ group, caps the pentagonal C₂B₃ plane of the *nido*-carborane dianion to form a 12-vertex *closo*-WC₂B₉ cluster. The W-Sn distance of 2.825 Å is similar to those observed in the structures of [(W(CO)₃(C₅H₅)₂SnPh₂)] (2.81 Å)⁴⁸ and [(μ-Cl)-(MeSnCl₂)W(CO)₃(MeSCH₂CH₂SMc)] (2.759 Å),⁴⁹ thus indicating dπ-dπ bonding between formal W⁰ and Sn^{IV} metals, that is consistent with the ¹¹⁹Sn NMR spectrum of the complex.⁴⁷ This work, together with the earlier study, suggests that a number of heteropolynuclear cluster complexes, including the mixed main group and transition metal species, can be synthesized. Since alkylidyne-metal cluster chemistry has been instrumental in the success of Fischer-Tropsch reactions and alkyne metathesis, a merger of chemistry between alkylidyne-metal and metallacarborane clusters has long been expected. In fact, the pioneering work of Stone and co-workers has profitably exploited the isolobal analogy between the organometallic species [W(≡CR)(CO)₂(η⁵-C₅R'₅)] and [W(≡CR)(CO)₂(η⁵-C₂B₉H₉R'₂)] (R' = H, Me). Since most of Stone's published work, prior to 1990, has been reviewed,⁴⁵ our discussion will be limited to the recently published work in this area of active research.

In series of papers, Stone and co-workers have studied the protonation reactions of alkylidyne(carborane) complexes of group 6 metals with HBF₄·Et₂O or HI alone or in the presence of varieties of unsaturated substrate molecules.⁵⁰⁻⁵⁶ The protonation of the salt [NEt₄][W(≡CR)(CO)₂(η⁵-C₂B₉H₉Me₂)] (where R = C₆H₄Me-4, Me) with HBF₄·Et₂O affords a product in which the CR group has migrated from tungsten to the C₂B₉ fragment. The migration of C₆H₄Me-4 group was confirmed by the crystal structure of [W(CO)₂(PPh₃)₂(η⁵-C₂B₉H₈(CH₂C₆H₄Me-4)Me₂)]⁵². The influence of the C_(cage)-substituents on the dicarbollide ligands has also been observed in most of the protonation reactions. This reactivity pattern is different from the isolobal cyclopentadienyl analogues [W(≡CR)(CO)₂(η⁵-C₅R'₅)] (where R' = H, Me).⁵⁷ The protonation probably proceeds via the initial formation of an alkylidyne-tungsten complex [W(≡C(H)R)(CO)₂(η⁵-C₂B₉H₉Me₂)] in which the metal center is electronically unsaturated. Addition of CO molecules presumably promotes the

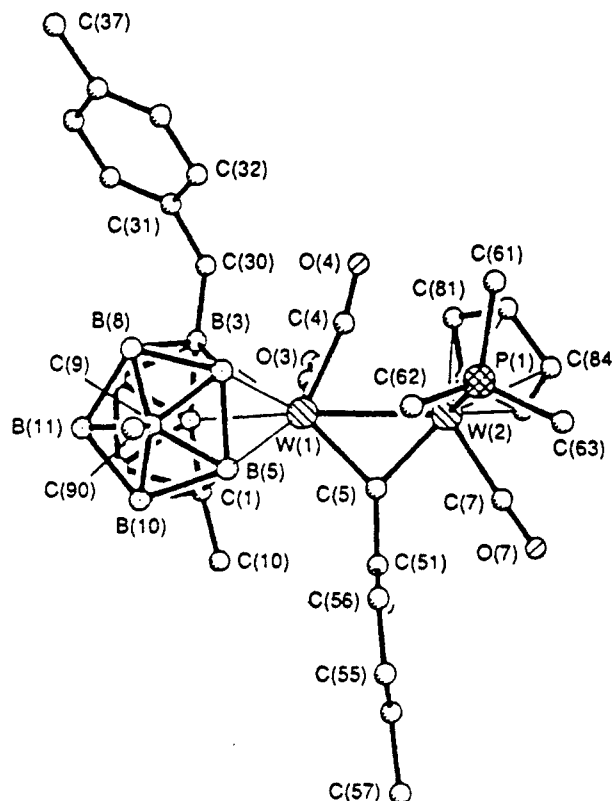


Figure 15. The molecular structure of [W₂(μ-CC₆H₄Me-4)(CO)₃(PMe₃)(η⁵-Cp){η⁵-2,8-C₂B₉H₈-10-(CH₂C₆H₄Me-4)-2,8-Me₂}]⁻. Reprinted from ref 54. Copyright 1992 Royal Society of Chemistry.

insertion of alkylidyne group into an adjacent B-H bond. However, the protonation of the complex in the presence of [M'(≡CR)(CO)₂(η⁵-C₅H₅)] produces the dinuclear cluster [MM'(μ-R)(CO)₃(η⁵-C₂B₉H₈-(CH₂C₆H₄Me-4)Me₂)(η⁵-C₅H₅)] (where M, M' = Mo, W; R = C₆H₄Me-4, Me).⁵¹ In the same report, these authors have shown the removal of a BH vertex from the C₂B₁₀ cage forming a stable C₂B₉ cluster along with the migration of CR group and the formation of M=M bond. The X-ray structures, presented in Figures 15-17, unambiguously show the presence of a metal-metal double bond (W=W 2.651 Å or W=Mo 2.702 Å) in each of these complexes.⁵¹

It has been demonstrated that the migration of alkylidyne group takes place during the protonation in the presence of a number of substrates including CO, PPh₃, PhPh₂, CNBu^t, Ph₂C₂, dppm, and dppe.⁵³⁻⁵⁵ However, the migration of a CR group to the P atom, forming a ylide of the type [W{CH(C₆H₄Me-4)-PPh₂(CH₂)_nPPh₂}(CO)₂(η⁵-C₂B₉H₉Me₂)]⁻, was observed when the substrate was either dppm or dppe.⁵⁶ Such ylide formations have been observed previously in alkylidyne chemistry.⁵⁸ Recently, the double migration of alkylidyne groups from tungsten to the borons on the C₂B₃ face of a dicarbollide ligand has been reported.⁵⁰ The crystal structures of the products confirmed these intriguing migrations of the alkylidyne moieties.⁵³⁻⁵⁵ Figure 18 represents the X-ray structure that clearly shows the double migration of CH₂C₆H₄Me-4 groups in a dicarbollide-tungsten complex.⁵⁰

A novel, anionic, "carbons apart" tungstacarborane derivative, [closo-1,8-Me₂-11-(CH₂C₆H₄Me-4)-2-Cl-2,2,2-(CO)₃-2,1,8-WC₂B₉H₉]⁻, was synthesized from the corresponding "carbons adjacent" analogue in a similar reaction involving aqueous HCl.⁵⁶ The crystal structure

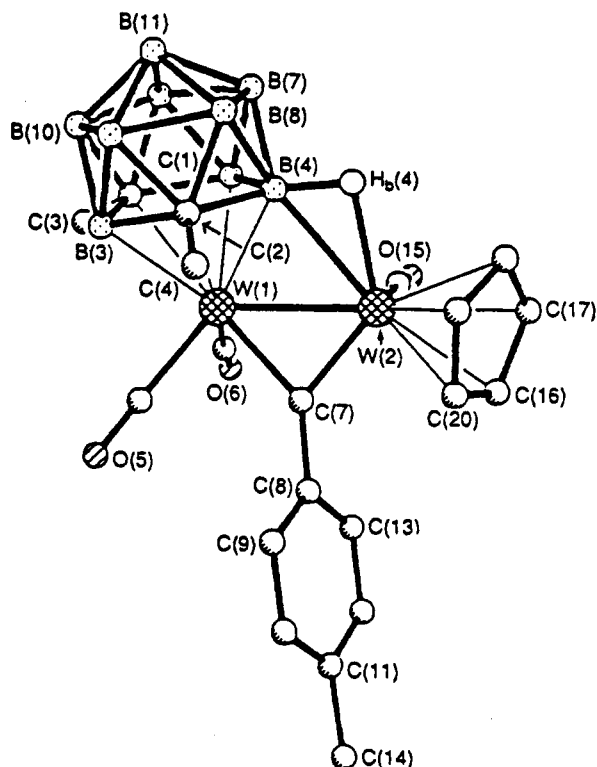


Figure 16. Molecular structure of $[W_2(\mu\text{-CC}_6\text{H}_4\text{Me-4})\text{-(CO)}_3(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)(\eta^5\text{-Cp})]$. Reprinted from ref 51. Copyright 1991 Royal Society of Chemistry.

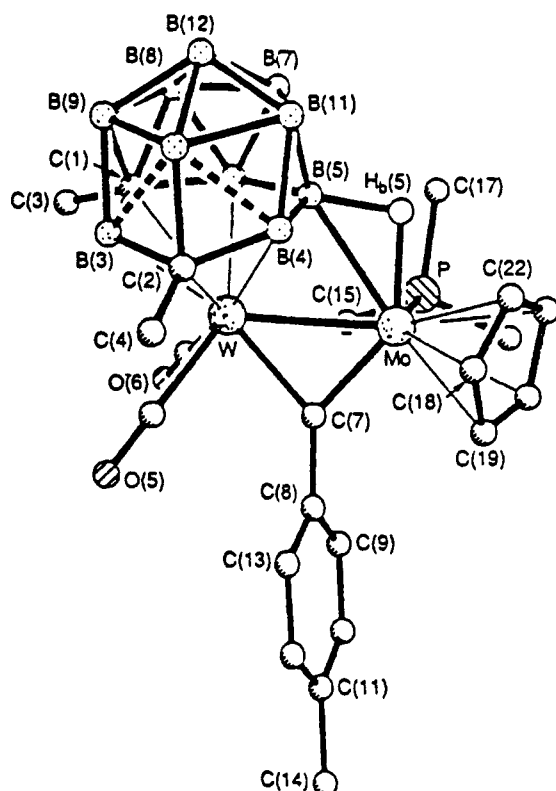


Figure 17. Molecular structure of $[MoW(\mu\text{-CC}_6\text{H}_4\text{Me-4})(CO)_2(PMe_3)(\eta^5\text{-C}_2\text{B}_{10}\text{H}_{10}\text{Me}_2)(\eta^5\text{-Cp})]$. Reprinted from ref 51. Copyright 1991 Royal Society of Chemistry.

(see Figure 19) unambiguously shows the "carbons apart" geometry of the complex with the tungsten metal, while capping the *nido*-icosahedral C_2B_9 cage, ligated by three CO groups and a Cl atom. Although a similar type of cage rearrangement was previously observed by Hawthorne et al. for a rhodacarborane complex,⁵⁹

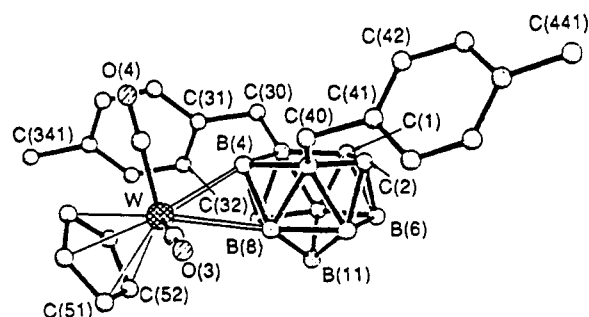


Figure 18. The molecular structure of $[exo\text{-}nido\text{-}9,11\text{-(CH}_2\text{C}_6\text{H}_4\text{Me-4)}_2\text{-}5,10\text{-}\{W(CO)_2(\eta\text{-Cp})\}\text{-}5,10\text{-(}\mu\text{-H)}_2\text{-}7,8\text{-C}_2\text{-B}_9\text{H}_8]$. Reprinted from ref 50. Copyright 1992 Royal Society of Chemistry.

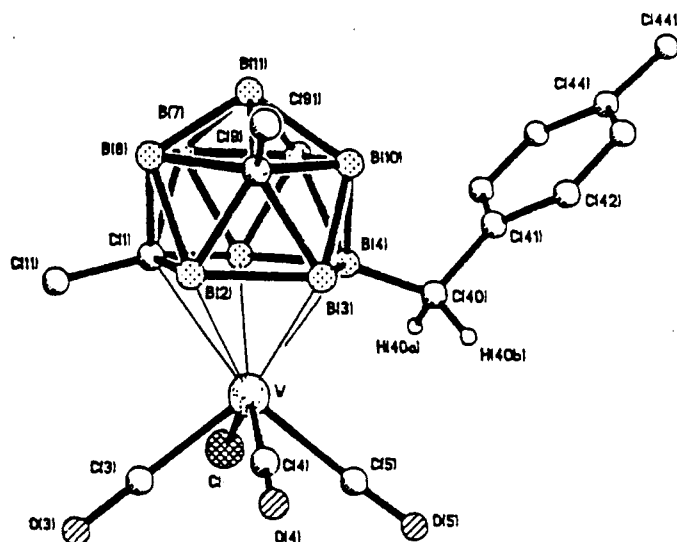


Figure 19. Structure of the anion of $[NEt_4][closo\text{-}1,8\text{-Me}_2\text{-}11\text{-(CH}_2\text{C}_6\text{H}_4\text{Me-4)}\text{-}2\text{-Cl-}2,2,2\text{-(CO)}_3\text{-}2,1,8\text{-WC}_2\text{B}_9\text{H}_8]$. Reprinted from ref 56. Copyright 1992 American Chemical Society.

this represents the first example of a *reversible* cage rearrangement in metallacarborane chemistry.

It is clear from the work of Stone and co-workers that the nature of the products, in all the cases of protonation reactions, is influenced not only by protonating agents, cage carbon substituents or the substrate molecules, but also by the reaction temperatures. As varieties of new compounds become available, the mechanistic details tend to complicate the "so-called" simple protonation reactions. Nevertheless, this area of research seems to be developing faster than ever and undoubtedly has dominated the chemistry of electronically unsaturated organometallic "clustered clusters".

The research on tungsten complexes has also been extended to mixed-metal clusters without the migration of alkylidyne moieties. The heteropolynuclear metallacarboranes of the types $[WPt(\mu\text{-CR})\text{-(}\mu\text{-}\sigma\text{-}\eta^x\text{-C}_2\text{B}_n\text{H}_{n-1}\text{Me}_2\text{)(CO)}_2\text{(PMe}_2\text{Ph)}]$ (where $x = 5$, $n = 9$; $x = 6$, $n = 10$)⁶⁰ and $[W_2Au_2(\mu\text{-CR})_2\{\mu\text{-Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\}\text{(CO)}_4(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (where $n = 2\text{--}6$) can be synthesized from a reaction involving $[Au_2Cl_2\{\mu\text{-Ph}_2\text{P(CH}_2\text{)}_n\text{PPh}_2\}]$ or $[PtCl(Me)(PMe_2Ph)_2]$ and a mixture of $TiBF_4$ and $[NEt_4]^+[W(\equiv CR)(CO)_2\text{-(}\eta^5\text{-C}_2\text{B}_9\text{Me}_2\text{)}]^-$.⁶¹ While the crystal structures of these mixed-metal species unambiguously show the formation of metal-metal bonds ($W\text{-Pt} = 2.720\text{--}2.738$ Å, and $W\text{-Au} = 2.798$ Å), the structure of the mixed W_2Au_2 species (see Figure 20), with $n = 4$, confirms the presence

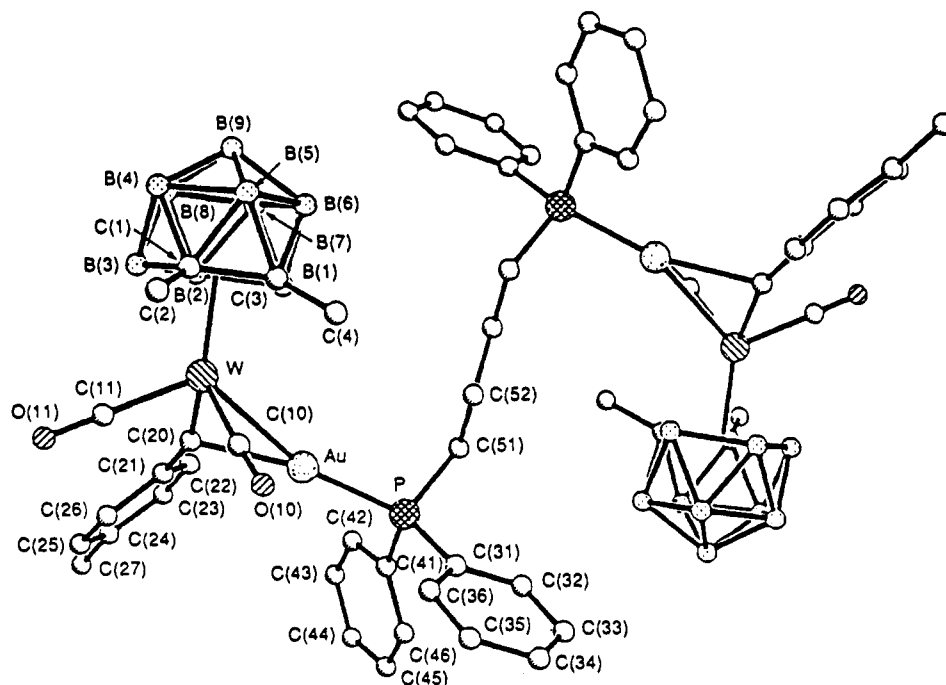
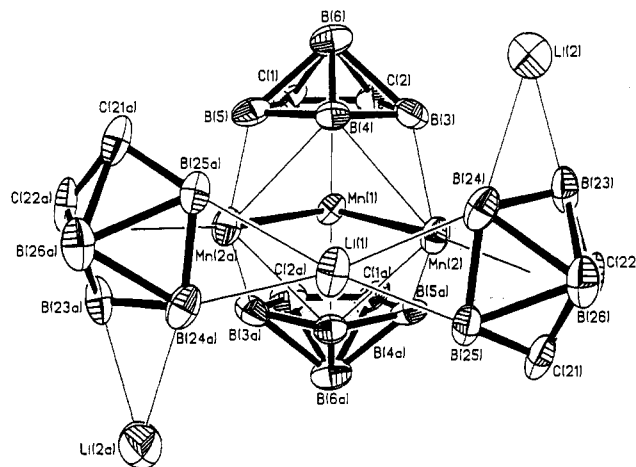


Figure 20. Molecular structure of $[\text{W}_2\text{Au}_2(\mu\text{-CR})_2(\mu\text{-PPh}_2)(\text{CH}_2)_4\text{PPh}_2](\text{CO})_4(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)_2$ showing W-Au bond. Reprinted from ref 60. Copyright 1990 Royal Society of Chemistry.

of two tungstacarboranes that are bridged by $[\text{Au-P}(\text{Ph})_2(\text{CH}_2)_2]_2$ unit, with a center of inversion at the midpoint of the chain of methylene groups. The overall geometry of the ligands at the W center can be described at best as a distorted square pyramid or a "four-legged piano stool". Despite an unsymmetrical bridging of the W-Au bond by the *p*-tolylmethylidyne ligand, the distance of tungsten from the C_2B_3 centroid (1.919 Å) of the dicarbollide ligand in each unit appears to be normal.⁶¹

The manganese or rhenium complexes of a number of carborane ligand systems have been known since the first report on $\text{Cs}[(\text{C}_2\text{B}_9\text{H}_{11})\text{M}(\text{CO})_3]$ ($\text{M} = \text{Mn}^{\text{I}}$ or Re^{I}) by Hawthorne and Andrews in 1965.⁶² However, most of the reported mangana-carborane complexes are half-sandwiched closo species with $\text{Mn}(\text{R}_3\text{P})_x(\text{CO})_{3-x}$ (R = alkyl or aryl group; $x = 0, 1$, or 2) unit occupying a vertex of either an icosahedron or its lower homologues.²⁵ Until recently, the only known mangana-carborane sandwiches have been the anionic complexes of the type $[\text{4,4'}\text{-Mn}^{\text{II}}(\text{1,6-C}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$ and $[\text{Mn}^{\text{IV}}(\text{CB}_{10}\text{H}_{11})_2]^{2-}$ whose geometries have not been confirmed by X-ray crystallography.⁶³ The synthesis and X-ray crystal structure of a novel zwitterionic and paramagnetic manganese sandwich complex, $\{[\text{Li}(\text{THF})][\text{Li}(\text{TMEDA})]_2\}\{\text{commo-Mn}_3[2,3\text{-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_4\}^{3-}$, was reported most recently.⁶⁴ The synthetic pathways are given in eq 3. A "butterfly" geometry for



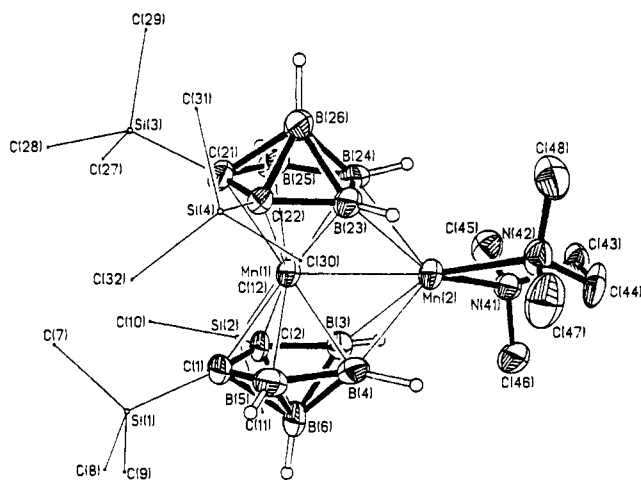


Figure 22. The crystal structure of a manganacarborane sandwich, $[\text{Mn}(\text{TMEDA})][\text{commo-1,1'}\text{-Mn}[2,3\text{-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_2]$ showing the exo-polyhedrally wedged second Mn atom. Reprinted from ref 67.

terminal Mn atoms. The shorter central Mn-centroid distance (1.708 Å), when compared to that of terminal Mn-centroid distance of 2.125 Å, is consistent with the high-spin $\text{Mn}^{\text{I}}\text{-Mn}^{\text{III}}\text{-Mn}^{\text{I}}$ trinuclear system. There was no signal in the X-band EPR spectrum of the complex at 25 °C.⁶⁴

An entirely different result was obtained when a trinuclear half-sandwich gadolinacarborane cluster, $\{\text{closo-Gd}_3[2,3\text{-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_3(\mu_2\text{-closo-Li}_3[2,3\text{-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_3)[\mu_2\text{-Li}(\text{THF})]_3(\mu_3\text{-OMe})(\mu_3\text{-O})\}$,⁶⁶ was reacted with MnCl_2 as in the previous reaction. In fact, the isolated product was a less complicated Mn-cluster system, $3,3',4,4'\text{-Mn}(\text{TMEDA})\text{-commo-1,1'}\text{-Mn}[2,3\text{-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_2$, indicating that a different reaction sequence is taking place when predominantly ionic lanthanacarboranes are used solely as the source for carborane ligands. The room temperature effective magnetic moment (7.6 μ_B) of the Mn_2 complex decreases monotonically with decreasing temperature and reaches 5.6 μ_B at 80 K, indicating that a significant antiferromagnetic coupling exists between the two Mn atoms. The crystal structure of the product (Figure 22) clearly shows that the Mn atom, formally in +2 oxidation state, is somewhat parallel sandwiched by two carborane cages (Mn-C = 2.167 Å, Mn-B = 2.243 Å, and Cnt-Mn-Cnt = 175.5°).⁶⁷ For charge balance, an additional exo-polyhedral $\text{Mn}^{\text{II}}(\text{TMEDA})$ unit is present within the coordination sphere by bonding to two borons of each cage and to the central Mn atom (Mn-Mn = 2.665 Å). The incorporation of a second metal atom into the structure of sandwich complexes as counterion has been observed previously in carborane complexes of Sc, Y, Zr, and Hf.^{26,28-31}

The study of cyclodextrin inclusion complexes with organometallic species, where they behave as the guest molecules is of current interest. Inspired by the success in forming inclusion complexes between *o*-carborane and cyclodextrins Chetcuti et al. have reported the formation of the first inclusion metallacarborane complexes of the general formula, $[\text{Cs}[\text{closo-3,3,3-(CO)}_3\text{-3,1,2-MC}_2\text{B}_9\text{H}_{11}\text{-}\alpha\text{ or } \beta\text{-(cyclodextrin)}]]$ (where M = Mn, Re).^{68a} The crystal structure of the Re complex shows that the cyclodextrins are packed in a head to tail manner, forming a channel structure, while the *closo*-rhenacarborane guest anions are present in the host channels with their alternatively tilted axis. An in-

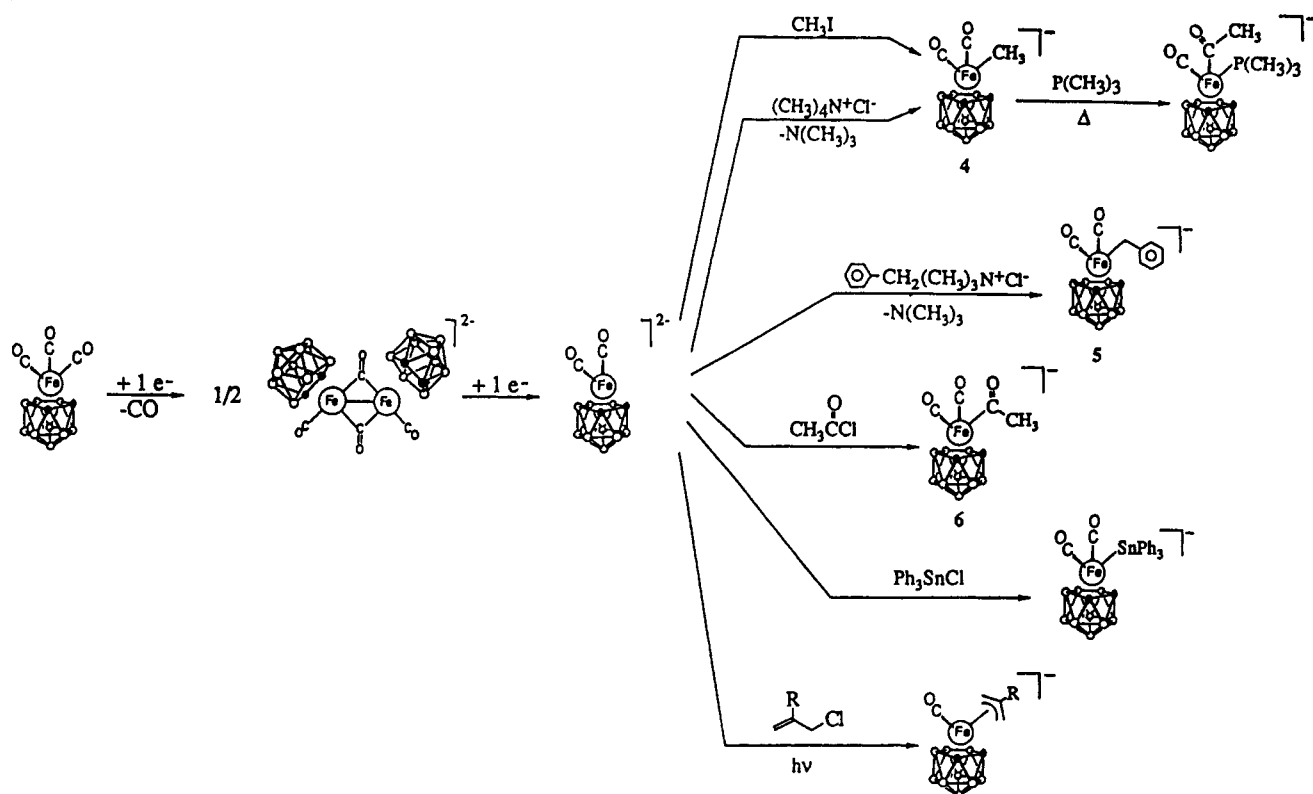
teresting structural feature is that adjacent channels are antiparallel to one another so as to align the guests of one channel in the opposite direction of the adjacent one.^{68a} The bond distances and lengths between the metal and the carborane cage are not changed from the values reported earlier for $\text{Cs}[\text{closo-3,3,3-(CO)}_3\text{-3,1,2-MC}_2\text{B}_9\text{H}_{11}]$.^{68b} Since inclusion compounds show increasing applications in catalysis⁶⁹ and for enzyme modeling,⁷⁰ there is a wealth of fascinating chemistry yet to be explored in this area of metallacarborane chemistry.

B. Middle and Late Transition Metal Complexes

The variety of known transition metal carborane complexes incorporating all types of carborane ligands, large or small, is very extensive since the discovery of the similarities of the dicarbollide dianions with the formally isolobal cyclopentadienide ion in the formation of the first metallocene-type sandwich complexes such as $[\text{Fe}^{\text{II}}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ and $[\text{Fe}^{\text{III}}(\text{C}_2\text{B}_9\text{H}_{11})_2]^{-}$.⁸ There are a number of review articles, monographs, and chapters in books that adequately cover most of the published work in this area until 1982.^{1,4,71} The transition metal complexes, based on mixed carborane and arene ligands, or incorporating purely the carborane ligands that contain one, three, or four carbons in the cage framework, and those complexes of linked cage and multidecker systems, are discussed separately in the following sections. Therefore, our discussions in this part of the review are limited to the sandwiched and half-sandwiched transition metal complexes.

In series of papers on metal-promoted face to face fusion of carborane cages, Grimes and co-workers have exemplified the formation of a single polyhedral C_4B_8 cluster involving either an iron sandwich ($\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{Fe}^{\text{II}}\text{H}_2$ or its cobalt analogue $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{Co}^{\text{III}}\text{H}$ (R = Me, Et, or *n*-propyl).^{3a,42,43,46,47,72-74} Nonetheless, the mechanism of this "oxidative ligand fusion" was not reported until recently. In a systematic study of the fusion process, these authors have confirmed that the reaction is predominantly intramolecular with respect to the ligands and no evidence of ligand exchange could be found even in the mixtures containing two dissimilar FeH_2 -carborane complexes. The finding of this study is the slow formation of a paramagnetic Fe_2 complex in THF from the corresponding diamagnetic mononuclear FeH_2 species known as the first intermediate, thus indicating the existence of the second intermediate in the ligand fusion process. An X-ray diffraction study confirmed the structure of this second intermediate as a dimetallic complex having one iron atom sandwiched between two C_2B_4 ligands and the second iron in a wedging position coordinated to the complex via four Fe-B bonds.⁷⁵ Since the diiron species is isostructural with the previously described dimanganese complex (see Figure 22),⁶⁷ it can also be regarded as a formal zwitterionic sandwich complex whose coordination sphere contains both the cation and the anion. Although, the two iron atoms are within the normal bonding distance (2.414 Å), the ⁵⁷Fe Mössbauer spectra can be interpreted, at best, as the species with no or very little direct Fe-Fe interaction. While the magnetic susceptibility and Mössbauer data suggest that both the iron atoms are formally in +2 oxidation state, the central and the outer Fe atoms are in low-spin (diamagnetic) and high-spin (paramagnetic) con-

Scheme IV. A Schematic Diagram Showing the Reactivity of Diiron Complex
 $\{[closo-3-CO-3,3'-(\mu-CO)-3,1,2-FeC_2B_9H_{11}]_2\}^{2-}$ (Reprinted from ref 80. Copyright 1991 American Chemical Society)



figurations, respectively. Presumably, the fusion of the two carborane faces at the B–B edges in the formation of the corresponding C_4B_8 species is induced by the presence of four outer Fe–B bonds as found in the crystal structure of the diiron complex.⁷⁵ The bonding in this “wedge”-bridged dinuclear sandwich as well as in its monoiron precursor, $(R_2C_2B_4H_4)_2Fe^{II}H_2$, has been investigated by using extended Hückel MO calculations. The results show that the electronic factors prevent the formation of stable bent-sandwich ferracarborane complexes, but prefer a wedging position for the second metal atom.⁷⁶

Although, the dicarbollide anions have been utilized continuously since the birth of the metallocarborane chemistry, ferracarboranes have been relatively less investigated except for a few studies.^{77,78} The recent reports from Hawthorne’s laboratory have demonstrated the synthetic versatility of mononuclear iron(II) ferracarboranes which are the relatively unexplored metallocarborane counterparts of $CpFe$ (Fp) derivatives.^{79,80} The mononuclear iron complexes of the type $[closo-3,3-(CO)_2-3-L-3,1,2-FeC_2B_9H_{11}]$ (where $L = PPh_3$, CH_3CN , $P(OCH_3)_3$, and CO) were prepared by the reaction of dimeric iron dicarbonyl carborane $[closo-3-CO-3,3'-(\mu-CO)-3,1,2-FeC_2B_9H_{11}]_2^{2-}$ with anhydrous $CuCl$ and the monodentate ligands. The ligand substitutions can also be carried out directly on the dianion $[closo-3,3-(CO)_2-3,1,2-FeC_2B_9H_{11}]_2^{2-}$ as shown in Scheme IV. The structural assignments of these complexes were supported by their X-ray crystal structures, each of which show the presence of a polyhedral FeC_2B_9 unit in which the iron adopts a pseudooctahedral coordination. The structure of the unsubstituted Fp analogue, $[closo-3,3,3-(CO)_3-3,1,2-FeC_2B_9H_{11}]$, is shown in Figure 23.⁸⁰ The structure shows that the C_2B_3 bonding face is almost planar and the $Fe(CO)_3$ unit is approximately centered over this face, giving rise to a Fe–centroid

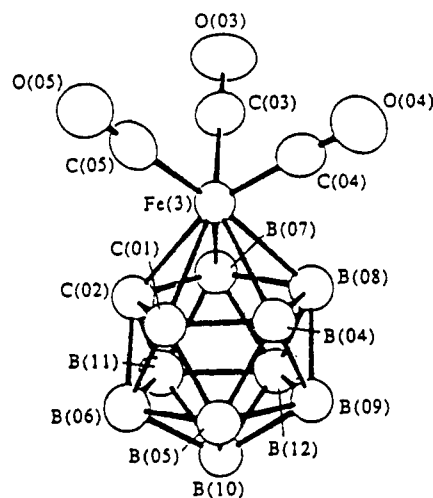


Figure 23. Molecular structure of $[closo-3,3,3-(CO)_3-3,1,2-FeC_2B_9H_{11}]$. Reprinted from ref 80. Copyright 1991 American Chemical Society.

distance of 1.562 Å. Although the C–O distances (1.131, 1.143, and 1.118 Å) are slightly greater than those of $[CpFe(CO)_3]PF_6$ (1.111, 1.112, and 1.113 Å),⁸¹ they are similar (1.136–1.138 Å) when compared to those in $[(CO)_3Fe(C_2B_3H_7)]$.⁸² With the exception of $SnPh_3$ unit occupying one of the facial coordination sites, the ferracarborane anion, $[closo-3,3-(CO)_2-3-[Sn(C_6H_5)_3]-3,1,2-FeC_2B_9H_{11}]^-$, adopts an identical closo structure as its precursor, and as such, the iron atom is approximately centered over the C_2B_3 face (Fe–centroid = 1.557 Å) (see Figure 24).⁷⁹ The Fe–Sn distance of 2.554 Å is comparable to that in $[Fp-Sn(C_6H_5)_3]$.⁸³ However, it has generally been observed in the crystal structures of these complexes that the metal center is slightly slipped toward the cage carbons above the C_2B_3 face while the opposite is true for the

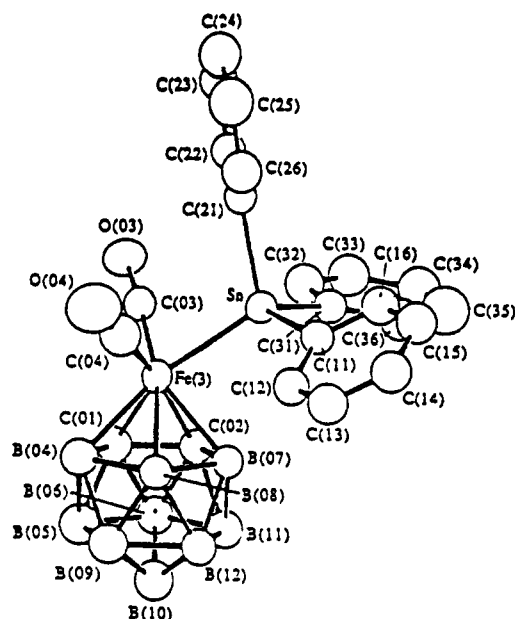


Figure 24. Structure of $[\text{closo-3,3-(CO)}_2\text{-3-[Sn(C}_6\text{H}_5)_3\text{]-3,1,2-FeC}_2\text{B}_9\text{H}_{11}]^-$. Reprinted from ref 79. Copyright 1991 American Chemical Society.

main group metallocarboranes.⁸⁴ Fehlner and co-workers have used Fenske–Hall quantum chemical technique to examine the structural distortions from an idealized closo geometry in metallocarborane clusters of the type $1,1,1\text{-(CO)}_3\text{-1-Fe-2,3-(Me)}_2\text{-2,3-C}_2\text{B}_4\text{H}_4$. The results indicated that the greater interaction of the metal with the cage carbons is predominantly due to normal cluster-bonding effects since the antibonding interaction between the “ t_{2g} ” metal set and the cage carbons is negligible as opposed to that in the main group system.⁸⁵

The dinegatively charged dicarbollide ligands promote the formation of anionic sandwich complexes with the metal when it is formally present in oxidation state less than +4.⁸⁶ The reduction of the charge by one unit on each ligand could result in the formation of neutral,⁸⁷ cationic,⁸⁸ or clustered sandwich complexes⁸⁹ in which the metals are present in accessible low oxidation states. Metallocarborane complexes incorporating charge-compensated ligands have been previously prepared by various methods including ligand rearrangement, reduction of a metal complex and addition of dialkyl sulfide.⁴ A general methodology has now been developed to synthesize a number of prototype *commo*-metallocarboranes of Fe and Co and their corresponding charge-compensated dicarbollide ligands.⁹⁰ The crystal structure of the neutral and charge-compensated Fe^{II} sandwich complex $[\text{commo-3,3'-Fe}\{8\text{-N(C}_2\text{H}_5)_3\text{-3,1,2-FeC}_2\text{B}_9\text{H}_{10}\}_2]$ is shown in Figure 25, and for comparison, the structure of the anionic species $[\text{commo-3,3'-Fe}\{3,1,2\text{-FeC}_2\text{B}_9\text{H}_{11}\}_2][\text{N(CH}_3)_4]_2$, prepared previously from the dinegatively charged dicarbollide ligand,⁹¹ was also determined very recently and is shown in Figure 26.⁹⁰ In both structures the Fe atom is sandwiched between the two planar pentagonal faces of the dicarbollide ligands with the average metal to cage distances of 2.05–2.20 Å in the charge-compensated species and 2.03 Å in the other that make the metal–centroid distances of 1.50, 1.56, and 1.48 Å, respectively. The stronger bonding of the metal in the anionic complex, as evidenced by the shorter Fe–carborane distances, could be rationalized on the basis of the dinegatively

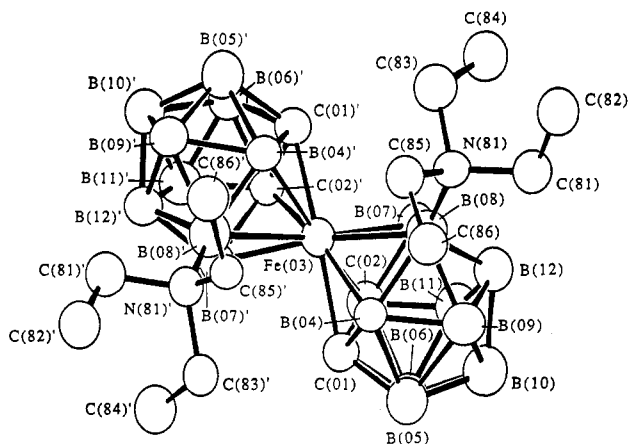


Figure 25. Structure of $[\text{commo-3,3'-Fe}\{8\text{-N(C}_2\text{H}_5)_3\text{-3,1,2-FeC}_2\text{B}_9\text{H}_{10}\}_2]$. Reprinted from ref 90. Copyright 1991 American Chemical Society.

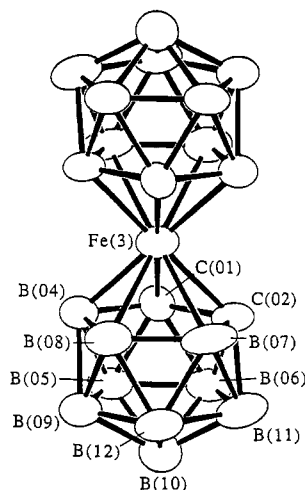


Figure 26. Structure of $[\text{commo-3,3'-Fe}\{3,1,2\text{-FeC}_2\text{B}_9\text{H}_{11}\}_2][\text{N(CH}_3)_4]_2$. Reprinted from ref 90. Copyright 1991 American Chemical Society.

charged dicarbollide ligand when compared to that in the neutral sandwich complex in which the ligands are charge-compensated monoanions.⁹⁰

The first charge-compensated metal complex of a C_2B_4 carborane system, $1\text{-Br-1-(PPh}_3\text{)}_3\text{-1-Ni}^{\text{II}}[2,3\text{-Et}_2\text{-5-(PPh}_3\text{)}_2\text{-2,3-C}_2\text{B}_4\text{H}_3]$, was isolated unexpectedly as a purple, diamagnetic, half-sandwich species from the reaction of the $[\text{nido-2,3-Et}_2\text{C}_2\text{B}_4\text{H}_5]^-$ monoanion with $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ in THF at room temperature.⁹² In the same report, the syntheses, structural characterizations and properties of neutral, diamagnetic Co complex and neutral, paramagnetic low-spin Fe^{III} complex of the general formula $(\text{Ph}_2\text{PCH}_2)_2(\text{Cl})\text{M}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ were also described. The crystal structures show the presence of a slightly distorted 7-vertex *closo*- MC_2B_4 cage in each complex. The presence of a halide ion facilitated some substitution reactions at the metal center in the presence of KCN and MeMgI , but the exchange with the H^- ion was unsuccessful unlike the analogous cyclopentadienyliron complex.⁹³ In addition, the reaction of the Co complex with Grignard reagent, MeMgI , proceeded quite differently, thus forming $1\text{-Co}[(\text{Ph}_2\text{PCH}_2)_2(\text{I})\text{-2,3-Et}_2\text{C}_2\text{B}_4\text{H}_4]$ as opposed to the expected $[(\text{Ph}_2\text{PCH}_2)_2(\text{Me})\text{Co}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]$.⁹²

Metal atom synthesis has been used widely in organometallic chemistry. This methodology has been

profitably exploited by Sneddon and co-workers in the synthesis of a number of unusual metallacarboranes.⁹⁴⁻⁹⁶ The reactions of thermally generated iron and cobalt atoms with *arachno*-2,6- $C_2B_7H_{13}$ and cyclopentadiene, toluene, mesitylene, or 2-butyne yielded a wide variety of unique, air- and water-stable metallacarborane clusters.⁹⁶ The resulting mixed-ligand sandwich complexes 2-($\eta-C_5H_5$)Co-1,4- $C_2B_7H_9$, 4-($\eta-C_5H_5$)Co-2,3- $C_2B_7H_{11}$, 2-(η^6-R)Fe-1,6- $C_2B_7H_9$, and 6-(η^6-R)Fe-9,10- $C_2B_7H_{11}$, (where R = toluene or mesitylene) were characterized by spectroscopy, and the structures of the iron species were also determined by X-ray crystallography.⁹⁶ A similar reaction involving hexaborane(10), bis(trimethylsilyl)acetylene, and cyclopentadiene gave an unusual mixed-ligand complex as a major product whose crystal structure shows a unique bridged structure consisting of a [1-($\eta-C_5H_5$)Co-2,3-(Me₃Si)₂C₂B₄H₃] sandwich in which the terminal hydrogen on the unique boron is replaced by a B₂H₅ moiety via a three-center B-B-B bond. Alternatively, the complex can be viewed as a metallacarborane-bridged diborane derivative.⁹⁵ Unfortunately, the metal atom synthesis cannot be applied to the targeted metallacarborane complexes since generality does not exist in the reaction pathways of these systems.

Metallacarboranes and their derivatives, formed by the addition of organic functional groups, have been used as synthons in the preparation of multidecker sandwich complexes.^{3a} The chemical reactivity of anions derived from (C₅Me₅)Co(Et₂C₂B₃H₅) toward electrophilic reagents to prepare a number of functionalized metallacarborane derivatives was explored recently by Grimes and co-workers.⁹⁷⁻⁹⁹ Consequently, the unique boron-substituted chloro, bromo, and iodo derivatives were prepared by the reactions of [(C₅Me₅)Co(Et₂C₂B₃H₄)]⁻ with MeSO₂Cl, BrCH₂CN, and CF₃I, while the reaction with C(O)CF₃Cl produced exclusively B(nonunique)-C(O)CF₃ derivative. Monohalo B(nonunique)-X derivatives were also obtained by the reaction of (C₅Me₅)Co(Et₂C₂B₃H₅) with *N*-halosuccinimides. The reaction of [(C₅Me₅)Co(Et₂C₂B₃H₄)]⁻ with acetyl chloride gave boron(unique)-substituted 2-vinyl acetate derivative instead of the acetyl one. The base-catalyzed cleavage of this complex produces B(unique)-substituted acetyl complex. The structure of this vinyl acetate-substituted cobaltacarborane complex was confirmed by X-ray crystallography.⁹⁷ Evidently, these B-substituents control the sandwich-stacking process.

Recently, Hawthorne et al. have synthesized systematically a variety of functionalized Venus flytrap-type metal cluster complexes of a C₂B₉ carborane system and demonstrated their utility in immunodiagnosis and radioimmunotherapy by binding radiotransition metals in the complex to tumor-associated monoclonal antibodies.¹⁰⁰ The structures of the pyrazole B_(cage)-bridged and alkylene carbon-bridged metallacarboranes were confirmed by X-ray diffraction studies.^{101,102a} The crystal structure of an alkylene carbon-bridged complex, [7,7'- μ -1,3-C₃H₆(7,8-C₂B₉H₁₀)₂Co][MePh₃P],^{102a} shown in Figure 27, is similar to the one reported for a disulfide boron-bridged cobaltacarborane complex, [HCS₂-(C₂B₉H₁₀)₂Co].^{102b}

In contrast to icosahedral systems, most of the reported metallacarboranes of C₂B₄ carborane systems are those in which the cage carbons reside in adjacent

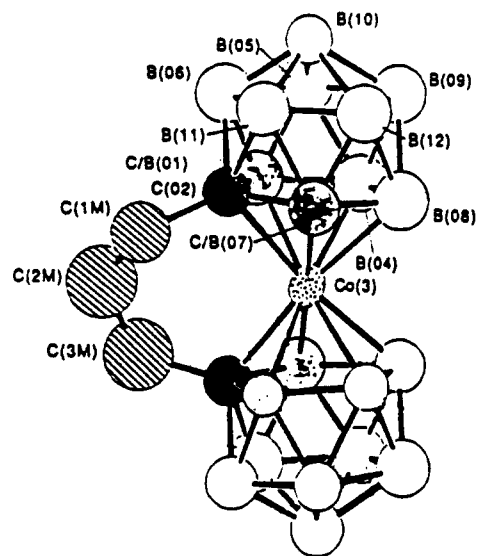
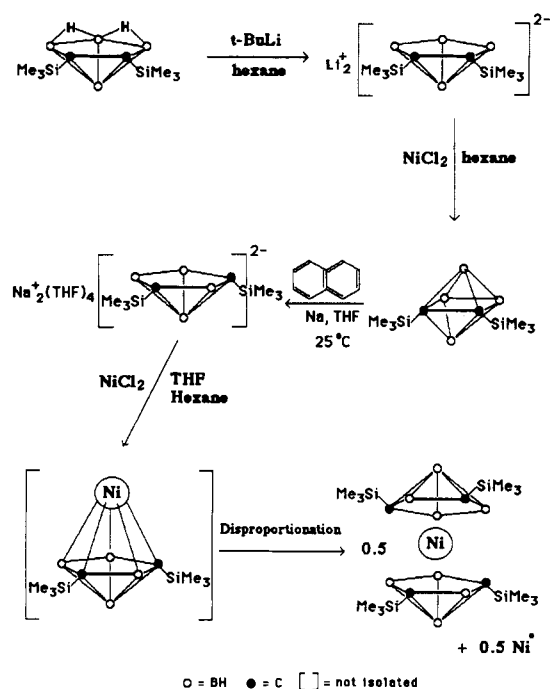


Figure 27. Molecular structure of [7,7'- μ -1,3-C₃H₆-(7,8-C₂B₉H₁₀)₂Co]⁻. Reprinted from ref 102a. Copyright 1992 American Chemical Society.

Scheme V. A Schematic Diagram for the Preparation of Ni(IV) Sandwich Complex Based on Carbons Apart C₂B₄ Carborane Ligands (Reprinted from ref 104)



positions. Exceptions to these have been observed in some cases where cage carbons were separated when the metal complex was heated at very high temperature.⁴ Until recently, neither the "carbons apart" anionic ligands nor a general methodology existed for the formation of such carbons apart metalla-C₂B₄ carboranes. Recent report on high-yield, room temperature synthesis of "carbons apart" C₂B₄ carborane dianion [2,4-(SiMe₃)₂-2,4-C₂B₄H₄]²⁻ along with its structure determination has provided a much needed diversity to the chemistry of small metallacarboranes.¹⁰³ Although this dianion was produced from the corresponding "carbons adjacent" analogue as shown in Scheme V, its reactivity toward NiCl₂ seems to be different. For example, the reaction of the dilithium salt of the carbons adjacent dianion, [2,3-(SiMe₃)₂-

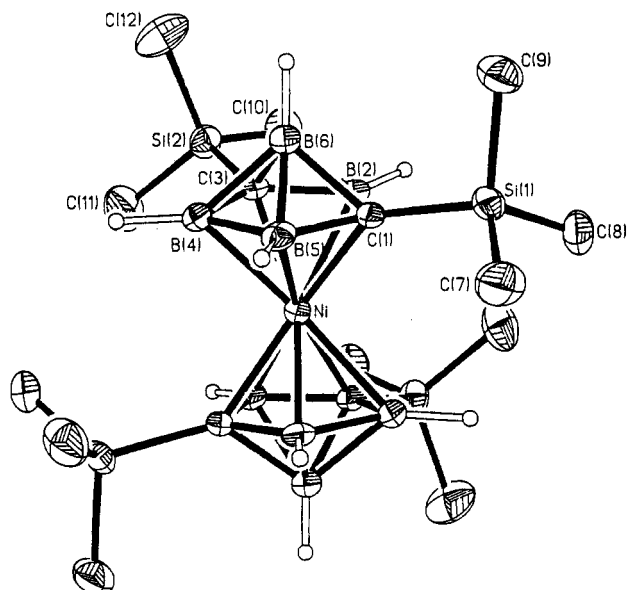


Figure 28. Molecular structure of a Ni(IV) sandwich complex showing the carbon apart geometry of carborane cages. Reprinted from ref 104.

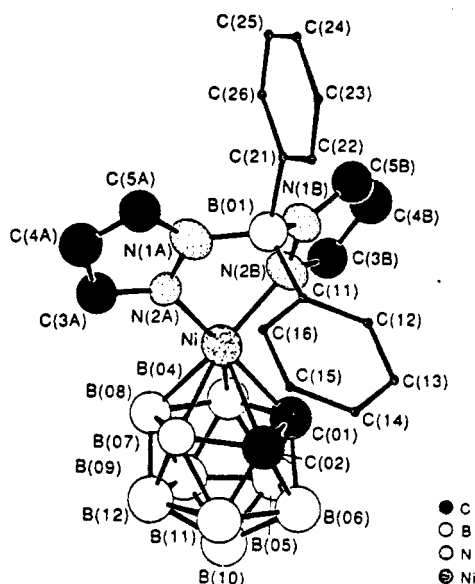


Figure 29. Structure of $[closo-3-(\eta^2\text{-Ph}_2\text{B}(\text{pz})_2)\text{-}3,1,2\text{-NiC}_2\text{B}_9\text{H}_{11}]$ without the hydrogen atoms. Reprinted from ref 105. Copyright 1990 American Chemical Society.

$2,3\text{-C}_2\text{B}_4\text{H}_4]^{2-}$, with anhydrous NiCl_2 failed to produce the expected *closo*-nickelacarborane, instead undergoes a redox reaction to yield Ni^0 and closed-cage product $1,2\text{-(SiMe}_3)_2\text{-}1,2\text{-C}_2\text{B}_4\text{H}_4$ which is the precursor for the "carbons apart" dianion. In contrast, a *commo*-nickel complex could be isolated from the reaction of the carbons apart dianion with NiCl_2 as shown in Scheme V.¹⁰⁴ The crystal structure of this Ni(IV) sandwich,¹⁰⁴ shown in Figure 28, unambiguously confirms its "carbons apart" geometry with the Ni atom approximately centered over the C_2B_3 face. A ligand exchange reaction between *closo*- $3,3\text{-(PhMe}_2\text{P)}_2\text{-}3,1,2\text{-NiC}_2\text{B}_9\text{H}_{11}$ and $[\text{Me}_4\text{N}][\text{Ph}_2\text{B}(\text{pz})_2]$ in THF has also been studied. The crystal structure of the product $[3\text{-(}\eta^2\text{-Ph}_2\text{B}(\text{pz})_2\text{)-}3,1,2\text{-NiC}_2\text{B}_9\text{H}_{11}][\text{Me}_4\text{N}]$, shown in Figure 29,¹⁰⁵ reveals that the six-membered $\text{Ni}(\text{N})_2\text{B}$ ring adopts a boat conformation. The anion shows no distortions from idealized *closo* geometry as measured by the slip parameter Δ in contrast to the metallacarborane

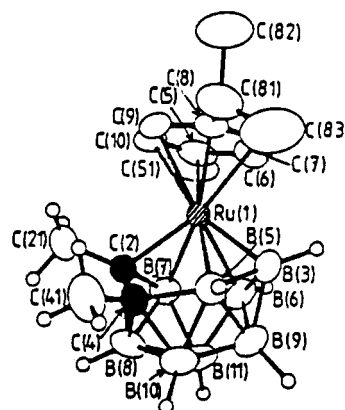


Figure 30. Molecular structure of $[1\text{-(}\eta^6\text{-MeC}_6\text{H}_4\text{-i-Pr)-}2,4\text{-Me}_2\text{-}1,2,4\text{-RuC}_2\text{B}_8\text{H}_8]$. Reprinted from ref 111. Copyright 1987 American Chemical Society.

complexes of other d^8 metals with dicarbollide ligands.¹⁰⁶ Nevertheless, it exhibits an unusual distortion in that the phenyl group of $[\text{Ph}_2\text{B}(\text{pz})_2]^-$ ligand interacts with the hydrogen atom at C(2) atom of the C_2B_3 face and consequently, the Ni-C(2) interatomic distance is lengthened to 2.26 Å as compared to Ni-C(1) distance of 2.04 Å. Similarly, the isomeric products of a rhodium complex, *closo*- $3\text{-(}\eta^3\text{-HB}(\text{pz})_3\text{)-}3,1,2\text{-RhC}_2\text{B}_9\text{H}_{11}$ were also prepared by the same authors and have been structurally characterized.¹⁰⁵

The molecular geometries of some 9-, 10-, and 11-vertex metallacarboranes that contain no other heteroatoms are central to the discussion because they do not obey the electron-counting rules.^{107,108} Consequently, there was an open question whether these complexes are indeed *closo* or so-called "isocloso" species. Without the X-ray data, it has been said that the 11-vertex metallacarboranes such as $\text{CpCoC}_2\text{B}_8\text{H}_{10}$, $[(\text{PPh}_3)_2\text{HfC}_2\text{B}_8\text{H}_{10}]$, and $[(\text{C}_6\text{H}_5)_2\text{RuC}_2\text{B}_8\text{H}_{10}]$,^{109,110} obey the Williams-Wade rules because their skeletal electron counts are straightforward and they are presumed to have simple *closo* deltahedral geometries.^{6,7} However, these proposed *closo* deltahedral geometries have been contradicted by the X-ray structure of $[1\text{-(}\eta^6\text{-MeC}_6\text{H}_4\text{-i-Pr)-}2,4\text{-Me}_2\text{-}1,2,4\text{-RuC}_2\text{B}_8\text{H}_8]$ (see Figure 30) that unambiguously exhibits a quadrilateral open face,¹¹¹ and hence it exemplifies the limitation of the skeletal electron-counting rules of Williams and Wade. This compound was prepared in 30% yield from the reaction between $[(\text{MeC}_6\text{H}_4\text{-i-Pr})\text{RuCl}_2]_2$ and *nido*- $\text{Me}_2\text{C}_2\text{B}_8\text{H}_{10}$. The crystal structure shows that the RuC_2B_8 cluster is considerably distorted from the idealized *closo* geometry. The $\text{Ru}(1)\cdots\text{C}(4)$ distance of 2.683 Å is approaching nonbonding compared to $\text{Ru}(1)\text{-C}(2)$ distance of 2.124 Å. As such an open face involving $\text{Ru}(1)$, $\text{C}(2)$, $\text{C}(4)$, $\text{B}(5)$ atoms is formed. The $\text{Ru}(1)\text{-B}(5)$ bond is also longer (2.363 Å compared to 2.29 Å). This type of structure has been previously reported for isonido 10-vertex iridacarborane $[(\text{PPh}_3)(\text{Ph}_2\text{PC}_6\text{H}_4)\text{-IrB}_9\text{H}_7\text{-C}(\text{OH})]$.^{112,113} These authors have also studied an interesting rotational fluxionality in $[1,1\text{-(PMe}_2\text{Ph)}_2\text{-}1,2,3\text{-PtC}_2\text{B}_8\text{H}_9\text{X}]$ complexes that is accompanied by a flexing of the 10-vertex $\eta^6\text{-}\{\text{C}_2\text{B}_8\text{H}_9\text{X}\}$ moiety between extreme *nido* and *arachno* 10-vertex geometries.¹¹⁴ The crystal structure of the 11-vertex platinumacarborane (where $\text{X} = \text{H}$) is shown in Figure 31. The $(\text{R}_3\text{P})_2\text{Pt}$ unit is bonded to a six-membered open face of the carborane ligand to form a *closo* geometry. These results demonstrate that the minor variation in cluster

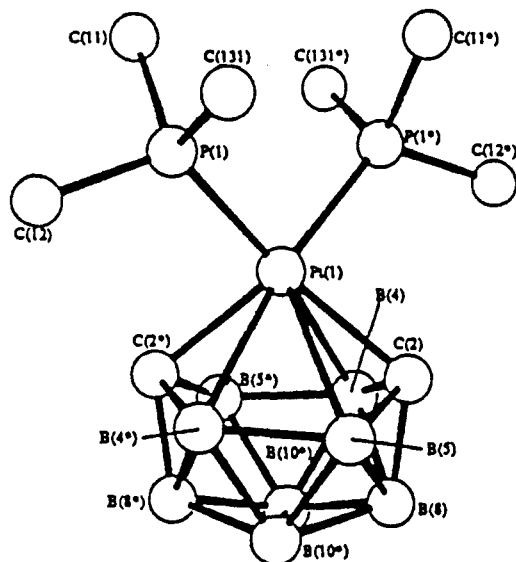


Figure 31. The structure of [1,1-(PMe₂Ph)₂-1,2,3-PtC₂B₉H₁₀]. Reprinted from ref 114. Copyright 1991 American Chemical Society.

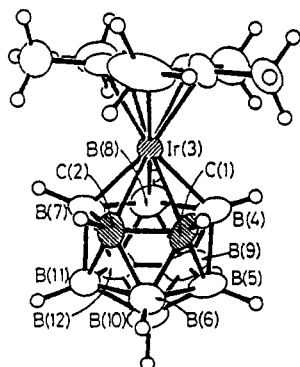
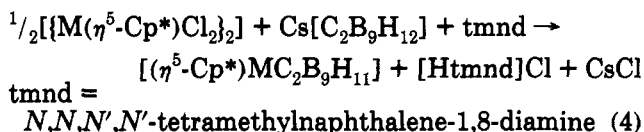


Figure 32. Molecular structure of [3-(η⁵-C₅Me₅)-3,1,2-IrC₂B₉H₁₁]. Reprinted from ref 115. Copyright 1990 Royal Society of Chemistry.

substitutions can induce an overall change in the geometries of the molecules.¹¹⁴ The rhodium and iridium compounds of the type [3-(η⁵-C₅Me₅)-3,1,2-MC₂B₉H₁₁] (where M = Rh, Ir) have been prepared recently according to eq 4.¹¹⁵



Since both complexes are isostructural, only the crystal structure of the iridium species, [3-(η⁵-C₅Me₅)-3,1,2-IrC₂B₉H₁₁], is shown here (see Figure 32). Despite the similarity between the two structures, the distortion of the MC₂B₉ cage is slightly greater in the rhodacarborane complex.¹¹⁵ The smaller magnitude of the distortion in these complexes is particularly noteworthy when compared to the open quadrilateral face in the 11-vertex ruthenium complex [1-(η⁶-MeC₆H₄-i-Pr)-2,4-Me₂-1,2,4-RuC₂B₉H₈] described previously.¹¹⁶ A comparison of the patterns in the NMR spectra of these metallocarboranes with those of *closo*-1,2-C₂B₁₀H₁₂, *nido*-7,8-C₂B₉H₁₃, and [*nido*-C₂B₉H₁₂]⁻ anion suggests that shielding similarities apparently exist between the anionic [*nido*-C₂B₉H₁₂]⁻ fragment and the metallocarborane rather than between the neutral species.¹¹⁵

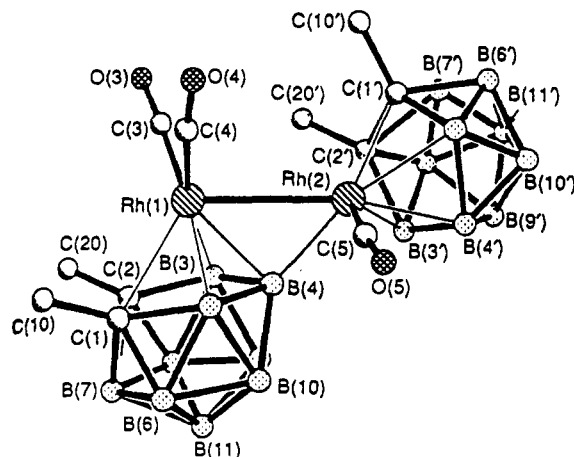


Figure 33. The structure of the anion [Rh₂(μ-σ:η⁵-C₂B₉H₈Me₂)(CO)₃(η⁵-C₂B₉H₈Me₂)]⁻. Reprinted from ref 117. Copyright 1991 Royal Society of Chemistry.

Nonetheless, the controversy still remains in the overall classification of these complexes with respect to *closo* or *nido* geometries.^{6,7}

Stone and co-workers have explored the reactivity of anionic rhodacarboranes in the preparation of polynuclear clusters with metal-metal bonds.¹¹⁶⁻¹¹⁹ The work reported prior to 1991 has been recently reviewed by Stone.⁴⁵ The rhodacarboranes of the type [NEt₄][Rh(CO)_{2-x}(PPh₃)_x(η⁵-C₂B₉H₉R₂)] (where x = 0 or 1; R = H or Me) have been used to prepare compounds with Rh-Rh, Rh-Re, Rh-Cu, Rh-Au, and Rh-Pt bonds. The crystal structures of these complexes show different roles of the carborane cages such as a spectator ion in [RhPt{σ-C(C₆H₄Me-4)=C(C₆H₄Me-4)H}(CO)(PEt₃)(PPh₃)(η⁵-C₂B₉H₁₁)] cluster,¹¹⁶ a bridging ligand via B-H-M bonds in complexes [CoRh(CO)₂(PPh₃)(η⁵-C₄Me₄)(η⁵-C₂B₉H₁₁)] and [Rh₂(CO)₂(PPh₃)₂(η⁵-C₂B₉H₁₁)]¹²⁰ or a linking group with the B-Rh σ bond as seen in [NEt₄][Rh₂(μ-σ:η⁵-C₂B₉H₈Me₂)(CO)₃(η⁵-C₂B₉H₉Me₂)]¹¹⁷. The crystal structure of [NEt₄][Rh₂(μ-σ:η⁵-C₂B₉H₈Me₂)(CO)₃(η⁵-C₂B₉H₉Me₂)]¹¹⁷ shows that the Rh-Rh distance of 2.876 Å is significantly longer than that in [Rh₂(CO)₂(PPh₃)₂(η⁵-C₂B₉H₁₁)] (2.692 Å)¹²⁰ and [Rh₂(PPh₃)₂(η⁵-C₂B₉H₁₁)₂] (2.763 Å).¹²¹ While the unique boron bridges the Rh-Rh bond with the distances of about 2.05–2.15 Å, the Rh-C_(cage) bonds seem to be longer (2.21–2.44 Å). As a result of the B_(unique) bridge, Rh(2) carries only one CO ligand.¹¹⁷

The mononuclear rhoda and iridacarboranes have produced some interesting metallacycles. In general, these cycloaddition reactions involved alkynes or aryl nitrile *N*-oxides and the selective *closo*-metallocarborane. The resulting metallacycles were isolated in good yields, and were characterized thoroughly including single-crystal X-ray diffraction studies.^{122,123} In all the structures, no change in the geometry of the MC₂B₉ (M = Rh, Ir) cluster was observed.

The *closo*-osmacarborane, 1-Os(CO)₃-2,3-(SiMe₃)₂-2,3-C₂B₉H₄, was prepared by the reaction of Os₃(CO)₁₂ with *nido*-2,3-(SiMe₃)₂C₂B₉H₆.¹²⁴ A pentagonal-bipyramidal geometry was assigned on the basis of multinuclear NMR spectra. The same compound was also obtained by heating the metal carbonyl with *closo*-1-Sn-2,3-(SiMe₃)₂C₂B₉H₄.¹²⁴ Supraicosahedral metallocarboranes of Pd and Ir incorporating [C₂B₁₀H₁₂]²⁻ ligand and an icosahedral platincarborane of the C₂B₉

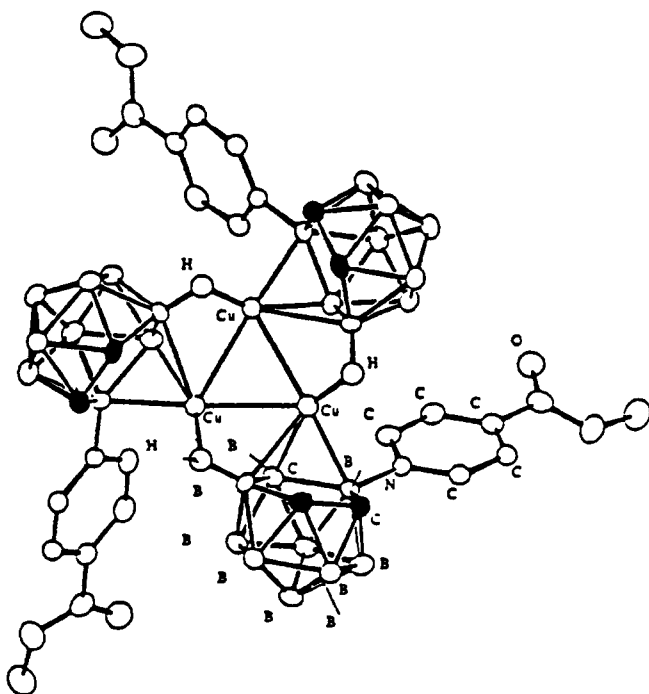


Figure 34. The crystal structure of $[\text{Cu}_3(\mu\text{-H})_3\{\text{C}_2\text{B}_9\text{H}_9(4\text{-(C}_5\text{H}_4\text{N)}\text{CO}_2\text{CH}_3)\}_3]$. Reprinted from ref 89. Copyright 1988 American Chemical Society.

system have been reported.¹²⁵ The reaction of $[\text{M-Cl}_2(\text{dppe})]$ (where $\text{M} = \text{Pd}, \text{Pt}$; $\text{dppe} = (\text{diphenylphosphino})\text{ethane}$) with $\text{Na}_2(\text{C}_2\text{B}_{10}\text{H}_{12})$ or $\text{Tl}_3\text{-(C}_2\text{B}_9\text{H}_{12})\text{O}$ gave the corresponding *clos*o species $[(\text{dppe})\text{PdC}_2\text{B}_{10}\text{H}_{12}]$ or $[(\text{dppe})\text{PtC}_2\text{B}_9\text{H}_{11}]$. When petroleum ether/methanol solvent mixture was employed with the iridium reagent, the reaction yielded an unexpected product $[(\text{PPh}_3)_2\text{IrC}_2\text{B}_{10}\text{H}_{11}(\text{OMe})]$, whose crystal structure shows that the methoxy group is bonded to the unique boron (between the two cage carbons) of the six-membered bonding face.¹²⁵

The mononuclear, $\text{PPN}[\text{c}los\text{o-3-(PPh}_3\text{)-3,1,2-CuC}_2\text{B}_9\text{H}_{11}]$ and dinuclear $[\text{c}los\text{o-exo-4,8-}\{(\mu\text{-H})_2\text{Cu(PPh}_3)\}\text{-3-(PPh}_3\text{)-3,1,2-CuC}_2\text{B}_9\text{H}_9]$ copper complexes were prepared by the reaction of thallium salt of the dicarbollide ion with Cu^+Cl in the presence of $(\text{PPN})\text{Cl}$. On the other hand, when Cu^+Cl is employed along with PPh_3 , either the mononuclear $[\text{c}los\text{o-3-(PPh}_3\text{)-4-(4-(C}_5\text{H}_4\text{N)}\text{CO}_2\text{CH}_3\text{)-3,1,2-CuC}_2\text{B}_9\text{H}_{10}]$ or the trinuclear $[\text{nido-Cu}_3(\mu\text{-H})_3\{\text{C}_2\text{B}_9\text{H}_9(4\text{-(C}_5\text{H}_4\text{N)}\text{CO}_2\text{CH}_3)\}_3]$ cluster can be produced depending upon the concentration of the PPh_3 ligand.⁸⁹ The structures of these mononuclear and trinuclear cupracarborane clusters were confirmed by X-ray crystallography. The structure of $[\text{nido-Cu}_3(\mu\text{-H})_3\{\text{C}_2\text{B}_9\text{H}_9(4\text{-(C}_5\text{H}_4\text{N)}\text{CO}_2\text{CH}_3)\}_3]$ is shown in Figure 34. This cluster contains three $[\text{CuC}_2\text{B}_9\text{H}_{10}(4\text{-(C}_5\text{H}_4\text{N)}\text{CO}_2\text{CH}_3)]$ units, which are linked by both Cu-H-B and Cu-Cu interactions about a crystallographic 3-fold axis that makes an interesting "pinwheel" ligand array around an equilateral Cu_3 core. The structure can also be viewed as a cluster consisting of three equilateral triangles of Cu_3 , H_3 , and B_3 atoms that are associated with the three Cu-H-B bridge bonds. The Cu-Cu distance of 2.52 \AA is relatively short compared to that in known Cu_3 triangles ($2.75\text{--}3.61 \text{ \AA}$).^{126,127}

The crystal structure of an unusual mercury complex of the $[\text{C}_2\text{B}_{10}\text{H}_{10}]^{2-}$ ligand system was reported recently by Hawthorne and co-workers.¹²⁸ Although the mercury atom in the complex is not an integral part the cage

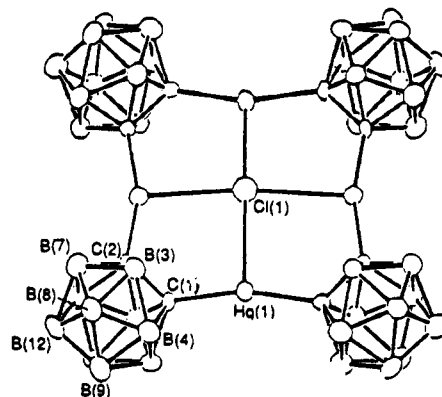


Figure 35. The crystal structure of an unusual mercury complex. Reprinted from ref 128. Copyright 1991 VCH Publishers.

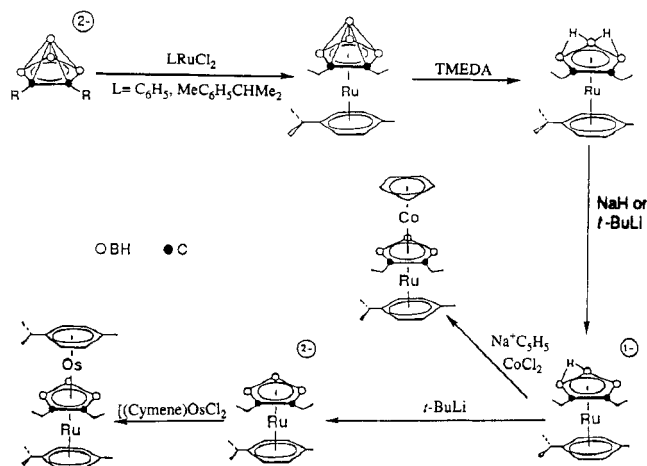
framework, it has demonstrated an unusual bonding mode in the solid state so as to form a $[12]\text{crown-4-macrocyclic}$ analogue. Therefore, our discussion on this complex is limited to the structural aspect only. The crystal structure of this complex (Figure 35) consists of four divalent carborane cages linked by four Hg atoms in a cyclic tetramer with a Cl ion located in the center ($\text{Hg-Cl} = 2.944 \text{ \AA}$). The Hg-Cl bonds are shorter than the sum of their van der Waals radii. Each Hg atom links carbon atoms of two carborane cages with distances of about $2.080\text{--}2.105 \text{ \AA}$ (av $\text{C-Hg-C} = 162^\circ$).

It is apparent from the above discussions that the synthetic, structural, bonding, and reactivity patterns have made the area of middle and late transition metal containing metallacarborane complexes as one of the forefronts of organometallic chemistry.

C. Linked-Cage and Multidecker Complexes

The synthesis of new materials having novel electronic, optical and conducting properties is of current interest. An approach to these materials is systematically linking the small sandwich units to form an extended multidecker sandwich system. Immediately following the discovery of the triple-decker structure of the type Cp_3Ni_2^+ ,¹²⁹ Grimes and co-workers were able to synthesize the first neutral triple-decker sandwich of a metallacarborane system in the early 1970's.¹³⁰ Since then, the research in this field has been dominated by the work of Grimes that has demonstrated how small metallacarboranes can be stacked and then linked systematically. Recent reviews by Grimes^{3a,131-133} and Siebert¹³⁴⁻¹³⁶ have adequately described the latest developments in this area of research. Therefore, our discussions in this section will cover only those results that need to be updated.

An effective procedure for the removal of apical BH units in metallacarboranes has been the treatment of a metallacarborane with TMEDA and H_2O or methanol at elevated temperatures.¹³⁷⁻¹⁴⁰ A reaction such as the one that involved methanol and $[\eta^6\text{-C}_6\text{H}_5\text{-(CH}_2\text{)}_3\text{FeC}_2\text{B}_4\text{H}_5]$ produced the corresponding *nido*-($\eta^6\text{-1-[C}_6\text{H}_5(\text{CH}_2)_3\text{Fe[2-C-3-(CH)}_3\text{B}_3\text{H}_5]$ incorporating two B-H-B bridge hydrogens to give the neutrality to the molecule.¹³⁸ As in previously developed methodology, removal of these bridge H 's with appropriate reagents affords the key anionic intermediates to construct a number of desired multidecker species systematically.^{131,137,139,141,142} Scheme VI illustrates the

Scheme VI. Reaction Pathways for the Formation of Multidecker Sandwich Complexes


synthesis of a particular class of triple-decker sandwiches, although a more general synthetic description, that can be applied to other stacked systems as well, can be found in ref 3a. Consequently, the synthesis of a red triple-decker complex, $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{NiCp}^*]$, was accomplished by removing an indenyl H in the presence of BuLi from $(\eta^6\text{-C}_9\text{H}_8)\text{-Fe}^{\text{II}}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$, followed by the addition of NiBr₂ and [Cp*]⁻ at -78°C .¹⁴³ The crystal structure of this complex, shown in Figure 36, exhibits an 8-vertex FeNiC₂B₄ cluster in which the nickel atom, cage carbon atoms, and one boron atom each occupy 4-coordinate sites, while the iron and the remaining borons reside in 5-coordinate vertices. Although the geometries of $\text{Fe}(\eta^5\text{-C}_9\text{H}_7)$ and $\text{Ni}(\eta^5\text{-Cp}^*)$ units are unexceptional, the arrangement of the metal atoms with respect to the carborane ligand is such that the overall geometry of the complex can be viewed as a bent triple-decker sandwich.¹⁴³

A linkage of two metallacarboranes can also be accomplished by using a bridging organic ligand along with the anionic carborane ligand and a metal reagent. Such an approach was employed by Sneddon and co-workers in the preparation of a linked metallacarborane complex $\text{CH}_2[\text{closo-1-(}\eta\text{-C}_5\text{H}_4\text{)Co(2,3-Et}_2\text{-C}_2\text{B}_4\text{H}_4\text{)}_2]$ from $[\text{nido-2,3-Et}_2\text{C}_2\text{B}_4\text{H}_5]^-$ anion with CoCl_2 and $\text{CH}_2(\text{C}_5\text{H}_5)_2^{2-}$ dianion, that included an additional oxidative workup.^{144a} The crystal structure of this complex, shown in Figure 37, exhibits two *closo-1-(}\eta\text{-C}_5\text{H}_4\text{)Co(2,3-Et}_2\text{C}_2\text{B}_4\text{H}_4) metallacarborane fragments joined by a cyclopentadienyl-bridging methylene group. The crystallographic parameters (see Table I) of the complex are similar to those observed in *closo-1-(}\eta\text{-C}_5\text{H}_5\text{)Co(2,3-Me}_2\text{C}_2\text{B}_4\text{H}_4).^{144b} The structural features are interesting in that while both the carborane and Cp ligands eclipse one another, the *closo*-cobaltacarboranes make a 90° angle between them with the closest intermolecular H...H contacts of 2.75 \AA [$\text{H}_{\text{B}(5)}\cdots\text{H}_{\text{Cp}(2)}$].^{144a}**

A similar linked metallacarborane of the type $\{[(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{FeH}(\text{C}_5\text{Me}_4)]_2\text{C}_6\text{H}_4\}$ has been synthesized from the reaction of $[\text{nido-Et}_2\text{C}_2\text{B}_4\text{H}_5]^-$ anion with the stoichiometric quantities of $[1,4\text{-(C}_5\text{Me}_4)_2\text{C}_6\text{H}_4]^{2-}$ dianion and FeCl_2 in THF.¹⁴⁵ The crystal structure of this diamagnetic complex shows the tilting of the central phenylene ring by about 55° relative to the cyclopentadienyl planes (see Figure 38). The location of the metal-bound hydrogen (1.63 \AA) is such that it could be considered as bridging the central Fe atom and two

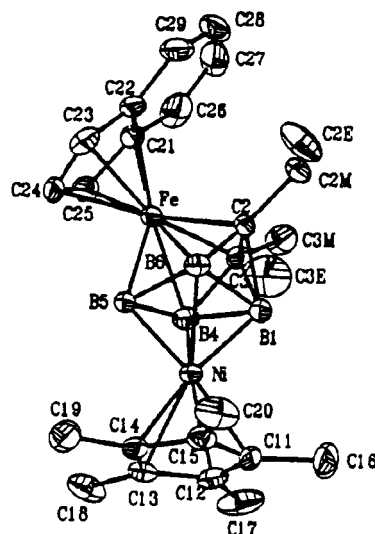


Figure 36. Molecular structure of $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{NiCp}^*]$ without the hydrogen atoms. Reprinted from ref 143. Copyright 1991 American Chemical Society.

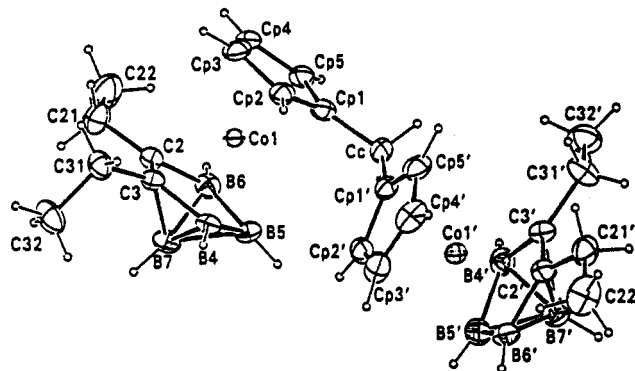


Figure 37. Molecular structure of $\text{CH}_2[\text{closo-1-(}\eta\text{-C}_5\text{H}_4\text{)Co(2,3-Et}_2\text{C}_2\text{B}_4\text{H}_4\text{)}_2]$. Reprinted from ref 144a. Copyright 1991 American Chemical Society.

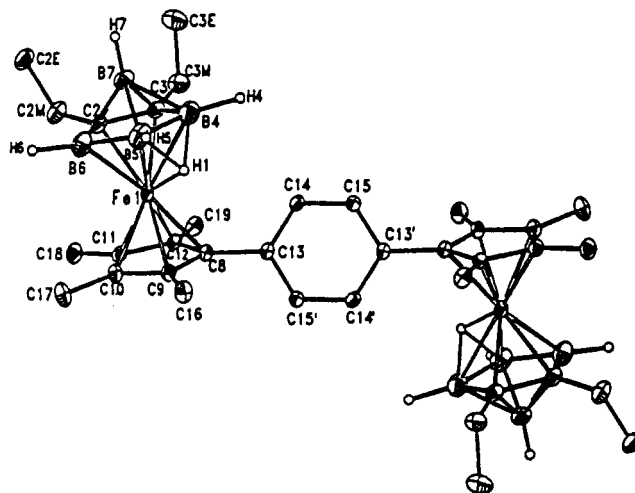


Figure 38. An ORTEP drawing of $\{[(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{FeH}(\text{C}_5\text{Me}_4)]_2\text{C}_6\text{H}_4\}$. Reprinted from ref 145. Copyright 1992 American Chemical Society.

neighboring boron atoms (ca. 1.45 \AA). Consequently, the distances of the metal to these boron atoms are longer than to the other ($2.213\text{--}2.262\text{ \AA}$ vs. 2.140 \AA).¹⁴⁵ The tilting of the Cp ring (6.6°) in the complex is in the opposite direction of that observed in the analogous linked Co species, $[(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)\text{Co}(\text{C}_5\text{Me}_4)]_2\text{C}_6\text{H}_4$ (7.2°),¹⁴² described in ref 3a. The linked diiron species also undergoes irreversible oxidation followed by a

reversible signal. However, the irreversible reduction generated a number of new and unidentified species.¹⁴⁵

Most recently, a number of C- and B-substituted double- and triple-decker sandwich complexes of Co have been prepared and thoroughly characterized.¹⁴⁶ Initially, the precursor, $\text{Cp}^*\text{Co}(\text{Me}_2\text{C}_2\text{B}_4\text{H}_4)$, was converted to the corresponding B-Me-substituted species, $\text{Cp}^*\text{Co}(\text{Me}_2\text{C}_2\text{B}_3\text{Me}_3\text{H}_2)$, in a number of steps involving decapitation by wet TMEDA and repeated deprotonations with butyllithium, followed by the reactions with methyl iodide. The crystal structure revealed that this intermediate complex is a decapitated mixed-ligand and staggered sandwich as in $(\text{Cp}^*_2\text{Co})^+$.¹⁴⁷ The shorter metal to carborane ring centroid distance, compared to that in the metallocene analogue (1.54 Å vs. 1.68 Å), demonstrates the stronger bonding capability of the carborane ligand than the cyclopentadienide as previously demonstrated.⁸ The synthetic utility of this complex as well as the corresponding $\text{C}_{(\text{cage})}\text{-H}$ or -SiMe_3 -substituted analogues has been demonstrated further in the preparation of a number of triple-decker sandwiches, $[\text{Cp}^*\text{Co}(\text{R},\text{R}'\text{-C}_2\text{B}_3\text{R}''_3)\text{Cp}^*\text{Co}](\text{R},\text{R}',\text{R}'' = \text{H}, \text{Me}, \text{or SiMe}_3)$.¹⁴⁶

The results to date indicate that the area of linked cage and multidecker sandwich complexes is still in its developing stage, and more advanced research needs to be done to find their applications, in an absolutely practical sense, as new materials in electronic industries. Nonetheless, the above results give every indication that this area of research will dominate the frontiers of organometallics for the next several decades.

D. Complexes of Arene and $\text{C}_8\text{H}_8^{2-}$ Ligands

During the last decade there has been an upsurge in the syntheses and characterizations of (π -arene)metallacarborane complexes, partly because of their utility in the preparation of multidecker clusters. Bicyclic or polycyclic arenes, coordinated to the transition metals, allow the construction of arene-bridged oligomers and polymers. Again, a recent article of Chemical Reviews described the latest developments in this area and, therefore, only the most recent results will be given here.^{3a,131}

There have been some reports on unusual syntheses and structures of d-block metallacarboranes incorporating both arene and small or large carborane ligands. In reactions of small carborane ligand of the type $[\text{Et}_2\text{C}_2\text{B}_4\text{H}_5]^-$ with $\text{C}_8\text{H}_8^{2-}$ anion and MCl_3 in THF, oxidation products such as $(\eta^8\text{-C}_8\text{H}_8)\text{M}^{\text{IV}}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ could be obtained in good yields when $\text{M} = \text{Ti}$ or V . A similar reaction with chromium reagent resulted in the formation of a tropylium complex $(\eta^7\text{-C}_7\text{H}_7)\text{-Cr}^{\text{III}}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ that could be the decomposition product of the expected $(\eta^8\text{-C}_8\text{H}_8)\text{Cr}^{\text{IV}}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ sandwich.⁴³ Although all three complexes are air stable in the solid state, the V and Cr species show remarkable stability toward O_2 in solution. It has also been shown that the B-substituted mono- and diiodo derivatives of the Ti complex can be made and, therefore, these derivatives could serve as valuable precursors to multidecker sandwich complexes.⁴³ The crystal structures of these mixed-ligand complexes show close 7-vertex pentagonal MC_2B_4 clusters in which the metal bonds to a planar $(\text{C}_8\text{H}_8)^{2-}$ or $(\text{C}_7\text{H}_7)^-$ ligand (Figures 39–41).⁴³ Although metal to arene distances do not vary signif-

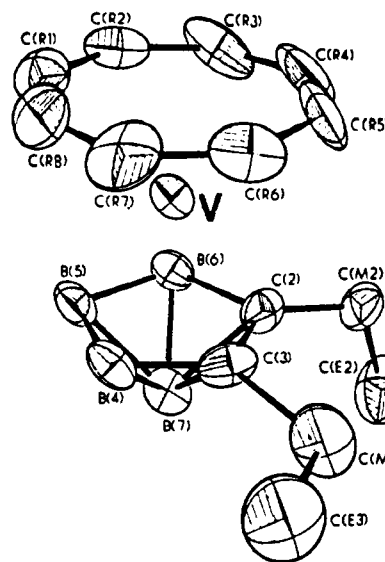


Figure 39. Molecular structure of $(\eta^8\text{-C}_8\text{H}_8)\text{V}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$. Reprinted from ref 43. Copyright 1984 American Chemical Society.

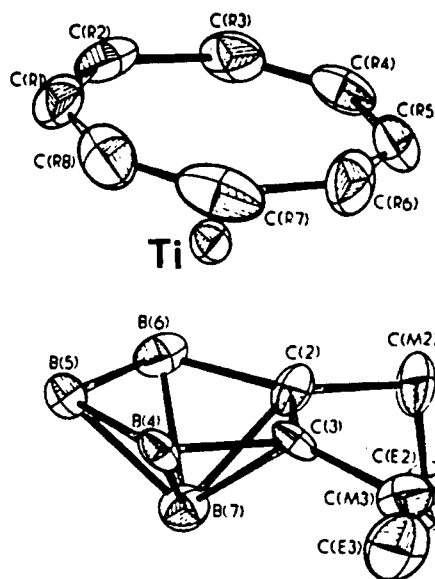


Figure 40. Molecular structure of $(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$. Reprinted from ref 43. Copyright 1984 American Chemical Society.

icantly, the shorter metal-(C_2B_3 centroid) distance in the structure of the vanadium complex (1.830 Å, see Figure 39), when compared to that in the titanium analogue (1.916 Å, see Figure 40) is consistent with the decrease in covalent radius of the metals going from group 4 to group 5. The magnetic susceptibility and ESR data of the paramagnetic vanadium sandwich are indicative of the formal +4 oxidation state of the metal. The room temperature solution ESR spectrum gave a g value of 1.94 with a vanadium hyperfine coupling ($\langle A \rangle = 155 \text{ G}$), but no ligand hyperfine splitting could be observed due to V-boron interactions.⁴³ The crystal structure of the chromium sandwich also shows essentially symmetric bonding of the metal with respect to both ligands with a dihedral angle of 2.76° .⁴³ Indeed, this work has demonstrated that such mixed-ligand systems can also stabilize the formal +4 oxidation state of the metals as in the purely carborane-based dianionic ligand systems.

Although the formation of $[\text{closo-3-}(\eta^6\text{-C}_6\text{H}_6)\text{-3,1,2-FeC}_2\text{B}_9\text{H}_{11}]$ was reported previously in the literature,

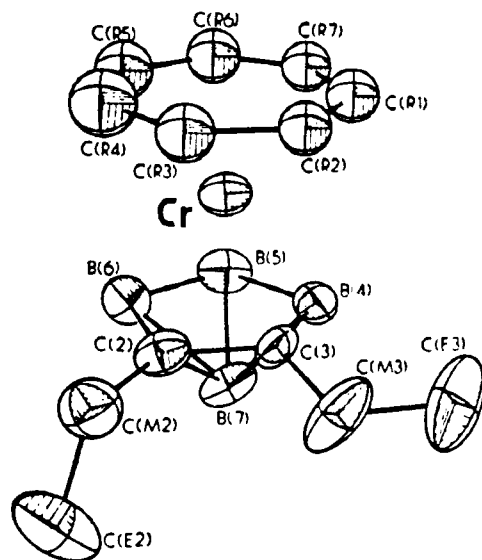


Figure 41. Molecular structure of $(\eta^7\text{-C}_7\text{H}_7)\text{Cr}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$. Reprinted from ref 43. Copyright 1984 American Chemical Society.

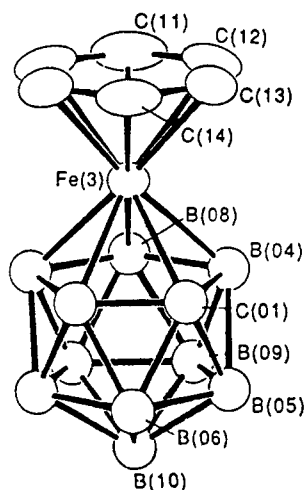


Figure 42. Molecular structure of $[\text{closo-3-(}\eta^6\text{-C}_6\text{H}_6\text{)-3,1,2-FeC}_2\text{B}_9\text{H}_{11}]$. Reprinted from ref 77. Copyright 1990 Elsevier Sequoia.

attempts to isolate this mixed-ligand species have been unsuccessful.^{78,148} However, a recent report describes the high-yield synthesis and isolation of this species involving the photolysis of *closo*-3,3,3-(CO)₃-3,1,2- $\text{FeC}_2\text{B}_9\text{H}_{11}$ in benzene.⁷⁷

The crystal structure, shown in Figure 42, exhibits a parallel sandwich geometry in which the Fe atom coordinates essentially the planar η^6 -benzene ring and the C_2B_3 face of a dicarbollide cage symmetrically with a dihedral angle of 2.1° . The metal to C_2B_3 and C_6H_6 centroid distances (1.487 and 1.571 Å) are unexceptional. Nonetheless, an interesting structural feature of the complex can be seen in the staggered conformations of the two ligands at the metal center.⁷⁷

The Ru and Os sandwich complexes of mixed subicosahedral carborane and π -arene ligands can also be prepared by the controlled cage degradation of the corresponding icosahedral analogue. Such a reaction involving *closo*-3,1,2-($\eta^6\text{-C}_6\text{H}_6$) $\text{RuC}_2\text{B}_9\text{H}_{11}$ gave the subicosahedral species, 1,2,4-($\eta^6\text{-C}_6\text{H}_6$) $\text{RuC}_2\text{B}_8\text{H}_{10}$ and 2,5,6-($\eta^6\text{-C}_6\text{H}_6$) $\text{RuC}_2\text{B}_7\text{H}_{11}$ in low yields.¹⁴⁹ A potential icosahedral osmium precursor, *closo*-3,1,2-($\eta^6\text{-C}_6\text{H}_6$) $\text{OsC}_2\text{B}_9\text{H}_{11}$, was synthesized by the reaction of (η^6 -

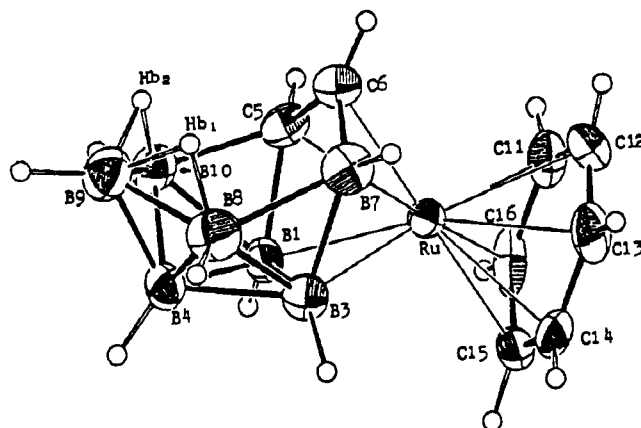
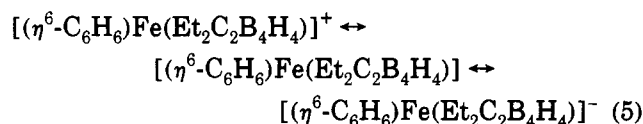


Figure 43. The crystal structure of 2,5,6-($\eta^6\text{-C}_6\text{H}_6$) $\text{RuC}_2\text{B}_7\text{H}_{11}$. Reprinted from ref 149. Copyright 1985 American Chemical Society.

C_6H_6) $\text{OsCl}_2\text{-NCCH}_3$ with $\text{Ti}[3,1,2\text{-TiC}_2\text{B}_9\text{H}_{11}]$.¹⁴⁹ Although the structures of this Os complex and the RuC_2B_8 species have not been determined in the solid state, the crystal structure of 2,5,6-($\eta^6\text{-C}_6\text{H}_6$) $\text{RuC}_2\text{B}_7\text{H}_{11}$ (see Figure 43) shows that the metal is not located on the six-membered open face, but occupies one of the lower ring vertices adjacent to the cage carbons. The average $\text{Ru-C}_{(\text{cage})}$, $\text{Ru-C}_{(\text{arene})}$, and Ru-B distances (2.15, 2.22, and 2.19 Å) are well within the range of those observed for ($\eta^6\text{-C}_6\text{H}_6$) Ru^{II} complexes¹¹¹. Thus, the structure represents a 24-electron, 10-membered *nido*-ruthenacarborane, similar to that of decaborane, and provides important information on the mechanism of the cluster degradation in metallacarborane systems.¹⁴⁹

The electrochemical properties of a number of mixed-ligand metal complexes of the type ($\eta^6\text{-arene}$) $\text{M}(\eta^5\text{-Et}_2\text{C}_2\text{B}_4\text{H}_4)$ (where $\text{M} = \text{Fe}, \text{Ru}$) have been reported recently by Grimes and co-workers.¹⁵⁰ The $\eta^6\text{-arene-Fe}^{\text{II}}$ species undergoes one oxidation and one reduction process, resulting in corresponding Fe^{III} and Fe^{I} complexes (eq 5). The electrolytic oxidation of (C_6Me_6)-



$\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)$ resulted in a green-brown solution displaying a strong ESR signal with g values 2.486 and 2.002 which are assigned to d^5 , Fe^{III} complex $[(\text{C}_6\text{Me}_6)\text{Fe}(\text{Et}_2\text{C}_2\text{B}_4\text{H}_4)]^+$.¹⁵⁰ The Ru complex also undergoes one-electron oxidation, but, unlike Fe, the oxidation product is unstable and no reduction was observed. Overall, this study clearly indicates that a carborane ligand such as $[\text{R}_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$ dianion imparts a significant thermodynamic and kinetic stabilization to Fe^{III} and Ru^{III} complexes unlike the Cp analogues.¹⁵⁰

The fluxional cluster isomerization in 10-vertex *closo*-2,1,6-ruthena- and -rhodacarboranes was studied in detail and the crystal structure of $[2\text{-(}\eta^6\text{-C}_6\text{Me}_6\text{)-closo-2,1,6-RuC}_2\text{B}_7\text{H}_9]$ was determined by Greenwood and co-workers.¹⁵¹ The $\text{Ru-C}(1)$ distance of 2.05 Å is significantly shorter than the $\text{Ru-C}(6)$ distance of 2.19 Å, while the Ru-B distances are in the normal range. A number of 18-electron rhodacarboranes of the type $[\text{closo-3,3-(}\eta^2\text{-}\eta^3\text{-C}_7\text{H}_7\text{CH}_2\text{)-1,2-R}^1\text{R}^2\text{-3,1,2-RhC}_2\text{B}_9\text{H}_9]$ and $[\text{closo-2,2-(}\eta^2\text{-}\eta^3\text{-C}_7\text{H}_7\text{CH}_2\text{)-2,1,7-RhC}_2\text{B}_9\text{H}_9]$ (where R^1

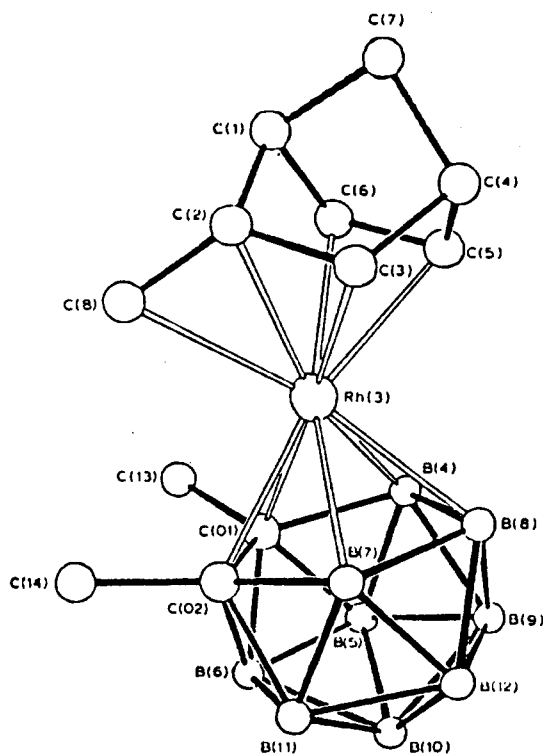


Figure 44. The molecular structure of the 18-electron rhodacarborane, *closo*-3,3-(η^2, η^3 -C₇H₇CH₂)-1,2-Me₂-3,1,2-RhC₂B₉H₉. Reprinted from ref 152. Copyright 1988 Elsevier Sequoia.

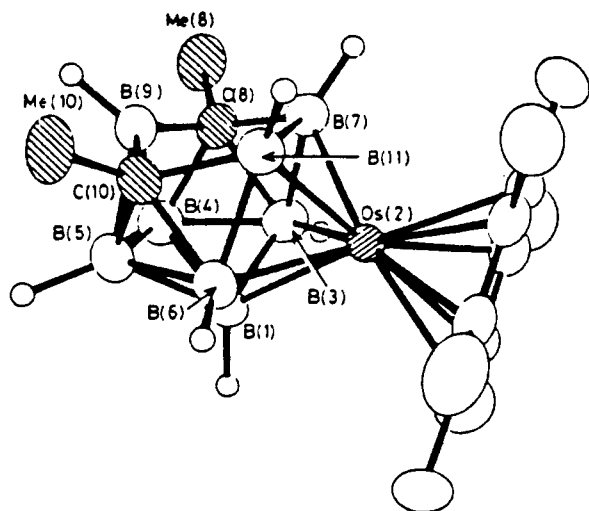


Figure 45. Molecular structure of the osmacarborane [2-(η^6 -C₆Me₆)-8,10-(Me)₂-nido-2,8,10-OsC₂B₈H₈]. Reprinted from ref 153. Copyright 1987 Royal Society of Chemistry.

$\text{R} = \text{H, Me or Ph}$) have been prepared by the reaction of {2-(hydroxymethyl)norbornadiene}(acetylacetonato)rhodium with mono- and disubstituted dicarbollide anions, followed by the acidification of the product with HPF_6 .¹⁵² The crystal structure of one of the mixed-ligand species, [*clos*-3,3-(η^2, η^3 - $\text{C}_7\text{H}_7\text{CH}_2$)-1,2-Me₂-3,1,2-RhC₂B₉H₉], shown in Figure 44, reveals that the Rh-C⁺(8) distance (2.354 Å) is considerably longer than the other Rh-C(norbornadienyl ligand) bonds (2.139–2.247 Å).¹⁵²

An orange, air-stable, mixed-ligand species of the Os metal, [2-(η^6 -C₆Me₆)-8,10-(Me)₂-*nido*-2,8,10-OsC₂B₃H₅] has been prepared quantitatively by thermal rearrangement of its so-called *closo* precursor, [1-(η^6 -C₆Me₆)-2,4-(Me)₂-1,2,4-OsC₂B₃H₃] at 400 °C for 14

min.¹⁵³ Unlike the "slipped" platinacarboranes, the crystal structure (see Figure 45) of the complex unambiguously shows a five-membered open face without the Os metal (BCBCB), resembling that of the "26-electron" $[nido-B_{11}H_{14}]^-$ anion.¹⁵⁴ The average Os-B and Os-C(arene*) distances are 2.175 and 2.26 Å, respectively. This work clearly demonstrates that the electron-counting rules should be supported by the crystallographically determined structures before predictions on the geometries of such complexes are made.^{6,7}

Clearly, the advances in this area have already reached a stage beyond the structural and bonding curiosities. The practical applications of monomeric species are being developed. Indeed, Grimes' elegant discovery of the utility of π -arene-metallacarboranes as basic building blocks in the construction of multidecker species (discussed in the previous section and elsewhere^{3a}) has given a new dimension to this area of metalla-C₂B₄ carborane chemistry, and as such a major breakthrough could be envisioned in these and other π -arene-metallacarborane systems.

E. Complexes of Mono-, Tri-, and Tetracarbon Carborane Ligands

In contrast to the vast number of metal complexes based on dicarbon-carborane ligand systems, the mono-, tri-, and tetracarbon containing metallacarboranes are relatively less explored area of organometallic chemistry. This is partly due to unavailability of their ligand precursors readily, and in many instances the carbon and other heteroatoms, such as N, P, S, Se, etc., are inserted along with the metal substrates simultaneously into polyhedral borane clusters.^{3a,71,84} Exceptions are the tetracarbametallaboranes which are prepared directly from the reaction of metal reagents with the dianionic $[R_4C_4B_3H_8]^{2-}$ ligand, produced from the corresponding neutral nido precursor, $R_4C_4B_3H_8$.⁷⁴ Nevertheless, the metal complexes of these systems represent a relatively young class of metallacarborane chemistry that has been developing slowly over the past 20 years or so, and the literature up to 1987 has been reviewed previously.¹⁵⁵ Therefore, we will discuss only those reports that appeared after 1987.

The C-substituted monocarba carborane ligand 9-(CH₃)₂S-7-[(Me₃Si)₂CH]-7-CB₁₀H₁₁, prepared from decaborane and Me₃SiC≡CSiMe₃ in the presence of Me₂S,¹⁵⁶ was reacted with [(η-Cp)Ni(CO)]₂ or [(η-Cp)Co(CO)]₂ in refluxing toluene or mesitylene to synthesize {2-(η-Cp)-1-[(Me₃Si)₂CH]-2,1-NiCB₁₀H₁₀} or {7-Me₂S-2-(η-Cp)-1-[(Me₃Si)₂CH]-2,1-CoCB₁₀H₁₀} in very low yields.¹⁵⁷ On the other hand, the metal atom synthesis involving this monocarbaborane with Co and toluene produced, in poor yields, the corresponding *closo*-monocarbacobaltaborane {2-(η⁶-C₆H₅CH₃)-1-[(Me₃Si)₂CH]-2,1-CoCB₁₀H₁₀} as an air-stable solid. The crystal structures of the Ni and Co mixed-ligand sandwich species have been determined, and only that of the Co complex is shown in Figure 46.¹⁵⁷ The Co-C distance of 2.14 Å, although similar to that in the structure of (η⁶-C₆H₅CH₃)Co(C₆F₅)₂,¹⁵⁸ is slightly longer than the average Co-B distance of 2.07 Å, thus showing a distorted MCB₁₀ cage. Consequently, the planes of the carborane and toluene ligands are tilted with respect to each other by about 7.6°. Perhaps, this tilting may purely be the result of steric crowding caused by the

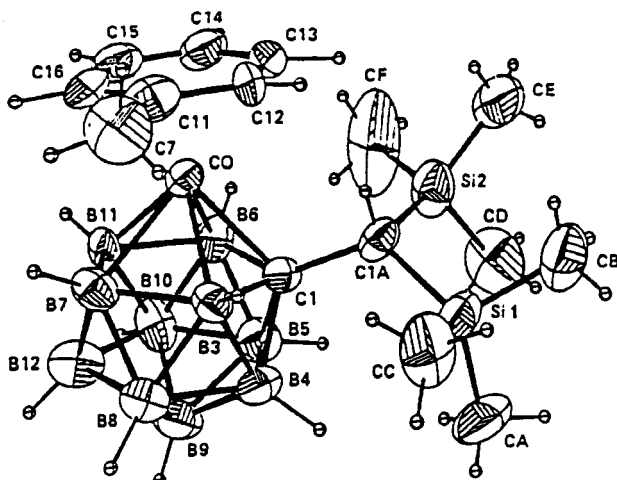


Figure 46. Crystal structure of $\{2-(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{-}1\text{-}[(\text{Me}_3\text{Si})_2\text{CH}]\text{-}2,1\text{-CoCB}_{10}\text{H}_{10}\}$. Reprinted from ref 157. Copyright 1988 American Chemical Society.

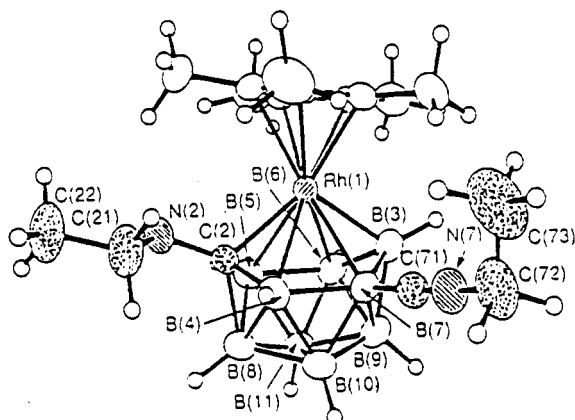


Figure 47. Molecular structure of the rhodacarborane $1-(\eta^5\text{-C}_5\text{Me}_5)\text{-}2\text{-(NHET)}\text{-}7\text{-(CNET)}\text{-closo-}1,2\text{-RhCB}_9\text{H}_9$. Reprinted from ref 159. Copyright 1990 Royal Society of Chemistry.

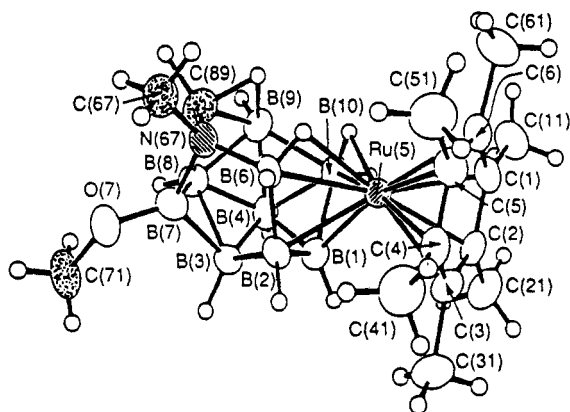


Figure 48. Molecular structure of the ruthenacarborane $5-(\eta^5\text{-C}_5\text{Me}_5)\text{-}7\text{-(OMe)}\text{-arachno-}5\text{-RuN(Me)C(H)B}_9\text{H}_{11}$. Reprinted from ref 159. Copyright 1990 Royal Society of Chemistry.

$(\text{Me}_3\text{Si})_2\text{CH}$ and the η^6 -toluene units near the metal center.¹⁵⁷

An insertion of C-atom into a metallaborane cluster could be accomplished as in the reaction involving 6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB₉H₁₃ or 6-($\eta^6\text{-C}_6\text{Me}_6$)-8-(OMe)-*nido*-6-RuB₉H₁₂ and RNC (R = Et, Me) that produced the corresponding C-inserted and both C- and B-substituted metallaborane derivative 1-($\eta^5\text{-C}_5\text{Me}_5$)-2-(NHR)-7-(CNR)-*closo*-1,2-RhCB₉H₉ or both CN-inserted and B-substituted unusual and unpredicted 5-($\eta^6\text{-C}_6\text{Me}_6$)-

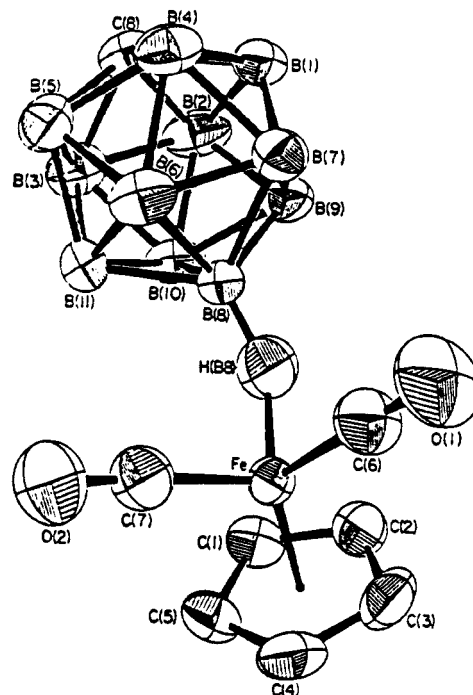
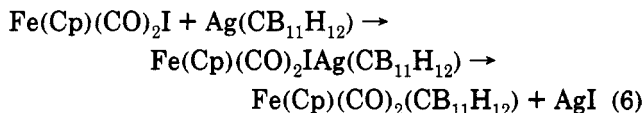


Figure 49. Molecular structure of $\text{Fe(Cp)(CO)}_2(\text{B}_{11}\text{CH}_{12})$. Reprinted from ref 160. Copyright 1989 American Chemical Society.

7-(OMe)-*arachno*-5-RuN(R)C(H)B₉H₁₁ in low yields.¹⁵⁹ The crystal structures of these complexes are shown in Figures 47 and 48. The rhodacarborane adopts an 11-vertex *closo* geometry, whereas the ruthenacarborane exhibits a unique 12-vertex RuNCB₉ cluster that has four-membered BBCN, five-membered BBBCN, and six-membered RuBBBCN open faces. The bond angles and lengths are unexceptional (Rh-B 2.121–2.461 Å and Ru-B 2.221–2.352 Å).¹⁵⁹ This is one of the prime examples of serendipity that exists in such insertion reactions.

The role of monocarbaborane anion $[\text{CB}_{11}\text{H}_{12}]^-$ as the least coordinating ligand to the metal substrates has been explored by Reed and co-workers in recent years. This property of the ligand has been further demonstrated by preparing exopolyhedrally linked Fe and Ir complexes from the reaction of argentacarboranes with the corresponding Fe or Ir salt as in eq 6.^{160–162} The



crystal structure of $\text{Fe(Cp)(CO)}_2(\text{B}_{11}\text{CH}_{12})$ (Figure 49) shows that the monocarbaborane anion is coordinated to iron via an Fe–H–B bridge with an angle of 141°. The Fe–H distance of 1.56 Å is significantly shorter than 1.82 Å found in iron(III) porphyrinate complex, $[\text{Fe(TPP)(B}_{11}\text{CH}_{12})]$,¹⁶² but is similar to those of “soft” ferracarboranes (1.56–1.61 Å).¹⁶³ The crystal structure of the argentacarborane precursor, $\text{AgB}_{11}\text{CH}_{12}\cdot 2\text{C}_6\text{H}_6$, shows that the silver is η^1 -coordinated to a benzene molecule (2.400 Å), while the second benzene molecule is present outside the coordination sphere even though identical C–C distances could be found in both rings (see Figure 50).¹⁶⁴ The two Ag–H distances (1.97 Å) arise from the interaction of the silver with one B–H_(terminal) bond of each cage resulting in a dimer in

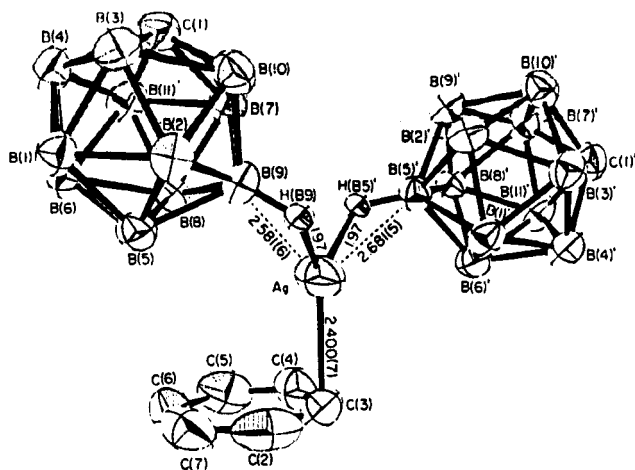


Figure 50. An ORTEP diagram of an argentamonocarborane. Reprinted from ref 164. Copyright 1986 American Chemical Society.

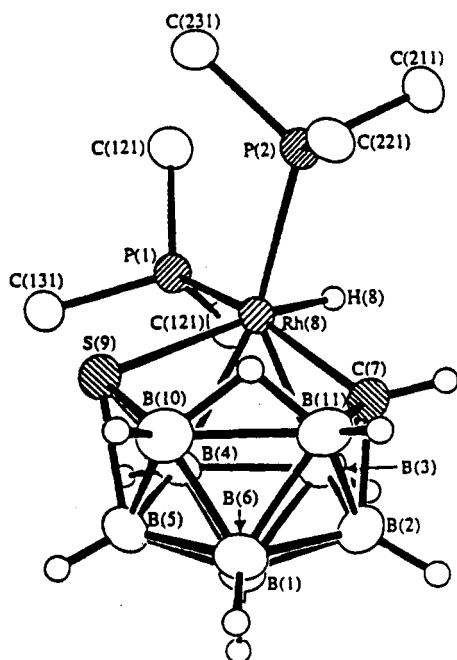


Figure 51. Molecular structure of *nido*-8,8-(PPh₃)₂-8-H-8,7,9-RhCSB₈H₁₀. Reprinted from ref 165. Copyright 1992 American Chemical Society.

which the monocarbaborane cage acts as a bridging ligand to give an alternating cation-anion chain. The bonding of Ag to two monoanionic polyhedral cages and to one arene ligand make the formal coordination number three for the metal. Although this structure represented the first example of a silver-hydrogen bonding, since then, more structures exhibiting such bonds have emerged from the same research group.¹⁶¹

A polyhedral metal complex that incorporates S, C, and Rh atoms as cluster vertices and simultaneously obeying the Williams and Wade's electron-counting rules, *nido*-8,8-(PPh₃)₂-8-H-8,7,9-RhCSB₈H₁₀, has been synthesized, in high-yield, from the reaction between *arachno*-6,9-CSB₈H₁₂ and RhCl(PPh₃)₃ in basic ethanol.¹⁶⁵ The X-ray diffraction analysis revealed the complex to be an open *nido* 11-vertex RhCSB₈ cluster (see Figure 51) with the Rh-S, Rh-C, and Rh-B distances of 2.447, 2.175, and 2.212 Å, respectively.¹⁶⁵ The thermolysis of this rhodathiamonocarborane species results in the formation of *closo*-1,1,1-(PPh₃)₂-1,1-RhCSB₈H₉ quantitatively, whose crystal structure

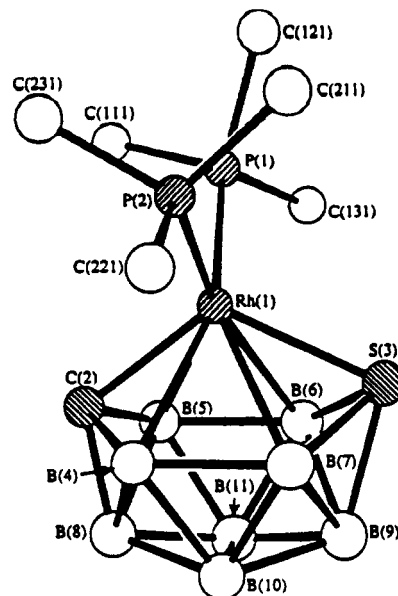


Figure 52. The crystal structure of a rhodathiamonocarborane. Reprinted from ref 165. Copyright 1992 American Chemical Society.

exhibits a *closo* deltahedral 11-vertex RhCSB₈ cluster (Rh-C = 2.11 Å, Rh-S = 2.34 Å, and Rh-B = 2.32–2.46 Å) that also follows the Wadman skeletal-electron counts (see Figure 52).¹⁶⁵

Metallacarboranes derived from tricarbon carboranes have not been explored in great detail with the exception of Siebert's work on diborolene.^{134–136} The low-yield syntheses of the tricarbaboranes restricted their synthetic utility in the production of the corresponding metallatricarbaborane complexes.^{166,167} The most recent report from Sneddon's group on the improved and high-yield (ca. 80%) synthesis of the monoanionic ligand [6-CH₃-5,6,8-C₃B₇H₉][−] and its subsequent conversion to a neutral precursor, *nido*-6-CH₃-5,6,9-C₃B₇H₁₀, has given hope for the rapid development of this area of metallacarborane chemistry.¹⁶⁸ The improved method has facilitated the high-yield syntheses of tricarbammetallaborane complexes of Mn, Fe, Co, and Ni metals such as [*commo*-M(1-M-2-CH₃-2,3,5-C₃B₇H₉)₂] (where M = Fe or Co), [1-M'-2-CH₃-2,3,4-C₃B₇H₉] (where M' = (Cp)Fe or Mn(CO)₃) and [9-(Cp)Ni-8-CH₃-7,8,10-C₃B₇H₉].^{168–170} The complexes were isolated by chromatography and were fully characterized including the X-ray diffraction studies. The crystal structures of the representative tricarbaborane complexes of iron and cobalt, [*closo*-1-(η⁵-C₅H₅)Fe-4-CH₃-2,3,4-C₃B₇H₉], [*commo*-Fe(1-Fe-5-CH₃-2,3,5-C₃B₇H₉)(1-Fe-4-CH₃-2,3,4-C₃B₇H₉)], and [*commo*-Co(1-Co-2-CH₃-2,3,5-C₃B₇H₉)₂], are shown in Figures 53–55. In the former complex, the iron atom is sandwiched between cyclopentadienyl and tricarbaborane monoanions, while in the other two species, the metal is sandwiched by the two tricarbaborane ligands. In these structures, the metal atom bonds more strongly to the two 4-coordinate C atoms than to the third one as evident in the M-C distances [Fe-C(2,3) = 1.977 Å vs Fe-C(4) = 2.265 Å; Co-C(2,3) = 2.029 Å vs Co-C(5) = 2.655 Å]. Consequently, the metallatricarbaborane clusters are significantly distorted and create open four-membered MCCB and five-membered MCCBC puckered faces, in Fe and Co complexes, respectively.^{168,169} In the same report, the cluster rearrangements in 11-vertex ferra- and cobalt-tricarbaborane complexes resulted in methyl group

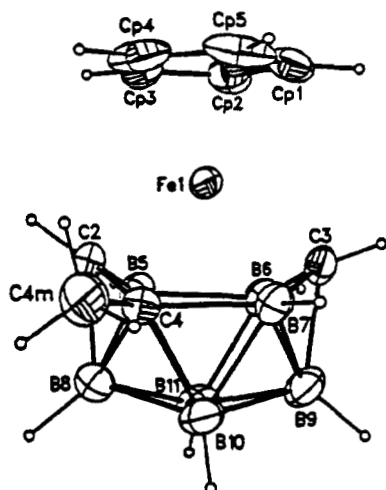


Figure 53. Molecular structure of 1-(η^5 -C₅H₅)Fe-4-CH₃-2,3,4-C₃B₇H₉. Reprinted from ref 168. Copyright 1992 American Chemical Society.

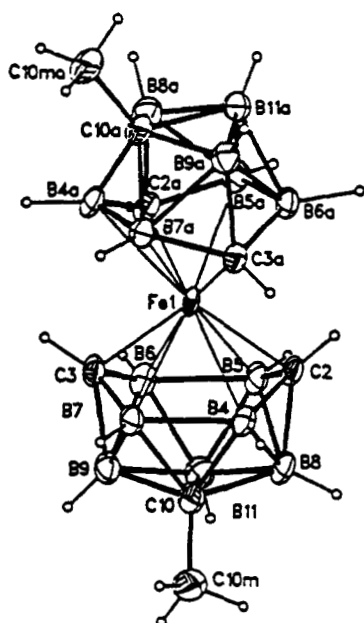


Figure 54. Molecular structure of *commo*-Fe(1-Fe-1-CH₃-2,3,10-C₃B₇H₉)₂. Reprinted from ref 169. Copyright 1992 American Chemical Society.

migrations from the four-coordinate carbon to the adjacent five-coordinate carbon at elevated temperatures. Isotope labeling studies¹⁷⁰ show that these reactions occur by means of cage-carbon skeletal rearrangements, rather than direct methyl migrations, thus resembling the mechanism observed in a metallocene (Cp₂Mo) system.¹⁷¹

Metal atom synthesis has also been employed in the preparation of four-carbon-containing mixed-ligand metal sandwich species 1-(η^6 -C₆Me₆)Fe-4,5,7,8-Me₄-C₄B₈H₈ and 2-(η^6 -Me₆C₆H₅)Fe-6,7,9,10-Me₄C₄B₈H₈ which were prepared from the reactions involving thermally generated iron atoms with pentaborane, toluene, and 2-butyne.¹⁷² The crystal structures show open arachno and nido geometries with Fe atoms occupying the five-coordinate apical and basal vertices, respectively.¹⁷² On the other hand, the conventional method involving the mixed dicarba- and tetracarborane anions, or just the tetracarborane anion such as [Et₄C₄B₈H₈]⁻, with MCl₂ has produced more or less the corresponding targeted metal derivatives. Evidently, a number of Fe

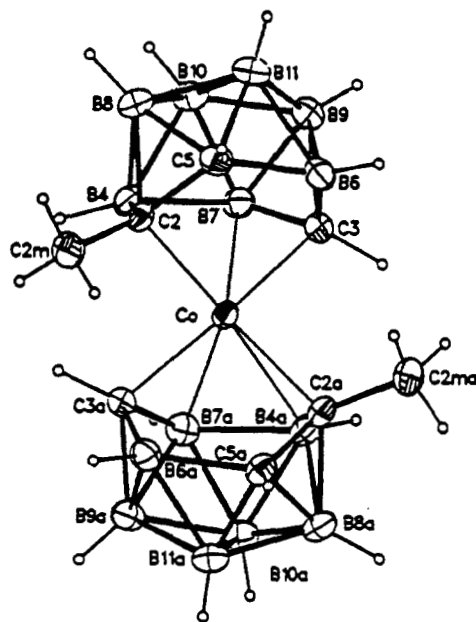


Figure 55. Molecular structure of *commo*-Co(1-Co-2-CH₃-2,3,5-C₃B₇H₉)₂. Reprinted from ref 169. Copyright 1992 American Chemical Society.

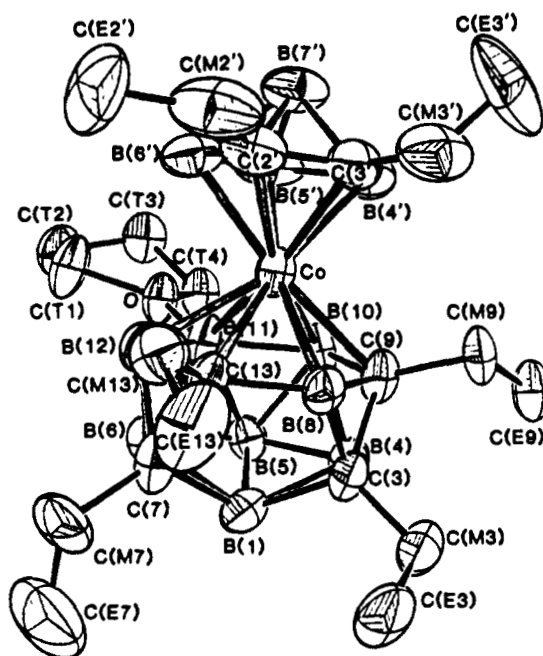


Figure 56. The crystal structure of an iron sandwich complex based on C₂B₄ and C₄B₈ carborane ligand systems. Reprinted from ref 173. Copyright 1985 American Chemical Society.

and Co complexes of a C₄B₈ ligand system has been synthesized.^{173,174} The crystal structure of (Et₂-C₂B₄H₄)Co(Et₄C₄B₈H₇OC₄H₈), shows the fusion between slightly distorted 7-vertex CoC₂B₄ cage (Co-C = 2.15 Å, Co-B = 2.11 Å) and the 13-vertex CoC₄B₈ cluster (Co-C = 2.23 Å, Co-B = 2.17 Å) with a pentagonal BCCBC open face away from the central metal atom (see Figure 56).¹⁷³ The 13-vertex *nido*-CoC₄B₈ cluster is formally derived from a closo 14-vertex cage (bicapped hexagonal antiprism) by removal of an equatorial vertex that makes the carbon atoms on the five-membered open face as low-coordinate ones as in the analogous Ni complex, (Ph₂PCH₂)₂NiMe₄C₄B₈H₈.¹⁷⁵ Nevertheless, the skeletal electron count in the molecule is consistent with the Williams-Wade rules.^{6,7}

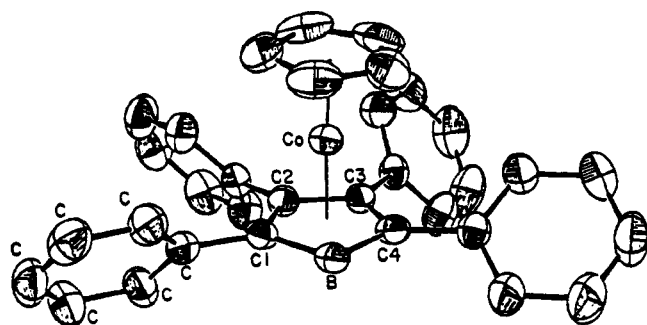
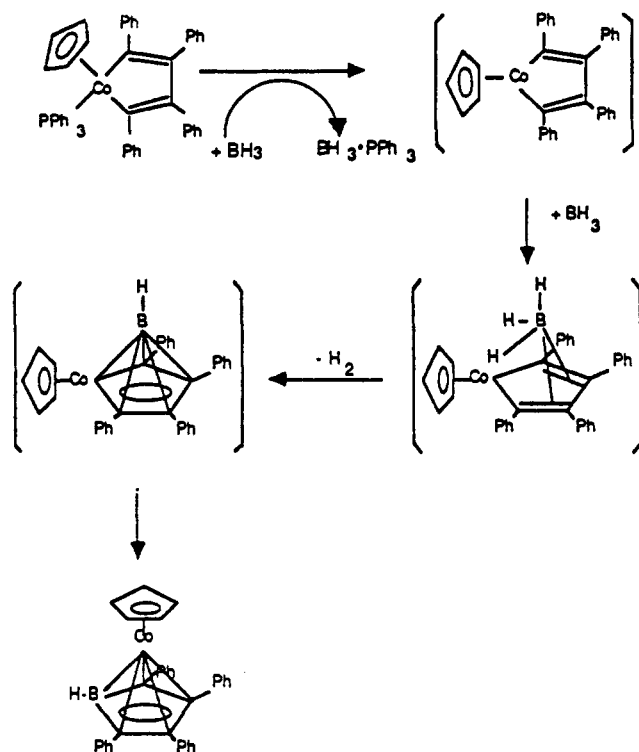


Figure 57. The solid-state structure of $(\text{CpCoC}_4\text{Ph}_4\text{BH})$. Reprinted from ref 176. Copyright 1989 American Chemical Society.

Scheme VII. Proposed Mechanism for the Insertion of a BH Unit into $\text{Cp}(\text{PPh}_3)\text{Co}(\text{CPh})_4$ (Reprinted from ref 176. Copyright 1989 American Chemical Society)



Preparation of several borabenzene complexes have been accomplished via insertion of a BH unit in an organometallic π -complex.¹³⁶ The methodology has now been extended to the metallocarborane chemistry. A cobalt sandwich compound, $(\text{CpCoC}_4\text{Ph}_4\text{BH})$ was prepared by reacting $\text{Cp}(\text{PPh}_3)\text{Co}(\text{CPh})_4$ with $\text{BH}_3 \cdot \text{THF}$ as shown in Scheme VII.¹⁷⁶ The crystal structure of this complex (Figure 57) reveals that the CpCo fragment is in the apical position, and the B-H fragment is in a basal position of the CoC_4B nido cluster core. The Co-B distance of 2.147 Å is significantly longer than the average cobalt distances to the C_4B ring carbons (2.045 Å). The Cp and BC_4 rings are coplanar and the boron atom is slightly below the plane defined by the cage carbons.¹⁷⁶

The results to date indicate that the patterns of reactivity are slowly emerging in the tricarbametallaborane systems and, to some extent, in the species containing four-carbon atoms as well. Nevertheless, the future investigations in this area hold the promise of being every bit as fascinating as the previous ones.

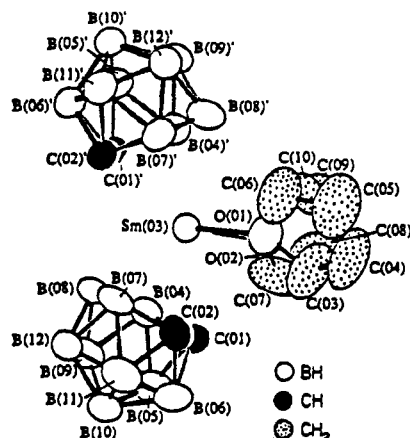


Figure 58. Molecular structure of $[3,3-(\text{THF})_2\text{-commo-3,3'-Sm}(3,1,2\text{-SmC}_2\text{B}_9\text{H}_{11})_2]$. Reprinted from ref 180. Copyright 1988 American Chemical Society.

III. Metallocarboranes of f-Block Elements

During the last decade or so, the chemistry of lanthanide elements has taken a new direction since it is no longer limited to the formation of purely ionic compounds. In fact, new classes of complexes, unusual structures, and novel reactivity patterns have emerged with the elements of lanthanides and a lanthanide congener, yttrium.^{25,28,177} Although a variety of ligands has been established in organolanthanide systems, the cyclopentadienide anion and its C-substituted derivatives have been widely utilized.¹⁷⁸ The chemistry of lanthanide complexes of C_2B_{10} , C_2B_9 , and C_2B_4 carborane ligand systems have just begun to be explored.

Consequently, Hawthorne and co-workers have prepared a number of lanthanacarboranes during the past four years or so from the reaction of Na salt of the dicarbollide dianion with LnI_2 ($\text{Ln} = \text{Yb}$ or Sm) in THF and further oxidation of the immediate closo species with the thallacarborane salt $[\text{PPN}][\text{closo-3,1,2-TiC}_2\text{B}_9\text{H}_{11}]$. The resulting half-sandwich and sandwich complexes of the general formulas $[\text{closo-Ln}^{\text{II}}(\text{C}_2\text{B}_9\text{H}_{11}) \cdot (\text{THF})_4]$ and $[\text{PPN}][\text{commo-Ln}^{\text{III}}(\text{C}_2\text{B}_9\text{H}_{11})_2 \cdot (\text{THF})_2]$, respectively, were obtained in good yields.^{179,180}

The weak coordination of the THF solvent to the metal was demonstrated by the substitution reactions with stronger bases such as MeCN and DMF. These novel lanthanacarboranes were fully characterized including NMR spectra, magnetic susceptibility, and X-ray diffraction. The crystal structures of the $[\text{PPN}][\text{salt of sandwich samaracarborane}, [3,3-(\text{THF})_2\text{-commo-3,3'-Sm}(3,1,2\text{-SmC}_2\text{B}_9\text{H}_{11})_2]$, and the half-sandwich ytterbacarborane, $[\text{Yb}(\text{C}_2\text{B}_9\text{H}_{11})(\text{DMF})_4]$, are shown in Figures 58 and 59.^{179,180} The structures reveal that the metal is essentially centered over the planar pentagonal C_2B_3 face(s). The coordination sphere of the Yb metal is completed by bonding to four DMF molecules and one dicarbollide ligand with the average Yb-B distances of 2.74 Å. On the other hand, the geometry of the Sm sandwich can be described as a distorted tetrahedron with two carborane cages and two THF molecules. While the centroid-Sm-centroid angle of 131.9° is similar to that reported for Cp^*_2LnL derivatives ($\text{L} = \text{other ligand}$),¹⁸¹ the Sm-centroid distances of 2.33 Å in the complex are significantly shorter than those (av 2.45 Å) of $\text{Cp}^*_2\text{Sm}(\text{Cl})(\text{THF})$ and $[\text{Cp}^*_2\text{Sm}(\text{I})(\text{THF})]$,¹⁸² thus confirming the tighter bonding of the lanthanide to the dicarbollide ligands than to the Cp^* anions.

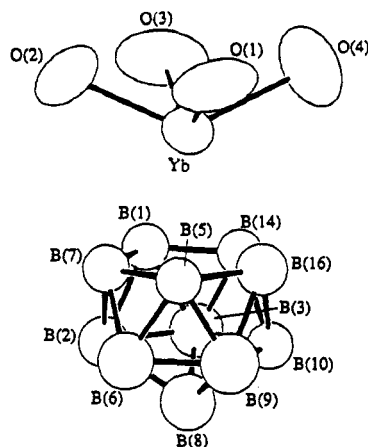


Figure 59. Molecular structure of $[\text{Yb}(\text{C}_2\text{B}_9\text{H}_{11})(\text{DMF})_4]$. Reprinted from ref 180. Copyright 1988 American Chemical Society.

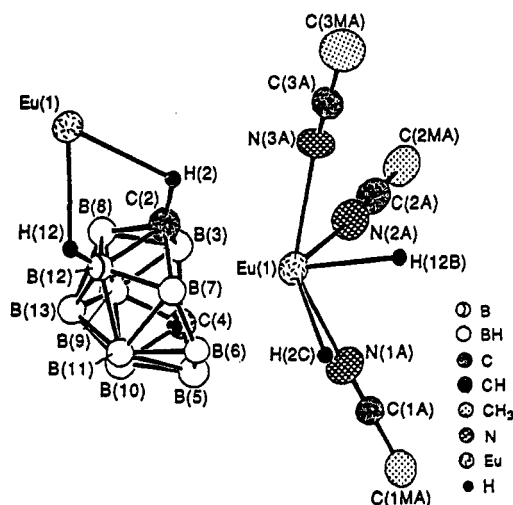


Figure 60. Structure of a polymeric Eu complex, $[\text{closo-1,1,1-(MeCN)}_3\text{-1,2,4-EuC}_2\text{B}_{10}\text{H}_{12}]$. Reprinted from ref 183. Copyright 1992 American Chemical Society.

The utility of $[\text{C}_2\text{B}_{10}\text{H}_{12}]^{2-}$ dianion in lanthanide chemistry has also been demonstrated in the synthesis of polymeric lanthanacarboranes of general formula, $[\text{closo-1,1,1-(THF)}_3\text{-1,2,4-Ln-C}_2\text{B}_{10}\text{H}_{12}]_\infty$, from the reaction of $\text{LnI}_2(\text{THF})_2$ (where $\text{Ln} = \text{Sm}, \text{Eu}$) in THF.¹⁸³ When $\text{Ln} = \text{Eu}$, the reaction can be carried out further with 1 equiv of $\text{Na}_2[\text{C}_2\text{B}_{10}\text{H}_{12}]$ to produce the corresponding Eu sandwich, $[\text{1,1-(THF)}_2\text{-commo-1,1'-Eu(1,2,4-EuC}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$ in 65% yield. Interestingly, this species can also be generated directly by the reaction of EuCl_3 with $\text{Na}_2[\text{C}_2\text{B}_{10}\text{H}_{12}]$.^{183,184} The molecular structures of polymeric half-sandwich complex $[\text{closo-1,1,1-(MeCN)}_3\text{-1,2,4-EuC}_2\text{B}_{10}\text{H}_{12}]_\infty$ and the anionic sandwich $[\text{1,1-(THF)}_2\text{-commo-1,1'-Eu(1,2,4-EuC}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$ are shown in Figures 60 and 61.^{183,184} The crystal structure of the *closo*-europacarborane is composed of two crystallographically independent spiral chains with the carborane moieties serving each as a ligand for two europium atoms while bonding to one via both upper and lower belt so as to form Eu-H-E (where $\text{E} = \text{B}$ or C) agostic structural arrangement ($\text{Eu-C} = 3.04$, $\text{Eu-B} = 2.96$, $\text{Eu-N} = 2.678 \text{ \AA}$).^{183,184} The coordination sphere about each europium atom is completed by three acetonitrile ligands and the repeat of this arrangement gave a polymeric structure as in the strontium analogue.¹⁸⁵ The commo complex $[\text{Et}_4\text{N}]_2[\text{1,1-(THF)}_2\text{-commo-1,1'-Eu(1,2,4-EuC}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$

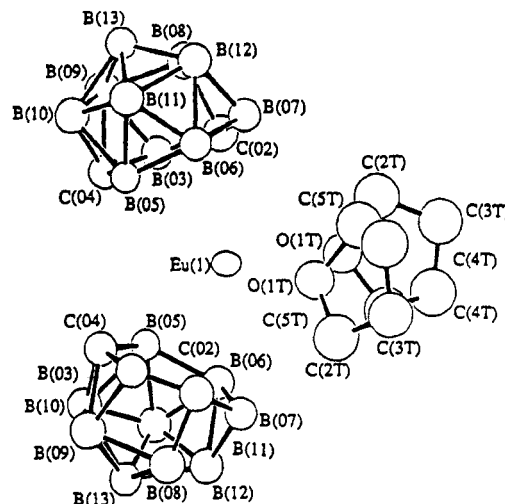


Figure 61. Molecular structure of an anionic europium sandwich complex $[\text{1,1-(THF)}_2\text{-commo-1,1'-Eu(1,2,4-EuC}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$. Reprinted from ref 183. Copyright 1992 American Chemical Society.

$\text{H}_{12}]_2]$ (see Figure 61; $\text{Eu-C} = 2.89$ and 3.20 \AA , $\text{Eu-B} = 2.98, 2.99, 3.09$ and $>3.09 \text{ \AA}$, $\text{Eu-O(THF)} = 2.63 \text{ \AA}$; centroid-Eu-centroid = 127.4° , centroid-Eu-O(THF) = 109.9 and 111.3° , $\text{O(THF)-Eu-O(THF)} = 74.8^\circ$).^{183,184} is isostructural with the Sm species shown in Figure 58.^{179,180}

Despite the success in syntheses and structural characterizations of a number of half-sandwiched and sandwiched Sm^{II} , Sm^{III} , Yb^{II} , and Eu^{II} complexes of both C_2B_9 and C_2B_{10} carborane ligand systems, there have been no reports on the analogous species incorporating other lanthanide metals. The preliminary report on a gadolinacarborane failed to confirm its molecular geometry in the solid state.¹⁸⁶ The most recent report on the synthesis and crystal structure of a *closo*-gadolinium(III)-carborane cluster of the type $\{[\eta^5\text{-1-Gd-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_3[(\mu_2\text{-1-Li-2,3-(SiMe}_3)_2\text{-2,3-C}_2\text{B}_4\text{H}_4)(\mu_3\text{-OMe})][\mu_2\text{-Li-(C}_4\text{H}_8\text{O)}]_3(\mu_3\text{-O})\}$ demonstrates that the Gd metal can also be incorporated as cluster vertices into carborane cages.⁶⁶ Since this complex is the first lanthanacarborane based on C_2B_4 carborane ligands, comparative reactivity and structural patterns are unavailable. In a reaction involving the THF-solvated $\text{Li}_2[2,3\text{-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]$ salt and anhydrous GdCl_3 in a molar ratio of 2:1 in dry benzene (C_6H_6), an unusual, trinuclear gadolinacarborane was produced in 58% yield. The crystal structure (Figure 62) shows that the molecule is constructed from six carborane cages, three solvated-THF molecules, three Gd atoms, and six Li atoms to form a tricapped trigonal prism with Gd atoms in the capping positions. The gadolinium metal in each *closo*-gadolinacarborane unit is η^5 -bonded to the carborane face with Gd-cage atoms and Gd-centroid distances ranging from 2.71 to 2.80 \AA and 2.38 to 2.4 \AA , respectively. As expected, the metal-centroid distances in the complex are shorter than those in $(\eta^5\text{-C}_5\text{H}_5)_3\text{Gd(THF)}_3$,¹⁸⁷ $[(\eta^5\text{-C}_5\text{H}_5)_2\text{-Gd(Br)}]_2$,¹⁸⁸ $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Gd}]_5(\mu_2\text{-OMe})_4(\mu_3\text{-OMe})_4(\mu_5\text{-O})\}$,¹⁸⁹ and in the polymeric complex $[(\eta^5\text{-C}_5\text{H}_5)_2\text{-Gd(Br)}]_\infty$.¹⁸⁸ While *closo*-gadolinacarboranes are bridged by both $\text{Li}^+(\text{THF})$ and *closo*-lithiacarborane moieties, in opposite directions, an O atom triply bridges the three Gd metals (av $\text{Gd-O}_{(\text{central})} = 2.193 \text{ \AA}$; $\text{Gd-O}_{(\text{central})}\text{-Gd} = 119.1^\circ$) slightly out of the Gd_3 triangular plane (0.22 \AA). Since each of the six carborane ligands bears

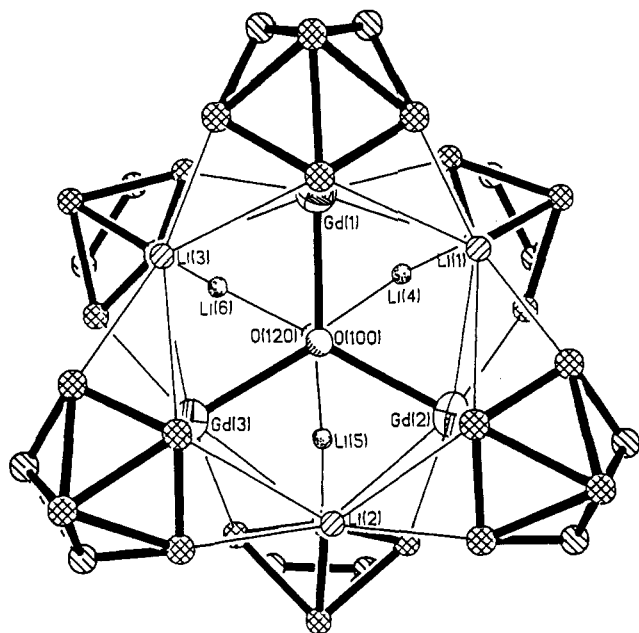


Figure 62. A perspective view (from above) showing the C_2B_4 cages and equilateral triangles of Gd and Li atoms in a trinuclear Gd complex. Reprinted from ref 66. Copyright 1992 VCH Publishers.

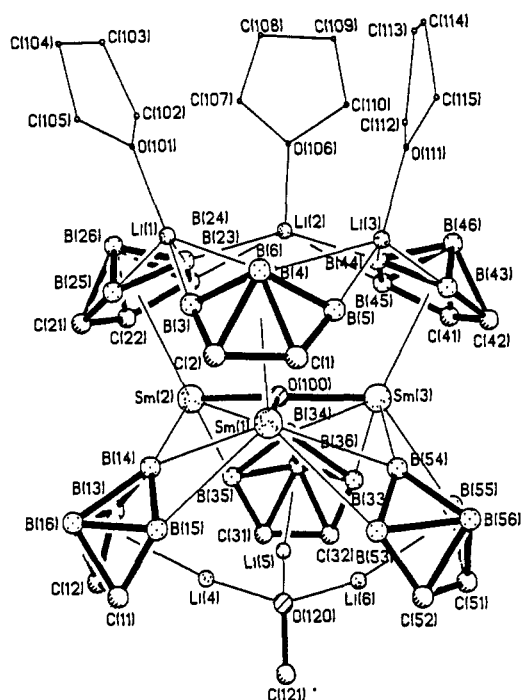


Figure 63. A perspective view of the isostructural trinuclear Sm(III) complex. Reprinted from ref 67.

a -2 charge and three Gd^{III} and six Li^I metals are present, for charge compensation an additional $(MeO)^-$ moiety is bound to the apical lithium atoms of the lower triangle of *closo*-lithiacarboranes in a tetrahedral fashion (av $Li-O-Li = 106^\circ$ and $Li-O-C = 113^\circ$). The source of the methoxide ion was discovered during the syntheses of a number of isostructural lanthanacarborane complexes incorporating Sm^{III} , Tb^{III} , Dy^{III} , and Ho^{III} metals. The representative structures, when $Ln = Sm$ and Ho , are shown in Figures 63 and 64.⁶⁷

It is commonly known that the Sm^{II} complexes tend to undergo oxidation with oxygen-containing substrates to form the corresponding Sm^{III} species because of their high reactivity and great oxophilicity.¹⁷⁸ This was tested

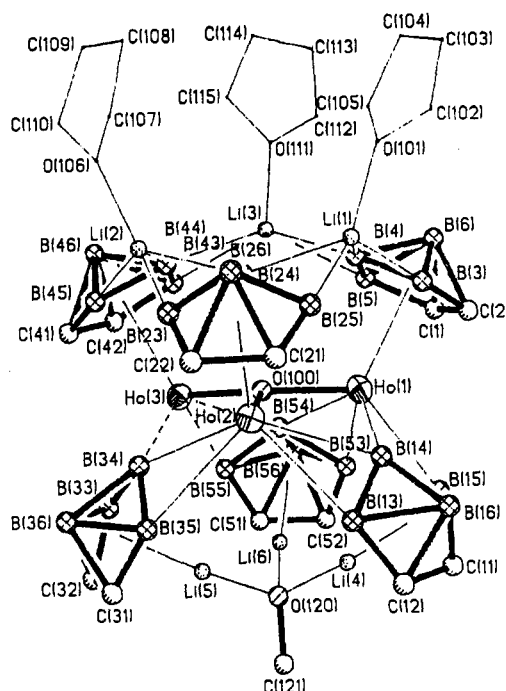


Figure 64. A perspective view of the isostructural trinuclear Ho(III) complex. Reprinted from ref 67.

by reacting $SmCl_3$ with 1 equiv of THF-solvated $Li_2[2,3-(SiMe_3)_2C_2B_4H_4]$ salt in dry benzene at $0^\circ C$ for 24 h and then treating the product with *tert*-butyl alcohol in order to isolate a Sm^{II} complex.⁶⁷ Since the complex was a pale yellow solid and most of the reported Sm^{II} species were found to be red solids,¹⁷⁸ formulation of the product as Sm^{II} -carborane was questionable although it was supported by its magnetic susceptibility data ($\mu_{eff} = 3.5 \mu_B$). This ambiguity was resolved by determining the crystal structure of the pale yellow solid that showed the complex to be a Sm^{II} -carborane species of the formula $[1,1,1-(t-C_4H_9OH)_3-2,3-(SiMe_3)_2-4,5-(Li(C_4H_9O)Cl)-closo-\eta^5-1-Sm-2,3-C_2B_4H_4] \cdot C_4H_9O$ (see Figure 65).⁶⁷ The C_2B_4 carborane ligand is essentially η^5 bonded to the Sm metal (Sm -centroid = 2.445 \AA), and three *tert*-butyl alcohol molecules are coordinated to Sm through oxygen. The three $Sm-O$ distances range from 2.10 to 2.31 \AA , while $O(13)-Sm-O(23)$ angle (77.3°) is severely contracted by about 36° when compared to the average value of 113.4° in other two $O-Sm-O$ angles. This is presumably due to second coordination of $O(13)$ atom to the THF-solvated Li metal with the distance of 1.98 \AA . Perhaps, the steric repulsion between the silyl and *tert*-butyl groups could be responsible for the unusual linear arrangement of Sm, $O(18)$, and $C(19)$ atoms (177.7°). Nonetheless, the average $O-Sm-Cnt$ angles of 113.3° constitute a distorted-tetrahedral geometry of the metal center in the complex. The incorporation of $LiCl$ salt within the coordination sphere of the complex is unusual and interesting. Since the complex can be converted to the corresponding trinuclear system in the absence of *tert*-butyl alcohol, it could be considered as an intermediate species in these systems.

These recent results clearly suggest that a number of novel mono-, tri-, and polynuclear lanthanide complexes of carborane systems could be synthesized and their reactivity patterns established.

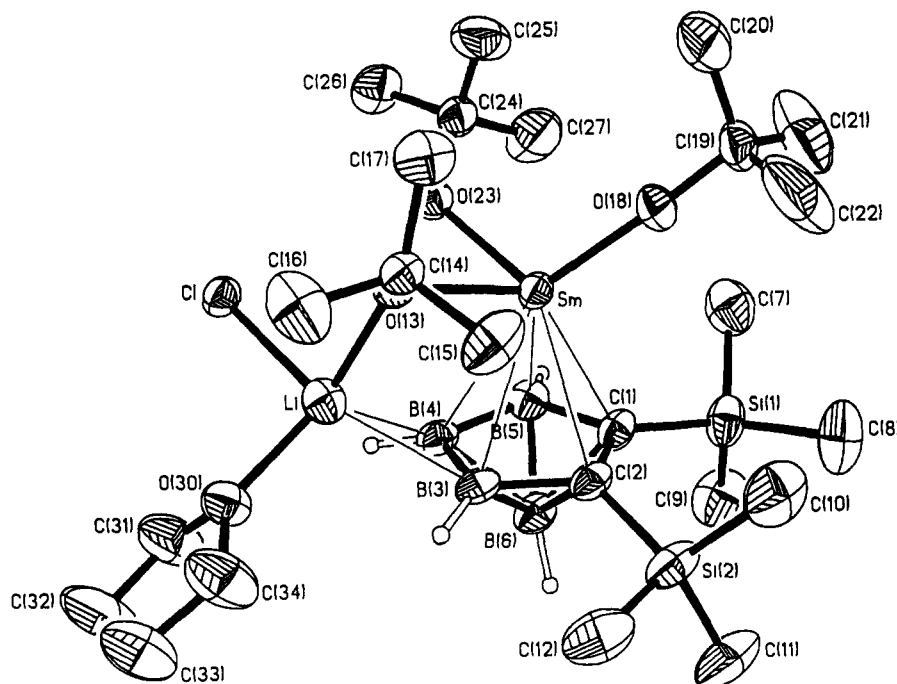


Figure 65. Molecular structure of a *closo*-samaracarborane showing the coordination of LiCl salt and *t*-BuOH molecules. Reprinted from ref 67.

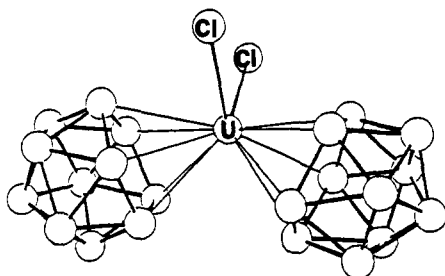


Figure 66. The crystal structure of an actinacarborane $[\text{Li}(\text{THF})_4]_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$. Reprinted from ref 190. Copyright 1976 American Chemical Society.

Except for one report, in 1977, there has been no activity at all in the area of actinacarborane chemistry.¹⁹⁰ Since this work has been cited continuously and none of the reviews described the synthesis and crystal structure of the uranium complex in the paper, we chose to discuss this particular and the *only known actinacarborane*. As per this report, the uranium sandwich compound $[\text{Li}(\text{OC}_4\text{H}_9)_4]_2[\text{U}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Cl}_2]$ was prepared, in excess of 75% yield, by the reaction of UCl_4 with $\text{Na}_2(\text{C}_2\text{B}_9\text{H}_{11})$ in THF. The crystal structure (Figure 66) shows the coordination geometry of the uranium as a distorted tetrahedron consisting of two η^5 -dicarbollide ligands and two σ -bonded Cl atoms. The average U to dicarbollide distances of 2.73 Å is comparable to those found in an uranocene derivative.²⁶⁷ The centroids of the dicarbollide bonding faces form an angle of 137° about the uranium atom. The bent-sandwich geometry of the complex is very similar to those of bent metallocenes and analogous $[3,3-(\text{THF})_2\text{-}commo\text{-}3,3'\text{-Sm}(3,1,2\text{-SmC}_2\text{B}_9\text{H}_{11})_2]^-$ and $[1,1-(\text{THF})_2\text{-}commo\text{-}1,1'\text{-Eu}(1,2,4\text{-EuC}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$ anionic complexes shown in Figures 58 and 61.^{179,180,183,184}

It is obvious that a lot more synthetic, mechanistic, structural, and theoretical research has yet to be done before this area of f-block metal-carborane chemistry becomes "predictably uninteresting".

IV. Metallocarboranes in Catalysis

Impetus for the study of metallocarboranes of d-block metals has been their potential as catalysts in olefin polymerization, hydrogenation, hydrosilylation, and isomerization of unsaturated organic substrates. The most studied species are the half-sandwich rhodacarboranes with the pioneering work by Hawthorne and co-workers in the early 1970s.^{17,59,191-197} Recently, Hawthorne¹³ and Grimes¹⁹⁸ have reviewed this aspect of the metallocarboranes adequately including the work published in 1989. Therefore, we will attempt here to summarize the most salient features of these findings.

A series of *closo* icosahedral rhodacarboranes bearing substituents at carbon has been synthesized by the reaction of $[(\text{PPh}_3)_3\text{RhCl}]$ with the corresponding C-substituted *nido*-7-R-8-R'-7,8- $\text{C}_2\text{B}_9\text{H}_{10}]^-$ (where R = H or D and R' = H, D, Ph, Me, and *n*-Bu). These rhodacarboranes were fully characterized by spectroscopic techniques and, in many cases, by X-ray crystallography.^{59,194} While *closo*-1-R-2-R'-3,3-(Ph_3P)₂-3-H-3,1,2- $\text{RhC}_2\text{B}_9\text{H}_9$ (where R = R' = μ -*o*-xylenyl) and *exo-nido*-[(PPh_3)₂Rh]- μ -4,9-(H)₂-[7-R-8-R'-7,8- $\text{C}_2\text{B}_9\text{H}_8$] (where R = R' = Me) exist as rapidly interconverting equilibrium mixture of *closo* and *exo-nido* isomers in solution, the derivatives of the latter (R = Me, R' = Ph and R = R' = μ -(CH_2)₃-) exist solely as the *exo-nido* isomer. The two isomeric forms of $[\text{closo-}3,1,2-(\text{Ph}_3\text{P})_2(\text{H})\text{RhC}_2\text{B}_9\text{H}_{11}]$ are shown in Figure 67.¹³ In a formal sense, the *exo-nido* species may be viewed as a complex consisting of a $[\text{L}_2\text{Rh}]^+$ cation complexed with the $[\text{nido-}7\text{-R-}8\text{-R'-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ anion via two Rh-H-B bridge bonds. A simplified and the most up to date mechanism, based on kinetic and deuterium-labeling studies on the *exo-nido* isomer, has been proposed by Hawthorne et al. for the hydrogenolysis of alkenyl acetate, alkene isomerization, and alkene hydrogenation as shown in Scheme VIII.¹⁹²

The mechanism involves the slow formation of rhodium monohydride species, containing B-Rh^{III}-H arrays, by the regioselective oxidative addition of

Scheme VIII. A Revised Mechanism for the Catalytic Processes Involving an *exo-nido*-Rhodacarborane Complex Based on Kinetic and Deuterium-Labeling Studies (Reprinted from ref 192. Copyright 1989 American Chemical Society)

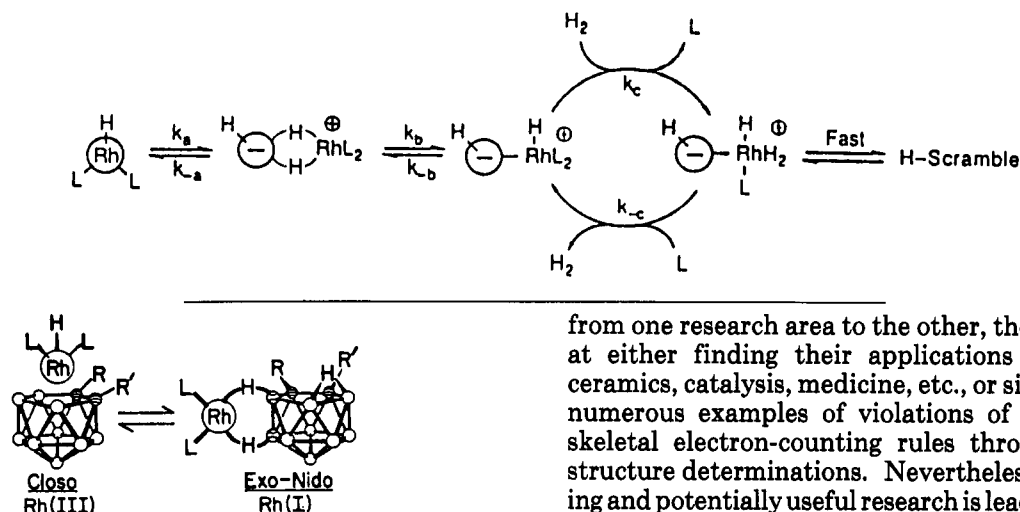


Figure 67. A schematic representation of the two isomeric forms of a rhodacarborane in solution. Reprinted from ref 13. Copyright 1988 VCH Publishers.

terminal B-H bonds to Rh^{I} centers. These highly reactive metal centers rapidly catalyze the addition of hydrogen to the substrates. Similarly, hydrosilanolyses of alkenyl acetates ($\text{CH}_3\text{CO}_2\text{CR}=\text{CH}_2$, $\text{R} = \text{CH}_3$, C_6H_5) with Et_3SiH in the presence of *exo-nido*-(PPh_3) $_2\text{Rh}$ -7,8-(μ -(CH_2) $_3$)-7,8- $\text{RhC}_2\text{B}_9\text{H}_{11}$ or *closo*-3,3-(PPh_3) $_2$ -3-H-3,1,2- $\text{RhC}_2\text{B}_9\text{H}_{11}$ were demonstrated by the same group in 1990. The mechanistic studies revealed that hydrosilanolysis predominates over hydrosilylation in a ratio of 20:1.¹⁹⁷ These recent findings clearly demonstrate the absence of previously proposed "cluster catalysis" mechanism involving the *closo*-rhodacarborane catalyst precursors.^{196,197}

A C-substituted Ir complex, 1-[Ir(CO)(PhCN)(P-Ph $_3$)]-7-Ph- σ -1,7- $\text{C}_2\text{B}_{10}\text{H}_{10}$, was found to be an effective catalyst for homogeneous hydrogenation of terminal olefins and acetylenes at room temperature and atmospheric or subatmospheric H_2 pressure. The hydrogenation takes place by a "hydride route". Thus the dihydro complex, formed initially by fast oxidative addition of H_2 to the iridacarborane, accommodates an unsaturated substrate in the coordination sphere by dissociating the nitrile ligand on the metal.¹⁹⁹ A similar study involving an unusual C-diphos-substituted rhodacarborane, 1,2-(Ph $_2\text{P}$) $_2\text{Rh}^{\text{I}}\text{CO}(\text{Cl})$]- σ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ in hydrogenation and hydroformylation reactions at elevated temperatures and high H_2 pressures has also been carried out.²⁰⁰

The preliminary reports on the reactivity studies, described in an earlier section, indicate that the early transition metal sandwiched carborane complexes^{26,28-32,38} have the potential to be active catalysts and/or catalyst precursors in Ziegler-Natta olefin polymerization, and as such more research in this area needs to be done in 1990s before their practical applications are developed.

V. Current and Future Directions

Our discussion summarizes the most promising research published during the past 10 years or so in the area of metallacarboranes of d- and f-block elements. Although the fundamental themes have varied greatly

from one research area to the other, they are all aimed at either finding their applications in electronics, ceramics, catalysis, medicine, etc., or simply providing numerous examples of violations of the traditional skeletal electron-counting rules through solid-state structure determinations. Nevertheless, this fascinating and potentially useful research is leading this unique area of organometallic chemistry toward the 21st century. As d^0 , 14-electron bent metallocene complexes of Ti, Zr, Hf, and Ta, found to be effective catalysts in Ziegler-Natta olefin polymerization, the metalla species based on purely carborane ligands,^{28,29-31} and those of the mixed Cp-carborane ligands^{26,32,38} hold great promise. The preliminary reports on metallacarboranes of early transition metals,^{28,29-31} with the speculation that these could be developed as better catalysts than the Cp analogues, have evidently inspired the researchers outside the traditional carborane chemistry (Jordan et al. and Bercaw et al., for example) who have found a "goldmine" in the area of catalysis that combines the well-established systems of Cp and carboranes. Since the structural and reactivity patterns in the lanthanide systems are similar to those of the organometallics of scandium and titanium groups, their useful applications in the field of catalysis are inevitable. The ionic nature of the lanthanacarboranes is an added advantage over the early transition metal species in terms of their further synthetic utility in other systems. This has been exemplified in the synthesis of a dinuclear "wedged" manganacarborane sandwich that could not be prepared by the conventional method involving dianionic carborane ligand and the metal reagent, thus demonstrating a superior directing ability of a lanthanide metal than the ligand itself in the formation of targeted species.^{66,67} These recent findings show that there is a wealth of fascinating and useful chemistry that needs to be explored in the near future.

The success of Fischer-Tropsch reactions and alkyne metathesis is largely due to alkylidyne-metal cluster chemistry and the work of Stone undoubtedly merged the metallacarborane with alkylidyne chemistry.⁴⁵ The mechanistic aspects of the protonation reactions, especially the ligand migrations and cage isomerizations, will be the guiding points for future research in this area. Nonetheless, this area of research has yet to demonstrate its true potential to be the forefronts of organometallics.

Although the chemistry of middle and late transition metal-carboranes has traditionally focused on the synthetic, structural, and bonding curiosities, a potentially useful chemistry has emerged in the area of mixed-ligand (carborane and Cp or arene) metalla- C_2B_4 carboranes.^{3a} In addition to Grimes' pioneering work

on multidecker sandwich complexes via the "decapitation" sequence, Hawthorne's unique way of making metallacarborane-metallacycles among other discoveries, Sneddon's high-yield route to tricarbametallaborane sandwiches, Chetcuti's method of preparing inclusion compounds, and eventual applications of all these species in variety of disciplines including BNCT, radioimmunotherapy, immunodiagnosis, electronics, ceramics, catalysis, polymers, and solvent extraction of radionuclides, etc., show every indication that this area of research will remain active for many years to come.

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