Structurally Diverse π-Cyclopentadienyl Complexes of the Main Group Elements

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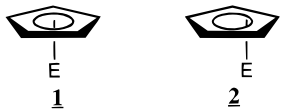
Contents

Introduction and Scope

The cyclopentadienyl anion, $[Cp]^-$, is one of the most versatile ligands. Complexes of the d and f elements usually engage the anion as a 6-electron π-donor, and the vast series of compounds is referred to as "metallocenes". Analogous complexes are now being developed for the main group elements of groups 1, 2, 13, 14, and 15, revealing a more diverse array of structural features. The range of electronegativities harbored by this series of elements is responsible for a highly variable Cp−E interaction, with complexes of the more electropositive elements, such as cesium, considered mainly ionic (i.e., $[E]^+[Cp]^-$) and those of the p block elements considered highly covalent. However, all main group π-cyclopentadienyl compounds display characteristics of both bonding types, and an understanding of the Cp−E interaction is further complicated by the fact that the projection points that the elements make onto the pentagonal plane of the Cp ligand is varied. This structural variability is referred to as "hapticity" for the transition metal complexes, but is less meaningful for main group element complexes because of the fluxional nature of most complexes. Most structurally characterized compounds exhibit a symmetric (local C_{5v} **1**) coordination of the Cp ligand, but displacement of the element from the C_5 axis of the ligand, **2**, is notable for the more electron-rich elements of groups 14 and 15.



1 **2**

Various aspects of π-cyclopentadienyl main group element complex chemistry have been previously reviewed in some detail. Supplemental discussions to the general overviews[1,2] include the importance of substitution around the Cp ligand,[3−9] the fluxional behavior of the Cp−element interaction,[10] and the potential utility of π-cyclopentadienyl alkaline earth metal derivatives as MOCVD sources.[11] In addition, assessments have been given for examples of cyclopentadienylelement complexes,[12−15] bis(cyclopentadienyl)element complexes,[7−9,15−16] tris(cyclopentadienyl)element complexes,[12] alkali metal π-cyclopentadienyl compounds,[18] and "p block metallocenes".[19]

In this review, an attempt has been made to provide a comprehensive account of the data currently available for compounds involving a main group element interacting with the π-cloud of one or more cyclopentadienyl ligands. We distinguish these complexes from the many compounds in which a p block element is σ-bound to one of the carbon centers within the Cp frame by specifying structures in which the element resides inside the pentagonal cylinder defined by the Cp ring. Although this discussion is restricted to complexes involving a formally 6π-electron cyclopentadienyl ligand, it is important to recognize that an extensive chemistry is also developing for complexes of main group elements involving cyclopentadienyl ligands with extended π-frameworks,[1] bridged cyclopentadienyls,[20] heterocyclopentadienyls,[21] and other isolobal analogues of Cp such

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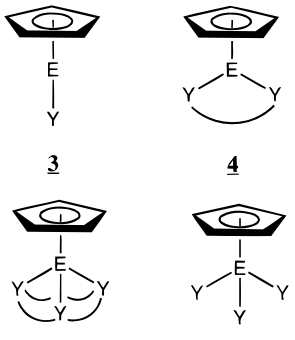
Peter Jutzi studied chemistry at the Technical University of Munich and received his Ph.D. degree under the supervision of Prof. Dr. M. Schmidt at the University of Marburg. After his habilitation at the University of Würzburg in 1971, he was appointed Associate Professor in 1974. In 1978 he moved as Full Professor in Inorganic Chemistry to the University of Bielefeld. His scientific interest is in the field of experimental organometallic chemistry. Topics of research are: I) Cyclopentadienyl chemistry of p- and d-block elements; II) Nanometer-sized materials; III) Organosilicon chemistry.

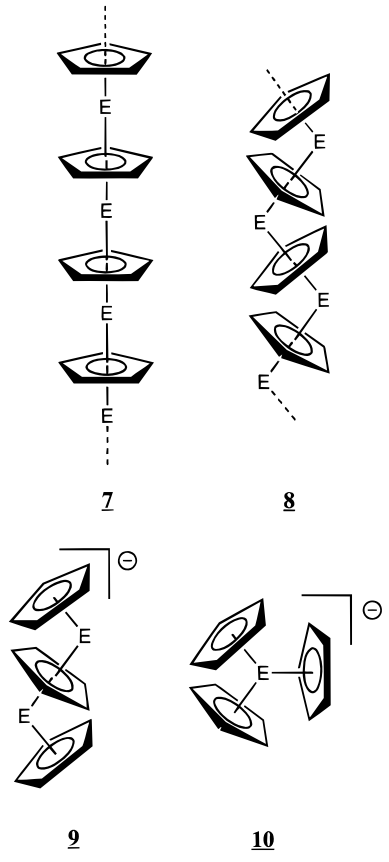
Neil Burford is a native of Liverpool, England. He obtained a BSc Honours degree in 1979 from the University of Wales, College Cardiff, and his Ph.D. research was supervised by Prof. T. Chivers at the University of Calgary. After a postdoctoral fellowship at the University of Alberta with Prof. R. Cavell and a Research Associateship at the University of New Brunswick with Prof. J. Passmore, he was appointed Assistant Professor at Dalhousie University in 1987, became Full Professor in 1995, and was appointed Killam Professor of Chemistry in 1998. His research is generally classified as synthetic chemistry involving the elements of group 15, with focuses on new structures and bonding and the bioactivity of bismuth compounds. In 1996, a collaboration with Prof. Dr. P. Jutzi was facilitated by an Alexander von Humboldt Fellowship.

as arene,[1,22] carbollyl,[1] and borazolyl.[23]



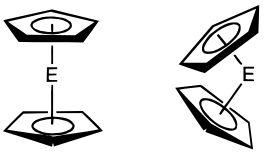
3 **4** **5** **6**

The now extensive list of known π-cyclopentadienyl complexes of the main group elements reveals some distinct structural trends, which we have separated into five categories and listed in tabular format. Table 1 lists molecular cyclopentadienylelement complexes in which the element bears a single Cp ligand and is composed of discrete molecular units in the solid state, **1** or **2**. These compounds may possess a number of auxiliary ligands, **3**−**6**, and may also be oligomeric by virtue of intermolecular interactions through the auxiliary ligands. Table 2 lists a small group of compounds of the group 13 and 14 elements, which are observed to form cluster structures in the solid state. Table 3 lists polymeric μ-cyclopentadienylelement systems, which have been established by X-ray methods and involve parallel **7** or nonparallel **8** "inverse sandwich" μ-Cp arrangements. Table 4 lists molecular μ-Cp complexes, which involve interactions similar to those responsible for the polymeric structures, but are composed of a finite number of units, e.g., **9**. This category also includes the structurally related tris(cyclopentadienyl)element complexes, **10**. Table 5 lists bis(cyclopentadienyl)element complexes, which involve two Cp ligands bound to an element center **11** or **12** as well the possibility of auxiliary ligands.



7 **8** **9** **10**

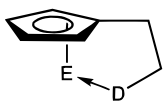
The listings of compounds in each category illustrate the extent and diversity of π-cyclopentadienyl main group element chemistry as well as the comprehensive nature in which many of the studies have been performed. The tables indicate the most convenient synthetic method or methods for each compound, according to the synthetic procedures outlined below, and the characterization techniques



11 **12**

employed for identification. In addition, pertinent structural parameters are given for compounds that have been structurally characterized in the solid state or gas phase. Most complexes are air sensitive and must be handled under inert conditions. In contrast to π-cyclopentadienyl transition metal complexes, they are usually colorless materials, involving standard formal oxidation states, although electronic spectroscopy has been used in isolated cases.

The structural and spectroscopic diversity observed for π-cyclopentadienyl main group element complexes has been responsible for the evolution of various nomenclatures, formulas, and structural drawings. The formats "cyclopentadienylelement", Cp_nE, and drawing type **1** are used throughout this article for consistency, but do not imply a type of bonding. Development of π-cyclopentadienyl main group element complexes has been facilitated by the use of substituted cyclopentadienyl ligands, abbreviated here as $Cp^{n\text{SUBSTITUTION}}$, where the superscript indicates the number ($n = 1-5$) and type of the substituents (M = methyl, I = isopropyl, B = tertiarybutyl, Ph = phenyl, Bz = benzyl, Bor = boryl, BorO = alkoxyboryl, BorN = aminoboryl, D = dimethylsilyl, T = trimethylsilyl, TS = trimethylstannyl, P = diphenylphosphino; $Cp^* = Cp^{5M}$; a number of unique and mixed substitution patterns are defined when referred to in the text; Cp′ is used as a general abbreviation for Cp and derivatives of Cp). The bulky nature of many of these derivatized Cp ligands is principally responsible for the relative stability[24] of the complexes, but it can also impose interesting distortion on the complex. Less obvious is the fact that these ligands are good leaving groups, allowing for substitution reactions with element−carbon bond cleavage in many situations.[25] Introduction of a side chain functionality (Cp^N, Cp^O, N = dimethylaminoethyl, O = methoxyethyl) with the potential for auxiliary, chelate coordination to the element center **13** offers another interesting dimension of structure and reactivity.[26,27]



13

Synthesis and Characterization

Most π-cyclopentadienyl main group element complexes are prepared by one or more of a number of general and often versatile synthetic procedures, which are summarized and classified below.

$$2E + 2Cp'H \rightarrow 2Cp'E + H_2$$

or

$$E + 2Cp'H \rightarrow Cp'_2E + H_2 \quad (1)$$

$$ER + Cp'H \rightarrow Cp'E + RH \quad (2)$$

$$EH + Cp'H \rightarrow Cp'E + H_2 \quad (3)$$

$$ENH_2 + Cp^*H \rightarrow Cp^*E + NH_3 \quad (4)$$

$$nMCp' + EX_n \rightarrow Cp'_nE + nMX$$

or

$$n/2MgCp'_2 + EX_n \rightarrow Cp'_nE + n/2MgX_m \quad (5)$$

$$2Cp'EX \rightarrow Cp'_2E + EX_2$$

and

$$2Cp'EX \leftarrow Cp'_2E + EX_2 \quad (6)$$

$$Cp'_nEY + A \rightarrow [Cp'_nE][AY] \quad (7)$$

$$Cp'_nEY + Z \rightarrow Cp'_nEZ + Y \quad (8)$$

$$Cp_nE + QR \rightarrow Cp^RECp_{n-1} + QH$$

or

$$Cp_nE + nQR \rightarrow Cp^R{}_nE + nQH \quad (9)$$

$$Cp'_nEX_2 + red \rightarrow Cp'_nE + redX_2 \quad (10)$$

$$Cp'_nE + [Cation][Cp'] \rightarrow [Cation][Cp'_{n+1}E]$$

or

$$2Cp'E + [Cation][Cl] \rightarrow [Cation][Cp'_{n+1}E] + ECl \quad (11)$$

$$Cp'_2E + MCp' \rightarrow [Cp'E][MCp'_2] \quad (12)$$

$$Cp'_nE + Y \rightarrow Cp'_nEY$$

or

$$Cp'_nEY + Z \rightarrow Cp'_nEY(Z) \quad (13)$$

$$Cp'_2E + HY \rightarrow [Cp'E][Y] + Cp'H$$

or

$$Cp'_2E + RY \rightarrow [Cp'E][Y] + Cp'R \quad (14)$$

$$Cp'_2E + MR \rightarrow Cp'ER + MCp' \quad (15)$$

$$Cp_nEYH \rightarrow Cp_{n-1}EY + CpH$$

or

$$Cp_nEY_2 \rightarrow Cp_{n-1}EY + CpY \quad (16)$$

The reaction equation numbers (1−16) are used in Tables 1−5 as a reference for the synthesis of a particular compound. In these equations, the symbol E designates the main group element; M refers to a metal such as lithium, sodium, magnesium, or thallium; X is a halogen atom; Y and Z are other substituents or auxiliary ligands; A is a Lewis acid; and "red" is a reducing agent. There are some specific or anomalous synthetic methods, which are described or referred to at the appropriate time in the discussion.

Table 1. Molecular Cyclopentadienylelement Complexes: Synthetic Approach (S, semicolon separates synthetic steps and comma refers to more than one synthetic method), Characterization Data Reported (CA = chemical analysis; IR = infrared; MS = mass spectrometry; X = X-ray crystallography; D = electron diffraction), NMR Nuclei Studied, and $Cp_{centroid}$−E Distances (Å) in the Solid State or Gas Phase

	S	CA	IR	MS	NMR	Cp_c−E	ref
CpLi·12-crown-4 (X)	2;13				^{1}H	2.06	63
Cp^{M}Li·TMEDA (X)	2;8					1.92	64
Cp^{BorO}Li·12-crown-4 (X)	1;13				^{1}H, ^{13}C	2.08	65
Cp^{4Ph}Li·THF_3	13	√	√	√	^{1}H, ^{13}C		66
Cp^{T}Li·TMEDA (X)	2	√			^{1}H	1.93	67
Cp^{3T}Li·L: L = quin (X), TMEDA (X), PMDETA (X)	2;13	√			^{1}H, ^{13}C, ^{7}Li, ^{29}Si	1.79, 1.99, 1.98	68,69
Cp^{3T}Li·L: L = Et_2O, THF (X), $^{n}Bu_2O$, 1,4-diox, DME, diglym, DAMP, pyr, bipy, BMTE	2;13	√			^{1}H, ^{13}C, ^{7}Li, ^{29}Si	1.80	70
[Li·$(TMEDA)_2$][CpM(Li·$TMEDA)_2$] (X)	5	√			^{1}H	2.00	71
Cp^{5D}Li·L: L = THF, $OCPh_2$ (X)	2;8				^{1}H, ^{13}C, ^{7}Li, ^{29}Si	1.82	72
^{isodi}CpLi·TMEDA (X)	8					1.91	73
LiCpCMe_2CMe_2CpLi, NaCpCMe_2CMe_2CpNa	2				^{1}H, ^{13}C		335
Cp*Na·pyr_3 (X)	1;13				^{1}H, ^{13}C, ^{23}Na (pyr)	2.40	74
Cp^{4Ph}Na·THF_3	2;13	√	√	√	^{1}H, ^{13}C		66
Cp^{4Ph}Na·$MeOCH_2CH_2OMe$ (X)	1					2.58	75
Cp^{CMeO}Na·THF (X)	1;9					2.56	76
Cp^{Sb}Na·THF_3[a] (X)	9				^{1}H, ^{13}C	2.52	77
Cp^{4Ph}K·THF_3	2;13	√	√	√	^{1}H, ^{13}C		66
Cp^{5Bz}K·THF_3 (X)	1;13					2.79	78
CpBeH[b]							79
CpBeR: R = Cl (D, X), Br (D), Me (D)	−6,5		√	√	^{1}H, ^{13}C, ^{9}Be	1.48, 1.45, 1.53, 1.50	80,81,82
CpBeCCH (D)	−6					1.49	80,83
Cp*BeMe·$YbCp^*_2$ (X)	13	√		√	^{1}H, ^{13}C	1.45	84
Cp*BeCl	5	√	√	√	^{1}H		85
$CpBeBH_4$ (D)						1.48	86
$CpBeB_3H_8$	8		√	√	^{1}H, ^{11}B		87
$CpBeB_5H_8$ (X)	8			√	^{1}H, ^{11}B	1.47	88
$CpBeB_5H_{10}$	5		√	√	1H, ^{11}B		89
Cp*BeP^tBu_2 (X), Cp*BeP^tBu_2·$AlMe_3$	8				^{1}H, ^{9}Be, ^{31}P	1.48	90
CpMgMe, CpMgPh	−6	√		√	^{1}H		91
CpMgR: R = Et, Bu, Me·TMEDA, $OEt·THF_2$; $\{CpMgOEt\}_4$ (X), THF_2·$CpMgCH_2CHCHCH_2MgCp·THF_2$, Cp*MgEt	16	√			^{1}H, ^{13}C, ^{25}Mg	2.11, 2.10	92,93
$CpMgC_4H_7$·L: C_4H_7 = 2methylallyl, L = THF, OEt_2	−6				^{1}H, ^{13}C, ^{25}Mg		93,94
CpMgMe·OEt_2	2		√		^{1}H		95
$\{Cp'MgCl·OEt_2\}_2$, Cp′ = Cp (X), Cp* (X)	−6					2.09, 2.09	96
CpMgBr·TMEDA (X)	13					2.21	97
Cp*MgBr·THF	2				^{1}H		98
Cp^{3T}MgBr·TMEDA (X)	2;13	√		√	^{1}H, ^{13}C, ^{25}Mg	2.17	99
[CpMg·PMDETA][Cp_2Tl] (X)	12	√	√		^{1}H, ^{13}C	2.08	100
$\{Cp^*CaI·THF_2\}_2$ (X)	5	√	√		^{1}H, ^{13}C	2.38, 2.39	101
$\{Cp^{4I}CaI·THF\}_2$ (X), Cp^{4I}CaI·DME, $\{Cp^{4I}CaI\}_n$, $\{Cp^*CaI\}_n$, $Cp^{4I}CaN(SiMe_3)_2$·THF (X), Cp^{4I}CaBHT·THF	5,−13;8	√	√		^{1}H, ^{13}C	2.38, 2.40, 2.39	102
$\{Cp^{4I}CaCCR·THF\}_2$: R = Ph (X), Fc, $SiMe_3$, Si^iPr_3, $SiPh_3$	8	√			^{1}H, ^{13}C	2.43	103
Cp^{4ME}CaI·THF, Cp^{4ME}CaBHT, Cp^{4ME}CaOtamp, BH$\{Cp^{4ME}Ca[RN]\}_2$ (X), Cp*$CaN(SiMe_3)_2$·THF_3, Cp*$CaCH(SiMe_3)_2$·THF_3	5,8	√	√		^{1}H, ^{13}C	2.45	104
$\{Cp^{2T}Ca·OC_5H_2$-1,3-$(SiMe_3)_2\}_2$ (X)	8					2.38	105
[Cp*BX][BX_4]: X = Cl, Br, I	7	√		√	^{13}C		106
[Cp*BBr][$AlBr_4$] (X)	*c*					1.18	107
Cp*BFe$(CO)_4$ (X)	8		√	√	^{1}H, ^{13}C, ^{11}B	1.35	108
$CpAlR_2$: R = Me (D, X), Et	5		√		^{1}H	2.66, 2.75	109,110
$CpAl^iBu_2$	2	√			^{1}H		111
CpAl$\{O(2,6$-$^tBu_2$-4-$MeC_6H_2)\}_2$ (X), Cp_2Al(O-2,6-$^tBu_2$-4-MeC_6H_2)	14	√			^{1}H, ^{13}C, ^{27}Al	1.92	112
$\{CpAlN(2,6$-$^iPr_2C_6H_3)\}_2$ (X)	15	√	√		^{1}H, ^{13}C, ^{27}Al	1.89, 1.89	113
$Cp^{M}AlR_2$: R = M, Et, ^{i}Bu	5				^{1}H		114
Cp_3Al					^{27}Al		115
$Cp^{3M}{}_3$Al (X)[d] {cf. $Cp^{4M}{}_3$Al (X)	5	√		√	^{1}H, ^{13}C, ^{27}Al	1.97	34
Cp*Al (D)	5					2.06	116,117
Cp*AlFe$(CO)_4$ (X)	8	√	√		^{1}H, ^{13}C, ^{27}Al	1.78	118
$\{Cp^*AlCl_2\}_2$ (X)	5	√	√	√	^{1}H	1.87	119

Table 1. (Continued)

	S	CA	IR	MS	NMR	Cp_c-E	ref
$Cp^*Al(DAB)$[e] (X)	*c*		√	√	^1H, ^{13}C, ^{27}Al	1.88	120
$\{Cp^{4ME}AlCl_2\}_2$ (X)	5	√	√	√	^1H	1.87	119
$\{Cp^*Al(Cl)R\}_2$: R = Me (X), Et, ^{i}Bu (X)	5		√	√	^1H, ^{13}C	2.00, 2.06	121
Cp^NAlR_2: R = Me (X), Et, Cl (X), Br, I	5	√		√	^1H, ^{13}C, ^{27}Al	2.51, 2.24	122
CpGa	5			√	^1H, ^{13}C, ^{71}Ga		46
Cp^BGa, Cp^*Ga, $Cp^{5Bz}Ga$, $Cp^{3T}Ga$	5			√	^1H, ^{13}C, ^{71}Ga		123
Cp^*Ga (D)	5					2.08	124
$CpGaR_2$: R = Me, Et	5		√		^1H		110,125
CpIn (D)	1,10	√	√			2.32	30,126,127,128,129
Cp^MIn (D)	5	√	√		^1H	2.31	130
Cp^*In (D)	5	√	√		^1H, ^{13}C	2.29	131
$Cp^{5Ph}*In$: Ph* = C_6H_4R, R = Et, C(O)Me, C(O)pentyl	5	√		√	^1H, ^{13}C		132
$Cp^{4MP}In$ (X)	5	√		√	^1H, ^{13}C	2.41	133,134
$\{Cp^{5Bz}In\}_2$ (X)	5	√	√	√	^1H, ^{13}C	2.38	135
$Cp^{3T}In$, $Cp^{3T}In$, $Cp^{3T}In$	5			√	^1H, ^{13}C, ^{29}Si		136
$CpInR_2$: R = Me, Et	5		√		^1H		109
CpTl (D)	5	√	√	√	^1H	2.41	30,137
Cp^MTl	2	√	√				138,139
$Cp^{Ph}Tl$	2	√			^1H		140,141
$Cp^{Bz}Tl$	2	√			^1H		140
$Cp^{C(O)M}Tl$, $Cp^{C(O)H}Tl$	2,5	√		√			140
Cp^ETl	5	√	√		^1H		142
$Cp^{2B}Tl$	2,5	√	√		^1H, ^{13}C		142,143
Cp^BTl, Cp^TTl	5	√	√				139,142
$Cp^{PhF}Tl$					^{19}F		144
$Cp^{BzF}Tl$, $Cp^{MBz}Tl$	2	√			^1H		145
$Cp^{4Ph}Tl$, $Cp^{5Ph}Tl$, $Cp^{4PhBPh}Tl$	2	√	√	√	^1H, ^{13}C		146
Cp^*Tl (D)	5					2.37	147
$Cp^{5Ph}*Tl$: Ph* = C_6H_4R, R = Me, Pr, pentyl, heptyl	2				^1H, ^{13}C		132
$Cp^{5Ph}**Tl$: Ph** = $C_6H_4C(O)R$, R = Me, Pr, pentyl, heptyl, OEt, Opentyl	2	√		√	^1H, ^{13}C		148
$Cp^{4Ph}**Tl$: Ph** = $C_6H_4C(O)R$, R = Me, Et, Pr, pentyl	2	√		√	^1H, ^{13}C		149
$Cp^{4MP}Tl$ (X)	5	√		√	^1H, ^{13}C	2.51	133
$\{Cp^{5Bz}Tl\}_2$ (X)	2	√	√	√	^1H, ^{13}C	2.49	146,150
Cp^ETl: E = CO_2Me, CHO, CO_2Et	5	√		√	^1H, ^{13}C		151
$Cp^{3T}Tl$	5			√	^1H, ^{13}C		152
Cp^PTl	2	√			^1H, ^{13}C		153
$Cp^{PM}Tl$: PM = PMe_2	2	√		√	^1H, ^{31}P		154
Cp^XTl: X = Cl, Br, I	2	√	√	√	^1H		155
$Cp^{5Cl}Tl$	2	√	√		^{35}Cl NQR		156
Cp^*GeCl (D)	5	√		√	^1H	2.11(pl)	157,158
Cp^NGeCl (X) [f]	5	√		√	^1H, ^{13}C	2.25	159
$Cp^*GeCH(SiMe_3)_2$ (X), $Cp^*GeN(SiMe_3)_2$, Cp*Gepip	8	√		√	^1H, ^{13}C	2.24	160
$[Cp^*Ge][BF_4]$, $[Cp^*Ge][SO_3CF_3]$, $[Cp^*Ge][AlCl_4]$, $[Cp^*Ge][GeCl_3]$	7,14	√		√	^1H, ^{13}C		161
$[Cp^*Ge][Cp^{5COOM}]$	14	√		√	^1H, ^{13}C		162
$[Cp^*Ge][SO_3CF_3]$, $[Cp^*Ge{\cdot}pyr][SO_3CF_3]$, $[Cp^*Ge{\cdot}pyraz][SO_3CF_3]$, $[Cp^*Ge{\cdot}bipy][SO_3CF_3]$	14,13	√		√	^1H		163
$[Cp^{**}Ge][GeCl_3]$[g] (X), $[Cp^{**}Ge][BF_4]$, $[Cp^{**}Ge][SO_3CF_3]$, Cp**GeCl	5;8	√		√	^1H, ^{13}C, ^{29}Si, ^{11}B, ^{19}F	1.93	164
$[Cp^{2B}Ge][BF_4]$	14	√		√	^1H, ^{13}C, ^{29}Si, ^{19}F		165
CpSnCl (X), CpSnBr	−6	√			^1H	2.34	166
$CpSn(\mu\text{-}OBu)_2M(OBu)$: M = Ge (X), Sn, Pb	5	√			^1H, ^{13}C, ^{119}Sn, ^{207}Pb	2.51	167
Cp^*SnCl (X), $Cp^{4M(S2MB)}SnCl$	−6,5	√		√	^1H, ^{13}C, ^{119}Sn	2.27	168
Cp^*SnBr	16	√		√	^1H, ^{13}C		169
$[Cp^*Sn][AlCl_4]$, $[Cp^*Sn][SO_3CF_3]$, $[Cp^*Sn][O_2CCF_3]$, $[Cp^*Sn][O_2CCCl_3]$	14	√		√	^1H		170,171
$[Cp^*Sn][Cp^{5COOM}]$	14	√		√	^1H, ^{13}C		162
$[Cp^*Sn][BF_4]$ (X), $[Cp^*Ge][BF_4]$	14	√			^1H, ^{13}C, ^{11}B ^{19}F	2.16	172,173
$[Cp^BSn][BF_4]$ (X)	14	√			^1H, ^{13}C, ^{11}B	2.18	174
$[Cp^{2B}Sn][BF_4]$	14	√	√		^1H, ^{13}C, ^{11}B, ^{19}F, ^{119}Sn		165
$[Cp^{**}Sn][BF_4]$[g] (X), $[Cp^{**}Sn][SO_3CF_3]$, Cp**SnCl	5;8	√		√	^1H, ^{13}C, ^{29}Si, ^{11}B, ^{19}F, ^{119}Sn	2.22	164
$[Cp^*Sn{\cdot}pyr][SO_3CF_3]$ (X), $[Cp^*Sn{\cdot}bipy][SO_3CF_3]$ (X), $[Cp^*Sn{\cdot}pyraz][SO_3CF_3]$, $[Cp^*Sn{\cdot}bipy][BF_4]$	13	√			^1H	2.24, 2.36	163
$\{CpSnN{=}C(NMe_2)_2\}_2$ (X)	15	√	√		^1H	2.43	175
$[Cp^{4M(SiB2M)}{}_6Sn_9Cl_{12}]$ (X)	2	√			^1H, ^{13}C, ^{119}Sn	2.21	176
$CpPbCl$, $CpPbBr$, $CpPbI$, $CpPbO_2CCH_3$	14						177
Cp^*PbCl, $[Cp^*Pb][BF_4]$ (X), $[Cp^*Pb][SO_3CF_3]$, $[Cp^*Pb{\cdot}bipy][SO_3CF_3]$, $[Cp^*Pb{\cdot}bipy][BF_4]$	14	√		√	^1H, ^{13}C, ^{11}B, ^{19}F, ^{207}Pb	2.27	178
$[Cp^{2B}Pb][BF_4]$	14	√		√	^1H, ^{13}C, ^{11}B, ^{19}F, ^{207}Pb		165

Table 1. (Continued)

	S	CA	IR	MS	NMR	Cp_c-E	ref
[Cp**Pb][BF_4], [Cp**Pb][SO_3CF_3][g]	5;8	√		√	^1H, ^{13}C, ^{29}Si, ^{11}B, ^{19}F, ^{207}Pb		164
Cp*PNMes* [h] (X), Cp*PN$SiMe_3$ (X)	5	√		√	^1H, ^{13}C, ^{31}P		179
[Cp*PNH^{t}Bu][$AlCl_4$] (X), [Cp*PNH^{t}Bu][SO_3CF_3]	7				^1H, ^{13}C	2.11	180
$CpSbCl_2$ (X)	5	√			^1H		181
Cp^*SbCl_2 (X)	5				^1H	2.40	182
$Cp^{4I}SbCl_2$ (X)	5	√		√	^1H, ^{13}C	2.36	183
$CpBiCl_2$ (X)	5	√			^1H	2.39	184
$Cp^{4I}BiCl_2$ (X), $Cp^{3B}BiCl_2$, $Cp^{4I}BiI_2$ (X), [$Cp^{4I}BiCl_2$]$_2$[$BiCl_3$]$_2$ (X)	5	√			^1H, ^{13}C	2.40, 2.40, 2.39	185

[a] Cp^{Sb} = Sb_4Cp_5 cage. [b] Microwave. [c] {Cp*Al}$_4$ + R. [d] Single π-coordinated Cp′ ligand. [e] DAB = MesNCHCHNMes. [f] Cp^N = $C_5Me_4(CH_2CH_2NMe_2)$. [g] Cp** = $C_5Me_4(SiMe_2C_5HMe_4)$. [h] Mes* = 2,4,6-tri-*tert*-butylphenyl.

Table 2. Molecular Cyclopentadienylelement Complexes that Adopt Cluster Structures in the Solid State, as Shown by X-ray Crystallography: Synthetic Approach (S), Characterization Data Reported (CA = chemical analysis; IR = infrared; MS = mass spectrometry), NMR Nuclei Studied, and $Cp_{centroid}-E$ Distances (Å)

	S	CA	IR/Ram	MS	NMR	Cp_c-E	ref
{Cp*Al}$_4$	5		√		^{27}Al	2.03, 2.00, 2.02	117,190
{Cp*AlZ}$_4$: Z = Se, Te	13	√	√	√	^1H, ^{13}C, ^{27}Al	1.95, 1.97	191
{$(Cp^*Al)_6P_4$}	*a*		√			2.70, 1.94, 1.94	192
{$(Cp^*Al)_3As_2$}	*a*			√	^1H, ^{27}Al	1.90	193
{$(Cp^*AlF)_4(SiPh_2)_2$}, {$(Cp^*Al)_3Sb_2$} (No X)	*a*	√	√	√	^1H, ^{13}C	2.09	194
{$NiCp_2(Cp^*Al)_2$}	*a*			√	^1H, ^{13}C, ^{27}Al	1.90, 1.92	195
{Cp*Ga}$_6$	5		√		^1H	2.08	196
{Cp*In}$_6$	5	√	√		^1H	2.30	131,197
{$Cp^{2T}Tl$}$_6$	2	√		√	^1H, ^{13}C	2.74−2.78	198
{Cp_2Pb}$_6$	5					2.44−2.53 (μ)	199

[a] {Cp*Al}$_4$ + R.

Cyclopentadiene carries a relatively acidic proton[28] and reacts smoothly with a number of main group elements according to eq (1), or when certain elements are co-condensed with the cyclopentadiene. Reaction (2) applies to reactive alkylmetal reagents and thallium salts (usually TlOEt), and sodium or potassium hydride are the most often used reagents to undergo reaction (3), which both take place in a variety of organic solvents, while the Cp* specific reaction (4) is performed in liquid ammonia.

The most generally applied preparative procedure for elements of groups 2, 13, 14, and 15 is the metathesis reaction (5) involving the appropriate stoichiometric combination of an element halide (X) or polyhalide with cyclopentadienyl-lithium, -sodium or -trimethylsilyl (M = Me_3Si), or bis(cyclopentadienyl)magnesium. Reaction (6) represents a redistribution reaction and might also be considered a thermal decomposition, which can involve reductive elimination of Cp ligands. The reverse reaction, (−6), can be used to obtain monocyclopentadienyl derivatives.

Lewis acids such as aluminum halides (A) and other anion (Y) abstraction agents generate a cationic system from a formerly neutral system in reaction (7), with a decrease in formal coordination number at the element. Compound derivatization can be achieved by exchange of the auxiliary ligand(s) in reaction (8), and by substitution onto the Cp ligand frame in reaction (9), which is usually performed on the more stable π-cyclopentadienyl complexes of thallium and tin.

Reductive dehalogenation according to reaction (10) is used for aluminum, silicon, germanium, and tin and is thermally induced for indium and lead. Additional cyclopentadienyl ligands can be introduced onto cyclopentadienyl-lithium, -sodium, -cesium, -thallium, -tin, and -lead compounds to give anionic multicyclopentadienyl complexes. This is achieved by reaction (11) involving more nucleophilic cyclopentadienide in salts with complex cations. Additional auxiliary ligands can also be introduced according to reaction (13). Decrease in the number of cyclopentadienyl ligands at an element site can be achieved by abstraction in reaction (12), protonation or alkylation in reaction (14), ligand substitution in reaction (15), and reductive elimination in reaction (16).

Theoretical Models for the Cp–E Interaction

Cyclopentadienyl compounds designated as σ-complexes are considered to involve sp^3 hybridization at the element bound carbon center; the bond lengths and angles within the Cp ring are nonequivalent and tend toward those of cyclopentadiene.[29] In contrast to bis(π-cyclopentadienyl) transition metal complexes, π-complexes of main group elements with the element displaced from the C_5 axis of the Cp ligand are sometimes described as involving peripheral coordination[2,30] and typically exhibit relatively minor perturbation of the C−C bonds within the Cp framework with retention of Cp planarity. Consistent with bis(π-cyclopentadienyl) transition metal complexes,[31] such systems are shown by NMR spectroscopy to routinely undergo haptotropic shifts and consequential fluxionality in solution[10] and in the solid state,[32] implying that all five of the carbon atoms in the Cp frame are involved in the element−Cp π-interaction. This is apparently frozen out in the solid state, revealing nonequivalent element−carbon distances obtained from X-ray crystallographic data. In this context, the energetic distinctions between various structures involving the element at different projection sites of the Cp ligand (different "hapticities") are

Table 3. Polymeric μ-Cyclopentadienylelement Complexes: Synthetic Approach (S, semicolon separates synthetic steps and comma refers to more than one synthetic method), Characterization Data Reported (CA = chemical analysis; IR = infrared; MS = mass spectrometry; X = X-ray crystallography; XP = X-ray powder), NMR Nuclei Studied, Selected Solid State Structural Parameters, $Cp_{centroid}$−E Distances (Å), Angles between Planes of Two Cp Ligands Bound to One Element Center (α°) and $Cp_{centroid}$−E−$Cp_{centroid}$ Angles (β°)

	S	CA	IR	MS	NMR	α	β	Cp_c−E	ref
CpLi (XP)	1,2	√	√				176	1.97	204,205,206, 207,208
Cp^{T}Li (X)	*a*					8, 5, 5	175	1.96	209
Cp^{M}Li	2								204
Cp^{Bor}Li, Cp^{BorO}Li, Cp^{BorN}Li	2				^{1}H, ^{13}C				65
Cp^{4Ph}Li	2		√	√	^{1}H, ^{13}C				66
Cp*Li	2								210,211
Cp^{3T}li	2	√			^{1}H, ^{13}C, ^{7}Li, ^{29}Si				68
^{isodi}CpLi	2				^{1}H, ^{13}C, ^{6}Li				61
^{camphor}CpLi	2				^{1}H, ^{13}C, ^{6}Li				212
CpNa (XP)	1	√	√		^{1}H		178	2.36	204,208,213, 214,215,216
CpNa·L: L = THF, TMEDA (X), pyr, 4-DApyr, bipy;	13	√	√		^{1}H	56, 63	119, 128	2.67, 2.69	213
CpNa·L: L = 1,2-DME, 1,4-diox, 1,3,5-triox, 15-crown-5, NEt_3	13	√	√		^{1}H				213
Cp^{M}Na·L: L = THF, TMEDA (X), pyr, 4-DApyr, bipy;	13	√	√		^{1}H				213
Cp^{M}Na	1	√	√		^{1}H				204,216
Cp^{Bor}Na, Cp^{BorO}Na, Cp^{BorN}Na	2				^{1}H, ^{13}C				65
Cp*Na	1;4				^{1}H, ^{13}C, ^{23}Na				74,210
Cp^{5Ph*}Na: Ph* = C_6H_4R, R = Me, Pr, pentyl, heptyl	4	√			^{1}H, ^{13}C				132
Cp^{5Ph**}Na: Ph** = $C_6H_4C(O)R$, R = Me, Pr, pentyl, OEt	4	√			^{1}H, ^{13}C				148
Cp^{4Ph**}Na: Ph** = $C_6H_4C(O)R$, R = Me	4	√			^{1}H, ^{13}C				149
Cp^{Bor}Na·THF_2 (X)	1;13					62	131	2.58, 2.63	65
Cp^{BorN}Na·THF (X)	1;13					44, 45	136, 136, 137	2.48, 2.50, 2.48, 2.48, 2.48, 2.53	65
Cp^{BorN}Na·THP (X)	1;13					42	141	2.44, 2.45	65
Cp^{THF}Na·THF[b] (X)	1								217
CpK (XP), Cp^{M}K	1;2						138	2.82	204,208
Cp^{T}K (X)	1			√	^{1}H, ^{13}C, ^{29}Si	30	151	2.78	218
Cp*K	3			√	^{1}H, ^{13}C (pyr)				74,210
CpK·$(Et_2O)_2$ (X)	3;13					34	145	2.77	219
Cp^{4MSi*}K·THF[c] (X)	3	√					146	2.81	220
Cp*K·pyr_2 (X)	3;13				^{1}H, ^{13}C	42	138	2.79	74
CpCs (XP)	1				^{1}H, ^{13}C		138	2.82	221,222
CpIn (X)	5		√		^{1}H	62	128	2.69, 2.73	130,223
Cp^{M}In (X)	5	√	√		^{1}H	56	130	2.61, 2.77	130
Cp^{4M}In (X)	5	√		√	^{1}H, ^{13}C	53	134	2.50, 2.81	224
Cp^{B}In (X)	5	√	√	√	^{1}H	66	128	2.53, 2.85	225
Cp^{T}In (X), Cp^{Ge}In	5	√	√		^{1}H	60	132	2.61, 2.82	226
Cp^{2Ph}In	5	√		√	^{1}H, ^{13}C				227
CpTl (XP)	5						137	3.19	228
Cp^{4M}Tl (X)	5	√		√	^{1}H, ^{13}C	53	134	2.68, 2.71	224
Cp*Tl (X)	5	√		√			145	2.71	229
Cp^{5Bz}Tl (X)	2	√	√	√	^{1}H			2.49	230
Cp^{T}Tl (X)	2	√		√	^{1}H, ^{13}C	34	149	2.71, 2.84	198
Cp^{4MPhS}Tl (X), Cp^{4MBzS}Tl (X)[d]	5	√		√	^{1}H, ^{13}C	41, 37	142, 147	2.63, 2.86, 2.74	231
Cp^{P}Tl (X)	2		√		^{1}H, ^{31}P	63	122	2.80, 2.88	232
$Cp^{Fluorenyl}$Tl (X)	2,5			√	^{1}H, ^{13}C	62	116	2.60, 3.12	233
$Cp^{tricyanovinyl}$Tl (X)	9	√	√		^{1}H	68	114	3.01, 3.06	234
Cp^{2Ph}Tl	2	√		√	^{1}H, ^{13}C				227
Cp^{2Ph}Tl·THF (X)	13					63, 63	119, 128	2.83, 2.87	227

[a] See text. [b] Cp^{THF} = $C_5H_4(CH_2OC_4H_7)$. [c] Cp^{4MSi*} = $C_5Me_4[SiMe_2(NCMe_3)]$. [d] Cp^{4MPhS} = $C_5Me_4(SiMe_2Ph)$; Cp^{4MBzS} = $C_5Me_4(SiMe_2CH_2Ph)$.

calculated to be small for main group elements,[33] and this is most convincingly demonstrated experimentally and theoretically for Cp'_3Al derivatives, with calculated differences of 4−8 kJ mol^{-1}.[34]

Although the "octet rule" generally provides useful simple models to appreciate the bonding in compounds of p block elements,[35] it is perhaps inappropriate for systems considered as coordination complexes or ion-paired systems. Moreover, the main group elements encompass a much wider range of electronegativities and hardness than the transition series, so that the Cp−E bond interactions are highly ionic for elements from group 1[36−38] and exhibit varying degrees of covalent character throughout the main group, with complexes of the elements from groups 14 and 15 predominantly covalent.

Table 4. Molecular (Oligomeric) μ-Cyclopentadienylelement Complexes and Tris(cyclopentadienyl)element Complexes: Synthetic Approach (S), Characterization Data Reported (CA = chemical analysis; IR = infrared; MS = mass spectrometry), NMR Nuclei Studied, Selected Solid State Structural Parameters, $Cp_{centroid}$−E Distances (Å), Angles between Planes of Two Cp Ligands Bound to One Element Center ($\alpha°$) and $Cp_{centroid}$−E−$Cp_{centroid}$ Angles ($\beta°$)

	S	CA	IR	MS	NMR	α	β	Cp_c−E	ref
$Cp^{5Bz}Li(\mu\text{-}Cp^{5Bz})Li\cdot C_6D_6$	2			√	^1H, ^{13}C, ^7Li	2	176	1.78, 2.03, 1.90	237
$[Ph_4P][Cp_3Cs_2]$	11	√			^1H, ^{13}C	64	116	3.13, 3.10	221
$[PBu_4\cdot THF][Cp_3Ba]$	11				^1H		106−115	2.90, 2.88, 2.92, 2.97	238
$[Li\cdot(12\text{-crown-}4)_2][Cp_3Tl_2]$	12		√		^1H	51, 55	134	2.63, 2.84(μ), 2.84, 2.64	239
$CpTl(\mu\text{-}Cp)Li\cdot PMDETA$	11					31, 36	150, 157	2.61, 2.82(μ), 2.85	100
$[Cp_2Sn(\mu\text{-}Cp)Sn\cdot THF][BF_4]$	*a*					60, 62, 79, 105	130, 138, 98, 102	2.29−3.66	240
$Cp[N(SiMe_3)_2]Sn(Cp)Li\cdot PMDETA$	13	√	√		^1H	56	126	2.57, 2.83	241
$[PMDETA\cdot Na](\mu\text{-}Cp)[Cp_2Sn]$	11	√	√		^1H	61, 64, 62	116, 119, 124	2.73, 2.55, 2.53	242,243
$[PMDETA\cdot Na](\mu\text{-}Cp)[Cp_2Pb]$	11	√	√		^1H		120, 123, 117	2.74, 2.60, 2.63	243
$[THF_6Mg][Cp_3Sn]_2$	11	√	√		^1H	71	119	2.65	243,244
$[THF_6Mg][Cp_3Pb]_2$	11	√	√		^1H		119	2.68	243
$[Li\cdot(12\text{-crown-}4)_2]_2[Cp_5Pb_2]\text{-}[Cp_9Pb_4]$	11	√	√		^1H	60, 60(μ), 62(μ)	128, 113(μ), 119(μ)	2.61, 2.54, 2.86(μ)	245
$[Li\cdot(12\text{-crown-}4)_2]_2[Cp_5Pb_2]\text{-}[Cp_9Pb_4]$						53, 57(μ), 69(μ)	124; 115(μ); 120(μ)	2.56, 2.92(μ), 2.70(μ), 2.51, 2.73(μ)	
$[(Me_2N)_3SCpS(NMe_2)_3][Cp]$	*b*				^1H			3.13, 3.22	246

[a] $Cp_2Sn + THF + BF_3$. [b] $CpSiMe_3 + [(Me_2N)_3S][Me_3SiF_2]$.

A general qualitative molecular orbital energy correlation diagram for Cp−E interactions of local C_{5v} symmetry **1** is given in Figure 1.[39] The most effective stabilization occurs between the fully bonding (lowest energy a_1) occupied π-orbital of the Cp ligand and the s and p (axis) orbitals of E. A secondary interaction involves the two occupied π-orbitals (e_1) of Cp with the degenerate p orbitals of E (perpendicular to the E−$Cp_{centroid}$ axis).

In Figure 1, Y is a coordinate bond if one invokes the model for the elements of group 1 and a covalent bond for elements of group 2 involved in neutral complexes. Cationic complexes of group 13 elements involve a covalent bond (e.g., $[CpBBr]^+$), while neutral group 13 (e.g., CpAl) complexes and cationic complexes of group 14 (e.g., $CpSn^+$) carry a nonbonding electron pair for Y. The validity of this model is demonstrated by calculated MO energies of beryllium complexes, which are in close agreement with measured vertical ionization energies obtained from PE spectra.[1,83] Most of the compounds for which this model is invoked are characteristic of *nido* clusters with a pentagonal pyramidal framework[40] when the Cp−E interaction is considered in isolation, but the three occupied bonding MOs[41] (a_1 and e_1) can also be described in terms of a "three-dimensional aromaticity" model.[37] A local C_{5v} symmetry structure represents a minimum for the Cp−element interaction in CpLi,[33,36,37,41−43] CpBeH,[37,41,44] $CpBe^+$,[37] $CpBeB_5H_{10}$,[45] CpB,[37] $CpBH^+$,[47] CpBeCl,[41] CpGa,[46] CpIn[41,47,48] CpTl,[37,49] $CpGe^+$,[50] and $CpSn^+$,[47] while model complexes of aluminum and germanium are distorted,[51] consistent with experimental observations (see below).

Covalent bonding in bis(cyclopentadienyl)element complexes can be modeled qualitatively by the general molecular orbital schemes for parallel planar (D_{5d}) and bent (C_{2v}) structures containing 14 valence electrons, shown in Figure 2. The stabilization of three electron pairs (D_{5d}: $1a_{1g}$, $1e_{1u}$; C_{2v}: $1a_1$, $2b_1$, $1b_2$) is primarily responsible for the Cp−element bond in both structures. The absence of an element orbital of a_2 symmetry in the C_{2v} structure and element orbitals of e_{1g} symmetry in the D_{5d} structure distinguishes the models from those for bis(π-cyclopentadienyl) transition metal complexes, imposing ligand-based nonbonding orbitals.

Most discussions of structural preferences for 14 electron bis(π-cyclopentadienyl) complexes focus attention on the energy and occupation of the $2a_{1g}$ orbital in a D_{5d} symmetry structure, which correlates with the 2_{a1} orbital in a C_{2v} symmetry structure. Structural adjustment from D_{5d} to C_{2v} symmetry effects a stabilization of the $2a_{1g}$ orbital due to incorporation of the a_1 p orbital of E. The observed structures of neutral Cp_2E (E = group 14) and cationic $[Cp_2E]^+$ (E = pnictogen) complexes are consistent with this model, which can be understood in more simple terms using a VSEPR arguments, implicating the $2a_1$ orbital (C_{2v}) as the so-called "lone pair". However, the energy of the $2a_{1g}$ orbital in the D_{5d} structure is also sensitive to the separation of the Cp ligands.[52] For a hypothetical parallel (D_{5d}) germanocene, the $2a_{1g}$ orbital is calculated to be above the $1e_{1g}$ level at small Cp−Cp separations (4.0 Å), it decreases in energy with increasing Cp−Cp separation, and is below the $1e_{1g}$ level for Cp−Cp separations in excess of 5.0 Å, consistent with the antibonding character of the $2a_{1g}$ orbital. In fact, the electronic imposition or consequences of the nonparallel structure may be minimal. Experimental support for the deep energy of the formal lone pair ($2a_{1g}$ or $2a_1$) on the element center is provided in the photoelectron spectroscopic data for Cp^*_2E (E = Si, Ge, Sn, Pb).[53] The ordering of the orbital energy levels for the heavier elements (Ge, Sn, Pb) is as shown in Figure 2, but the 2_{a1} orbital is anomalously high in relative energy in the silicocene, consistent with the relatively close proximity of the Cp* ligands and the more effective overlap of the 3p valence orbitals of silicon in comparison with the heavier elements.

The wide variety of theoretical molecular orbital studies on 14 electron systems has been comprehensively reviewed[7,9] and concludes that although non-

Table 5. Bis(cyclopentadienyl)element Complexes: Synthetic Approach (S, semicolon separates synthetic steps and comma refers to more than one synthetic method), Characterization Data Reported (CA = chemical analysis; IR = infrared; MS = mass spectrometry; X = X-ray crystallography; XP = X-ray powder; D = electron diffraction), NMR Nuclei Studied, Selected Solid State or Gas Phase Structural Parameters, $Cp_{centroid}-E$ Distances (Å), Angles between Planes of Two Cp Ligands Bound to One Element Center (α°), and $Cp_{centroid}-E-Cp_{centroid}$ Angles (β°)

	S	CA	IR	MS	NMR	α	β	Cp_c-E	ref
$[Ph_4P][Cp_2Li]$ (X)	11				^1H, ^{13}C	0	180	2.01	247
$[(NMe_2)_3S][Cp_2Li]$ (X)	11				^1H, ^{13}C	0	180	1.97, 1.99	248
$[Ph_2PMe_2][Cp^B{}_2Li]$ (X)	11	√	√		^1H, ^{13}C, ^{31}P				249
$[Li(12\text{-crown-}4)_2][^{iso}Cp_2Li]$ (X)	11				^1H, ^{13}C	0	180	1.99, 2.01	73
$[Ph_4P][Cp_2Na]$ (X)	11				^1H, ^{13}C	0	180	2.37	335
$[(NMe_2)_3SCpS(NMe_2)_3][Cp_2Na]$ (X)	11				^1H	0	180	2.33	248
$[Ph_4P][C_2Me_4(C_5H_4)_2Na\cdot THF]$ (X)	11				^1H, ^{13}C	121	122	2.38	335
Cp_2Be (D, X)	2	√	√		^1H, ^{13}C, ^9Be	4		1.47, 1.92, 1.50	204,250,251
Cp_2Mg (D, X)	1,2	√	√	√	^{25}Mg	0	180	2.01, 1.99	251,252
$Cp^M{}_2Mg$	2								253,254
$Cp^*{}_2Mg$ (D, X)	2	√	√	√	^1H, ^{13}C, ^{25}Mg	0	180	2.02	92,254,255
$Cp^B{}_2Mg$ (X)	2				^1H, ^{13}C, ^{25}Mg	0	180	2.00	256
$Cp^{3T}{}_2Mg$ (X)	2	√	√	√	^1H	8	171	2.02−2.04	99
$Cp^{5OMe}{}_2Mg$	2	√	√	√	^1H				257
$Cp_2Mg\cdot L$: L = pyr, TMEDA, TMBDA, THF, diox, DME, DMPE, PMe_3, OEt_2	13	√			^1H, ^{13}C, ^{25}Mg				92
$Cp_2Mg\cdot bipy$	13	√							85
$Cp^*{}_2Mg\cdot carbene^a$ (X)	13	√			^1H, ^{13}C		139	2.24, 2.17	258
Cp_2Ca (X)	1	√		√	^1H	57	118	2.48, 2.59	259,260,261
$Cp^*{}_2Ca$ (D, X)	1,5	√			^1H, ^{13}C	20, 33, 36	154, 147	2.31, 2.33−2.36	262,263,264
$Cp^{3I}{}_2Ca$ (X), $Cp^{3I}{}_2Ca\cdot THF$	5	√	√		^1H		170	2.33	265,266
$Cp^{4I}{}_2Ca$ (X)	5	√	√		^1H, ^{13}C	21	162	2.35, 2.35	267
$Cp_2Ca\cdot THF_2$	1;13,5	√	√		^1H, ^{13}C				268,269,270, 271
$Cp_2Ca\cdot DME_2$, $Cp_2Ca\cdot pyr_2$, $Cp_2Ca\cdot bipy$	8	√	√		^1H				268
$Cp_2Ca\cdot NH_3(THF)$	1;13	√	√		^1H				269
$Cp^B{}_2Ca\cdot THF$, $Cp^B{}_2Ca\cdot THF_2$ (X)	1;13				^1H, ^{13}C	48	133	2.46, 2.46	256
$Cp^{2B}{}_2Ca\cdot THF$	1;13	√			^1H, ^{13}C				271
$Cp^M{}_2Ca\cdot DME$ (X)	1;13	√	√		^1H	40	135	2.40	272
$Cp^*{}_2Ca\cdot carbene^a$ (X)	13	√			^1H, ^{13}C		144	2.38, 2.38	258
$Cp^*{}_2Ca\cdot THF_2$	1;13	√	√		^1H, ^{13}C				270,271
$Cp^*{}_2Ca\cdot THF$, $Cp^*{}_2Ca\cdot DME$	1;13	√			^1H, ^{13}C				271
$Cp^*{}_2Ca\cdot L$: L = bipy, $(xCN)_2$, PEt_3	13	√	√						85
$Cp^*{}_2Ca\cdot(Me_3SiCCCCSiMe_3)$ (X)	13		√		^1H, ^{13}C	36	144	2.35−2.37	273
$[Cp^*{}_2Ca]_2\cdot pyraz$, $Cp^*{}_2Ca]_2\cdot Me_4pyraz$	13	√	√		^1H				274
$Cp^T{}_2Ca\cdot THF$	1;13	√			^1H, ^{13}C				271
$Cp^{2T}{}_2Ca\cdot THF$ (X)	1;13	√			^1H, ^{13}C	46	135	2.40	271,275
$Cp^{O'}{}_2Ca^b$ (X), $Cp^{N'}{}_2Ca^c$ (X)	5	√		√	^1H, ^{13}C	40, 40	140, 137	2.38, 2.40	276
$[Cp^*{}_2Ca\cdot MeAlMe_2THF]_2$ (X)	8		√		^1H	39	143	2.41, 2.42	277
$Cp^*{}_2Ca\cdot Cl_2MCp^*{}_2$: M = Zr, Hf (X), Th, $Cp^*{}_2Ca\cdot(CO)Crmes$, $Cp^*{}_2Ca\cdot(CO)_2ZrCp^*{}_2$	13	√	√		^1H, ^{13}C	36	144	2.36, 2.38	278
$Cp^N{}_2Ca$, $Cp^O{}_2Ca$ (X)^d	2,5	√	√	√	^1H, ^{13}C	42	137	2.39, 2.40	279,280
$C_2Me_4(C_5H_4)_2Ca$, $CMe_2CEt_2(C_5H_4)_2Ca$, $C_2Me_4(C_5H_4)_2Ca\cdot BuNCHCHNBu$ (X), $CMe_2CEt_2(C_5H_4)_2Ca\cdot BuNCHCHNBu$	1	√	√	√	^1H				281
$(BuC_5H_5)_2Ca\cdot THF$ (X)	5	√			^1H	133			282
Cp_2Sr	1	√			^1H				259,261
$Cp^*{}_2Sr$ (D)	1,5	√			^1H, ^{13}C	25	149	247	85,264,283, 284
$Cp^{3I}{}_2Sr$	−13	√	√		^1H				284
$Cp_2Sr\cdot THF$, $Cp^*{}_2Sr\cdot THF_2$	5	√	√		^1H, ^{13}C				265
$Cp^*{}_2Sr\cdot(carbene)_2{}^a$ (X)	13	√			^1H, ^{13}C		131	2.66, 2.67	258
$Cp^B{}_2Sr\cdot THF$, $Cp^B{}_2Sr\cdot THF_2$ (X)	1;13				^1H, ^{13}C	48	133	2.61, 2.60	256
$Cp^{2T}{}_2Sr\cdot THF$ (X)	1;13	√			^1H, ^{13}C	48	134	2.55	275
$Cp^{3I}{}_2Sr\cdot THF_2$, $Cp^{3I}{}_2Sr\cdot THF_2$	5	√	√		^1H				265
$Cp^*{}_2Sr\cdot L$: L = bipy, OEt_2, $(xCN)_2$, PEt_3	13	√							85
$Cp^N{}_2Sr$ (X), $Cp^O{}_2Sr$	2	√	√		^1H, ^{13}C	42	141	2.58	280
$C_2Me_4(C_5H_4)_2Sr\cdot THF_2$	1	√	√	√	^1H				281
Cp_2Ba	1	√			^1H				259,261
$Cp^*{}_2Ba$ (D, X)	1,5	√			^1H, ^{13}C	26, 47, 49	148, 131	2.63, 2.70−2.78	85,263,264, 283,284,285
$Cp^{3I}{}_2Ba$	−13	√	√		^1H				265
$Cp^{4I}{}_2Ba$ (X)	5	√	√		^1H, ^{13}C	27	154	2.68	267
$Cp^*{}_2Ba\cdot carbene^a$ (X)	13	√			^1H, ^{13}C		137	2.74, 2.74	258
$Cp_2Ba\cdot THF_{0.25}$, $Cp^*{}_2Ba\cdot THF_2$	5	√	√		^1H, ^{13}C				85,268
$Cp^B{}_2Ba\cdot THF_2$	1;13				^{13}C				256
$Cp^{3I}{}_2Ba\cdot THF$, $Cp^{3I}{}_2Ba\cdot THF_2$ (X)	5;13	√	√		^1H	55	132	2.79	265

Table 5. (Continued)

	S	CA	IR	MS	NMR	α	β	Cp_c−E	ref
$Cp^{4Ph}{}_2Ba\cdot THF$	2	√	√		^1H, ^{13}C				286
$Cp^*{}_2Ba\cdot L$: L = bipy, $(xCN)_2$, PEt_3	13	√							85
$[Cp^*{}_2Ba]_2\cdot$pyraz (X), $[Cp^*{}_2Ba]_2\cdot Me_4$pyraz	13	√	√		^1H	44	138	2.47−2.73	274
$Cp^N{}_2Ba$, $Cp^O{}_2Ba$	2	√	√		^1H, ^{13}C				280
$Cp^{OO}{}_2Ba$[e]	5	√	√		^1H, ^{13}C				287
$Cp^*{}_2BCl$	5	√		√	^1H, ^{11}B				288
$[Cp^*BCp^*][BCl_4]$	7	√			^{11}B				289
$[Cp_2Al][MeB(C_6F_5)_3]$	7	√			^1H, ^{13}C, ^{27}Al				289
$[Cp^*{}_2Al][Cp^*AlCl_3]$ (X)	*f*			√	^1H, ^{27}Al	0	180	1.84	290
$[Cp^*{}_2Al][LiCp^{5Bz}{}_2]$ (X)	*g*								237
Cp_2AlMe (X), Cp_2AlEt, $Cp_2AlMe\cdot Et_2O$	5	√			^1H, ^{13}C, ^{27}Al	75	158	2.34, 2.21	291
$[CpMg\cdot PMDETA][Cp_2Tl]$ (X)	12						157	2.72	239
$Cp^*{}_2Si$ (X)	10	√		√	^1H, ^{13}C, ^{29}Si	22, 0; 25	180, 167	2.13, 2.11, 2.12, 2.12	54,292
Cp_2Ge (X)	5					50	152	2.23	293
$Cp^M{}_2Ge$ (D)	5	√	√	√	^1H, ^{13}C	34		2.22	52,294
$Cp^{2B}{}_2Ge$	5	√		√	^1H, ^{13}C				165
$Cp^*{}_2Ge$ (X)	5,10	√			^1H, ^{13}C	22		2.21	169,295
$Cp^T{}_2Ge$, $Cp^{2T}{}_2Ge$, $Cp^{3T}{}_2Ge$ (X)	5	√		√	^1H, ^{13}C	15, 21	170, 172	2.25, 2.26, 2.25, 2.25	296
$Cp^{4Ph}{}_2Ge$, $Cp^{B4Ph}{}_2Ge$	5	√	√	√	^1H, ^{13}C				66
$Cp^{5Ph}{}_2Ge$	5	√	√	√	^{13}C				297,298
$Cp^{5Bz}{}_2Ge$ (X)	5	√	√	√	^1H, ^{13}C	31	163, 163	2.24, 2.29, 2.24, 2.29	299,300
$C_2H_4(SiMe_2)_2(C_5Me_4)_2Ge$	5	√		√	^1H, ^{13}C				301
Cp_2Sn (D, X)	5	√	√		^1H	55, 46, 47	144, 147	2.42, 2.41, 2.37, 2.44	30,251,302,303, 304,305,306, 307
$Cp^M{}_2Sn$ (D)	5	√	√	√	^1H, ^{13}C	50	130	2.40	52,294,307
$Cp^{2B}{}_2Sn$	5	√		√	^1H, ^{13}C, ^{119}Sn				165
$Cp^*{}_2Sn$ (X)	5	√		√	^1H; ^{13}C, ^{119}Sn	36, 35	155, 155	2.39, 2.40	169,173,292, 295,308,309
$Cp^{3I}{}_2Sn$, $Cp^{4I}{}_2Sn$ (X)	5	√	√		^1H, ^{13}C	28	165	2.42, 2.24	310
$Cp^{5I}{}_2Sn$ (X)	5	√		√	^1H, ^{13}C, ^{119}Sn	0	180	2.49	311
$Cp^{4Ph}{}_2Sn$, $Cp^{B4Ph}{}_2Sn$	5	√	√	√	^1H, ^{13}C				66
$Cp^{5Ph}{}_2Sn$ (X)	5	√	√	√	^{13}C	0	180	2.40	297,298,312
$Cp^{5Bz}{}_2Sn$ (X)	5	√	√	√	^1H, ^{13}C	33	156	2.43, 2.45	300
$Cp^T{}_2Sn$, $Cp^{PN}{}_2Sn$[h] (X)	9				^1H, ^{13}C	47	149	2.38, 2.39	313
$Cp^{4MBS}{}_2Sn$[i] (X)	5	√			^1H, ^{13}C, ^{29}Si; ^{119}Sn	0	180	2.38	314
$Cp^{2T}{}_2Sn$, $Cp^{3T}{}_2Sn$ (X)	9				^1H, ^{13}C	16	162	2.27, 2.68	315
$Cp^{Sn}{}_2Sn$	9	√			^1H				316
$Cp^{5Ph}SnCp$ (X)	8	√		√	^{13}C	44	151	2.39, 2.49	297,298
$Cp^{MeCO}SnCp$, $Cp^{MeOCO}SnCp$, $Cp^{EtOCO}SnCp$	5		√	√	^1H				317
$[Cp^{PN}SnCp][AlCl_4]$	9				^1H, ^{13}C, ^{27}Al; ^{31}P				318
$C_2Me_4(C_5H_4)_2Sn$	1	√	√	√	^1H, ^{13}C, ^{119}Sn				319
$C_6H_4(CH_2C_5H_4)_2Sn$, $C_6H_4(CH_2C_5H_4)_2Sn_2(C_5H_5)_2$, $C_6H_4(CH_2C_5H_4)_2Sn\cdot BF_3$	5	√	√	√	^1H, ^{13}C				320
$Cp_2Sn\cdot BF_3$	13	√	√	√	^1H, ^{19}F				321
$Cp_2Sn\cdot$TMEDA (X)	13	√	√	√	^1H		131	2.52	322
$C_2H_4(SiMe_2)_2(C_5Me_4)_2Sn$	5	√		√	^1H, ^{13}C				301
Cp_2Pb (D, X)	5	√				45, 67, 52, 60	135, 123, 120, 117	2.55, 2.83, 2.82	30,199,204,236, 251,303,304, 323,324,325
$Cp^M{}_2Pb$	5				^1H, ^{13}C				294
$Cp^{2B}{}_2Pb$	5	√		√	^1H, ^{13}C, ^{207}Pb				165
$Cp^*{}_2Pb$ (X)	5	√			^1H, ^{13}C, ^{207}Pb	37	151	2.48, 2.52	292,305,326
$Cp^{3I}{}_2Pb$ (X)	5					0	180		7
$Cp^{3B}{}_2Pb$, $Cp^{4I}{}_2Pb$, $Cp^{5I}{}_2Pb$	5	√		√	^1H, ^{13}C				327
$Cp^{4Ph}{}_2Pb$, $Cp^{B4Ph}{}_2Pb$	5	√	√	√	^1H, ^{13}C				66
$Cp^T{}_2Pb$, $Cp^{2T}{}_2Pb$, $Cp^{3T}{}_2Pb$	5	√		√	^1H, ^{13}C				328
$Cp^{4MBS}{}_2Pb$[i] (X)	5	√		√	^1H, ^{13}C, ^{29}Si, ^{207}Pb	0	180	2.46	329
$Cp^{5Ph}{}_2Pb$	5	√	√	√	^{13}C				297,298
$Cp^{5Bz}{}_2Pb$ (X)	5	√	√	√	^1H, ^{13}C	33	154	2.50, 2.51	300
$[Cp^{PN}PbCp][AlCl_4]$					^1H, ^{13}C, ^{27}Al, ^{31}P				318
$C_2Me_4(C_5H_4)_2Pb$	1	√	√	√	^1H, ^{13}C, ^{207}Pb				319
$Cp_2Pb\cdot$TMEDA (X), $Cp_2Pb\cdot Me_2$bipy (X)	13	√	√		^1H		129, 140	2.59, 2.59	330
$[Cp^*{}_2As][BF_4]$ (X)	5;7				^1H, ^{13}C, ^{11}B, ^{19}F	36	173	2.14, 2.17	331
$Cp^{3B}{}_2SbCl$, $[Cp^{3B}{}_2Sb][AlCl_4]$ (X)	5,7	√		√	^1H, ^{13}C	12			332

Table 5. (Continued)

	S	CA	IR	MS	NMR	α	β	Cp_c−E	ref
$[Cp^*_2Sb][AlI_4]$ (X)	*j*					36			333
Cp^{3B}_2BiCl		√				36			333
Cp^{3B}_2BiCl (X)	5	√			^1H, ^{13}C	18	145	2.52, 2.55	185
$[Cp^{3B}_2Bi][AlCl_4]$ (X)	7	√			^1H, ^{13}C	10	173		334

[a] Carbene = 1,3,4,5-tetramethylimidazol-2-ylidene. [b] $Cp^{O'} = C_5Me_4[CH_2C(Ph)HOMe]$. [c] $Cp^{N'} = C_5Me_4[CH_2C(Ph)HNMe_2]$. [d] $Cp^N = C_5Me_4(CH_2CH_2NMe_2)$, $Cp^O = C_5H_4(CH_2CH_2OMe)$. [e] $Cp^{OO} = C_5H_4[CH_2CH_2O\ CH_2CH_2OMe]$. [f] $\{Cp^*Al\}_4 + AlCl_3$. [g] $\{Cp^*Al\}_4 + LiCp^{5Bz}$. [h] $Cp^{PN} = C_5H_4[P(N^iPr_2)_2]$. [i] $Cp^{4MBS} = C_5Me_4[SiMe_2(^tBu)]$. [j] $\{Cp^*Al\}_4 + SbI_3$.

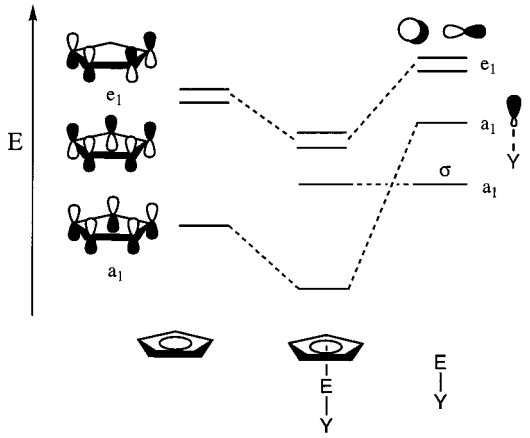


Figure 1. General molecular orbital diagram for Cp−main group element interactions of local C_{5v} symmetry, showing only occupied orbitals.

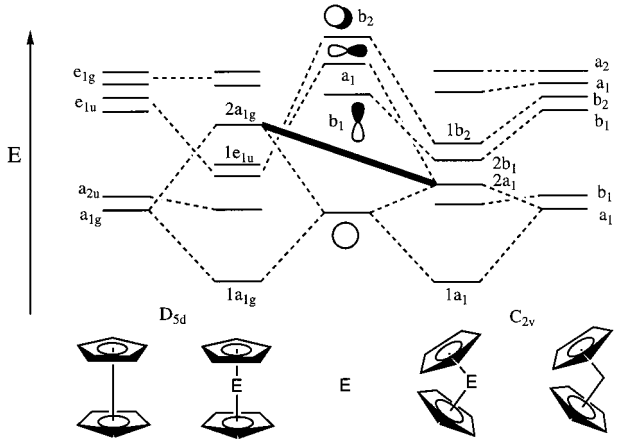


Figure 2. General molecular orbital diagrams for 14 electron bis(cyclopentadienyl)main group element complexes with parallel (D_{5d}) and bent (C_{2v}) structures, showing only occupied orbitals.

parallel (bent) structures represent global minima, this can only be recognized with higher order theory, as very small energy differences (<10 kJ mol^{-1}) distinguish parallel from nonparallel structures. This is borne out in the experimental observation of both parallel and nonparallel structures for silicocene in the same crystal.[54,55] Similar conclusions can be drawn for the hypothetical, isoelectronic phosphorus cation $[Cp_2P]^+$, although a surprisingly large interplane angle (α) of 110.8° is computed for the lowest energy structure.[56]

Modification of the D_{5d} section of Figure 2 involving destabilization and vacancy of the $2a_{1g}$ orbital provides a model for 12 electron systems, which is consistent with the observed structures for anionic $[ECp_2]^-$ (E = alkalimetal) and cationic $[Cp_2E]^+$ (E = group 13) complexes. However, observation of nonparallel structures for the neutral 12 electron Cp_2E alkaline earth complexes are inconsistent with this model (see below), so that these complexes have attracted intense theoretical studies.[57,58]

Structural Classifications

Characteristic infrared and Raman spectroscopic features and mass spectrometry were pivotal in the early identification and assignment of π-cyclopentadienyl main group element complexes, and the advent of routine multinuclear NMR spectroscopy realized a distinctive element upfield chemical shift for the π-cyclopentadienyl bound main group element center (for elements with NMR active nuclei), which is rationalized in terms of ring current phenomena.[59−61] Unfortunately, the ^{13}C chemical shifts of the Cp ligand are not useful criteria for assessment of Cp−element bonding.[62] As with many areas of modern inorganic chemistry, X-ray crystallography has played the leading role in the discovery and development of these compounds.

For the purpose of comparison between various derivatives, we define the following structural parameters, which are listed in the tables. The $Cp_{centroid}$−E distance (where possible, we have calculated values which have not been explicitly reported) indicates the intimacy or relative strength of the interaction between the Cp ligand and the main group element and can be informative in cases where the Cp ligand behaves as a μ-bridge between two element centers. For polymeric μ-Cp, molecular μ-Cp, and bis(cyclopentadienyl)element complexes, the angles α (between the Cp ligand planes) and β ($Cp_{centroid}$−E−$Cp_{centroid}$) help define the position of the element with respect to the Cp ligands. When α = 0°, the Cp ligands are parallel and β is usually 180°, however, if the element is displaced from the C_5 axis of the Cp ligand, the β angle will be significantly less than 180°.

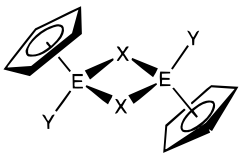
Molecular Cyclopentadienylelement Complexes

Complexes involving a single π-coordinated Cp ligand are often referred to as "half-sandwich" structures and relate to the "milking stool" ***1*** or "piano stool" designation used for certain π-cyclopentadienyl transition metal complexes. Derivatives are known for all elements of groups 1, 2, 13, 14, and 15, except cesium, francium, carbon, silicon, and nitrogen, as presented in Table 1.

The alkali metal parent compounds CpE (E = Li, Na, and K) and Cp^TLi have been shown to adopt polymeric structures in the solid state (see Table 3),

but strong donors such as THF, TMEDA[64] and 12-crown-4[63] effect cleavage of the polymer and have enabled isolation of a wide range of molecular species. Structural data available for an extensive series of compounds with the general formulas Cp′Li·Y_n, where Y_n can represent a mono-**3**, di-**4**, or polydentate ligand **5**, reveal that the donor strength of the auxiliary ligand (Y) has a significant effect on the magnitude of the Cp−Li interaction. In contrast, the polymeric array is often retained for derivatives of sodium and potassium in the presence of an auxiliary donor (see Table 3), and a sterically bulky[75] Cp ligand or excess donor[66] give rare examples of the general formula Cp′E·Y_3 **6**.

Beryllium complexes of the general formula Cp′BeR are monomeric in solution, in the gas phase, and in the solid state, with a consistent C_{5v} structure **3** (Y = R) and a narrow range of $Cp_{centroid}$−Be distances, despite the possibility of varying degrees of π-interaction between the auxiliary ligand and beryllium. Cp complexes of the heavier alkaline earth metals require the stabilizing influence of either an auxiliary donor or bulky Cp units. Monomeric structures are observed for complexes with monocoordinate, bidentate, and tridentate ligands, while dimeric arrangements are bound together by halide or amino bridges **14**.

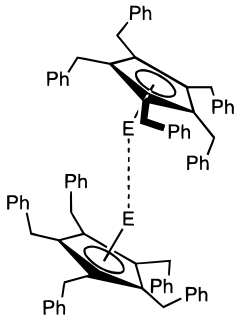


14

Neutral Cp-substituted boranes are σ-bonded compounds,[186] but cationic complexes of the form [Cp′BR]$^+$ have structures comparable to the isoelectronic CpLiY and CpBeR complexes **3**. ^{11}B, ^{1}H, and ^{13}C NMR spectral data are unambiguously interpreted in terms of π-complexation, and this is confirmed in a crystallographic study on [Cp*BBr][$AlBr_4$].[107]

The general binary formula Cp′E **1** is consistently observed in the gas phase for the heavier group 13 elements (E = Al, Ga, In, Tl), and NMR spectroscopic data and mass determination indicate that Cp′Ga, Cp′In, and Cp′Tl derivatives have a similar structure in solution.[123] The ring-substituted Cp′Ga complexes have a considerably higher thermal stability than the parent compound, and Cp*Ga can be distilled at ambient pressure (bp 150 °C) and is stable under MOCVD conditions up to 600 °C. Solid-state studies show oligomerization or polymerization as a common property for the heavier Cp′E derivatives as listed in Table 3.

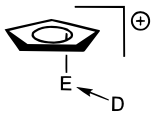
Pentabenzyl-substituted derivatives of indium[135] and thallium[146,150] adopt an unusual isostructural element−element bonded dimeric structure **15** in the solid state, which is described as a trans bent geometry. The dimer presumably represents the thermodynamically favored arrangement, and a weak element−element interaction, which has an identical distance in the two compounds (3.63 Å), may be responsible for extra stabilization energy. Although theoretical assessment at various levels implicates element−element interactions, they are weak and the {$Cp^{5Bz}E$}$_2$ dimers likely involve both element−element and ligand−ligand attractive interactions.[187,188]



15

The availability of vacant valence orbitals on high oxidation state group 13 centers might be expected to support π-coordination of Cp ligands; however, examples are relatively rare. While $CpAlMe_2$ is monomeric in the gas phase and is interpreted as a π-complex, alkyl derivatives of $CpAR_2$ are typically polymeric in the solid state with bridging σ-bound Cp ligands,[109,110] and $CpGaMe_2$ has a similar structure. Haloaluminum complexes involving cyclopentadiene ligands adopt typical dimeric bis-halogen bridged structures,[119,121] and dimerization can be prevented with the presence of a side chain donor functionality on the cyclopentadiene ligand (Cp^N), which imposes a chelate interaction in place of the bridge **13**, but most derivatives are best considered as σ-complexes.[26,27,189] The delicate energetic distinction between σ- and π-coordination is illustrated by the unique solid-state structure of $Cp^{3M}{}_3Al$,[34] which exhibits two π-bonded ligands and one σ-bonded ligand. It seems that π-coordination can be imposed by the presence of auxiliary electron withdrawing substituents on aluminum in CpAl{O(2,6-^{t}Bu$_2$-4-MeC_6H_2)}$_2$.[112]

The group 14 element cations [Cp′E]$^+$ (E = Ge, Sn), which are isoelectronic with the neutral group 13 element compounds Cp′E (E = Ga, In, Tl) described above, were first observed by mass spectrometry, but use of the Cp* ligand enabled the isolation of salts containing [Cp*Ge]$^+$,[161−163] [Cp*Sn]$^+$,[162,170−173] and [Cp*Pb]$^+$.[178] [Cp*Pb][BF_4] adopts a dimeric structure in the solid state bound by bridging anions, but the crystal structure of [Cp*Sn][BF_4] confirms the presence of isolated ions with C_{5v} symmetry **1**.[172,173] The nucleophilicity of [Cp*E]$^+$ cations (E = Ge, Sn) is demonstrated by the formation of coordination complexes with neutral ligands such as pyridine to give representatives of "slipped half sandwich" structures **16**.[163] Similar structural features are observed for the isoelectronic neutral derivatives of general formula Cp′ECl (E = Sn, Pb).[168,178] The solid state structure of CpSnCl involves a short Sn−Cl bond and a long Sn−Cl contact, which are responsible for a coordination polymeric array.



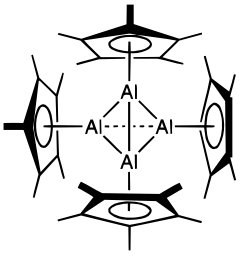
16

The rare examples of π-cyclopentadienyl phosphorus complexes (Cp*PNMes* and Cp*PNHBu from Table 1) all involve formal cationic low coordinate phosphorus centers (phosphenium),[179,180] whereas the more routine $CpSbCl_2$ adopts a chiral polymeric arrangement due to long-range intermolecular Cp−element π-interactions,[181] and chlorine bridges between bismuth centers are responsible for the polymeric solid-state structure of $CpBiCl_2$.[184] Thermal stability imposed by the Cp^{4I} ligand has enabled the isolation and structural characterization of an homologous pnictine series, $Cp^{4I}ECl_2$ (E = P, As, Sb, Bi), allowing for useful comparisons.[185] The solubility in common aprotic solvents decreases from P to Bi, and the color varies from yellow (P) to red-orange (Bi). Fluxional behavior observed in the ^1H NMR spectra can be frozen out for P and As but not for Sb and Bi. In the solid state, the position of the pnictogen center shows a smooth progression of the element from outside (P), to inside (Bi) the pentagonal cylinder. A halogen bridged dimer structure and a cluster arrangement have also been reported for bismuth.[185]

Cyclopentadienylelement Clusters

Complexes involving monovalent elements of group 13 (Cp*E), which are monomeric in the gas phase, adopt highly symmetric cluster arrangements in the solid state as listed in Table 2.

Cp*Al forms a unique tetrahedron of aluminum atoms with the apexes capped by Cp* ligands **17**,[117,190] which has been extensively modeled, and the calculated Al−Al bond length (2.79 Å) is consistent with that observed,[200] but is longer than that calculated for $\{AlX\}_4$ tetrahedra (X = H, Si^{t}Bu$_3$, SiH$_3$, Cl, F; 2.62−2.64 Å).[200,201] In contrast to the solid-state polymeric structure of Cp*Tl (see Table 3), the indium analogue Cp*In adopts an unusual hexameric structure with Cp* ligands surrounding an octahedral element cluster **18**.[131,197] $\{Cp^*Ga\}_6$[196] is isostructural with $\{Cp^*In\}_6$ including identical element−element bond lengths (363 Å) despite the differing atomic sizes of indium (atomic radius 1.55 Å) and gallium (atomic radius 1.30 Å). While the gallium cluster is colorless, the indium cluster is yellow, implicating more effective element−element interactions made possible by the larger atomic size. Interestingly, the octahedral cluster structures are distorted from O_h to S_6 symmetry by the slight offsetting of the $Cp_{centroid}$−normal from the center of the octahedron. $Cp^{2T}Tl$ also forms a hexameric cyclic cluster structure **19**, but involves only -μ-Cp interactions between element centers and can also be classified as a molecular -μ-Cp complex.[198] A similar structure is observed for one of three crystalline forms of plumbocene **20**.[199]



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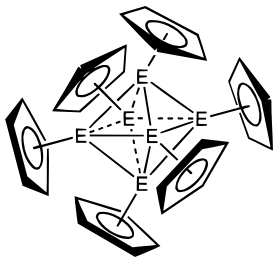

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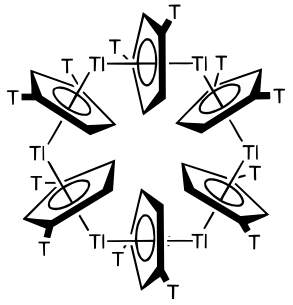

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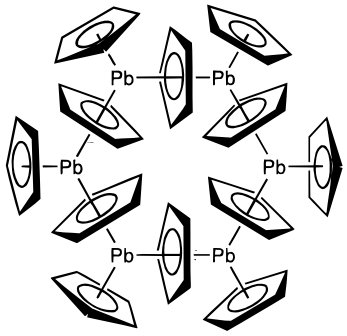


20

Reaction of $\{Cp^*Al\}_4$ with elemental selenium or tellurium gives heterocubanes of the general formula $\{Cp^*AlZ\}_4$ (Z = Se or Te),[191] where the tetrahedral array of aluminum atoms is retained. The higher oxidation state for aluminum effects a significant shortening of the $Cp_{centroid}$−Al distances relative to the starting material $\{Cp^*Al\}_4$, but the gallium analogues $\{Cp^*GaSe\}_4$,[202] $\{Cp^*GaTe\}_4$[203] involve σ-coordination of the Cp* ligands. Reaction of $\{Cp^*Al\}_4$ with elemental phosphorus (P_4) results in cleavage of all Al−Al and P−P bonds and formation of an unusual $\{(Cp^*Al)_6P_4\}$ cage.[192] Related clusters $\{(Cp^*AlF)_4(SiPh_2)_2\}$ and $\{(Cp^*Al)_3Sb_2\}$ are also accessible,[194] as well as $\{NiCp_2(Cp^*Al)_2\}$, which shows the Cp*Al monomer as a bridging ligand.[195]

Polymeric μ-Cyclopentadienylelement Complexes

The elements of group 1 as well as indium and thallium form equimolar cyclopentadienyl compounds with polymeric solid-state arrays involving alternating element and μ-Cp ligands, as listed in Table 3. Although few Cp′Li and Cp′Na complexes have been crystallographically characterized, we expect the

polymeric solid-state structure observed for a number of derivatives to be general. The planes of the Cp ligands may be parallel or almost parallel **7** (referred to as "super-sandwich") or nonparallel **8**.

The colorless microcrystalline solid formulated as CpLi was first prepared in 1901,[235] but low solubility restricted structural characterization until recently when it was determined by high-resolution powder X-ray diffraction.[208] The structure is analogous to that of CpNa and involves eclipsed and almost parallel-planar Cp rings **7**, consistent with the monosilylated derivative $Cp^{T}Li$, which was unexpectedly isolated as a crystalline byproduct of the reaction between $[(\eta^5Cp^{T})Y(O^{t}Bu)]_2$ and $LiCH_2SiMe_3$.[209] It crystallizes as a "super-sandwich" of stacked half sandwiches, with the Cp ligands staggered and the positioning of the $SiMe_3$ groups describing a screw trace along the stack. In contrast, CpK[208] and CpCs[222] adopt a "zigzag" pattern **8**. The presence of a silyl substituent in $Cp^{T}K$ (cf. $Cp^{T}Li$, $\beta = 175°$) imposes a slightly larger β angle at potassium (151°).[218] Nevertheless, the availability of additional coordination sites made possible by the nonparallel arrangement of the Cp ligands predictably influences the accommodation of auxiliary ligands. The structure of Cp*K·(pyridine)$_2$ ($\beta = 138°$)[74] can be considered a modification of Cp*K* ($\beta = 138°$)[208] and $Cp^{T}K$ (β 151°),[218] in which the interchain Cp−K contacts are replaced by the two auxiliary ligand interactions, but with minimal or no impact on the structure of the polymer. The auxiliary coordination in CpNa·TMEDA ($\beta = 128°$ and 119°)[213] effects a dramatic distortion of the polymeric backbone, relative to the base free CpNa polymer ($\beta = 178°$).[208] Nevertheless, the super sandwich structure is retained in contrast to derivatives of Cp′Li.

π-Cyclopentadienyl Cp′E complexes of indium and thallium with relatively minimal Cp substitution typically form "zigzag" polymeric structures in the solid state, which are analogous to those observed for π-cyclopentadienyl alkalimetal complexes. A branched polymeric structure is adopted by Cp_2Pb in the solid state with a tricoordinate environment for each lead center composed of two -μ-Cp ligands and one terminal Cp ligand.[236] The heavily substituted $Cp^{5Bz}Tl$ is observed in two crystalline forms depending upon the rate of crystallization. Rapid precipitation gave a structure in which the monomeric units are aligned in a super-sandwich polymeric array,[230] while the unusual E−E bonded dimer **15** was isolated by slow crystallization (Table 1).[146,150]

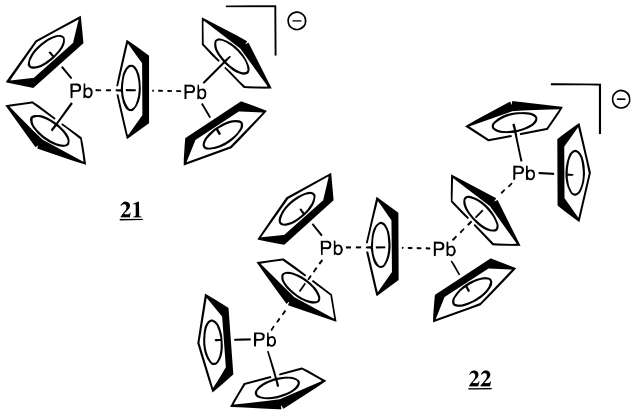
Molecular (Oligomeric) μ-Cyclopentadienylelement Complexes

Association of element centers by π-bound -μ-Cp ligands is a general feature of polymeric structures (see above), but is also evident in a number of molecular anionic systems, representing neutral π-cyclopentadienyl complexes bound together by an additional cyclopentadienyl anion, as listed in Table 4.

A dimeric structure is observed for the heavily substituted salt $Cp^{5Bz}Li$, where a benzene solvate molecule can be viewed as fragmenting the polymer which would be analogous to CpLi.[237] This interruption of coordinative polymerization is complete with more effective donor sites, such as nitrogen or oxygen, which enhance the solvation of Cp′Li derivatives, and numerous derivatives have been comprehensively characterized (Table 1). The dilithium cationic complex $[Cp^{M}(Li{\cdot}TMEDA)_2]^{+}$ [71] and the related mixed metal complexes $Cp[(SiMe_3)_2N]Sn(\mu\text{-}Cp)Li{\cdot}PMDETA$[241] and $CpTl(\mu\text{-}Cp)Li{\cdot}TMEDA$[100] involve μ-Cp or "inverted sandwich" interactions, which are substantially weaker (longer) than those in the "super-sandwich" structure of CpLi[208] and $Cp^{T}Li$.[209]

Nucleophilic addition of the cyclopentadienyl anion to CpTl gives either the unique anionic bis(π-cyclopentadienyl) thallate "sandwich" in [CpMg·PMDETA]-$[Cp_2Tl]$, or the "multidecker sandwich" $[Cp_3Tl_2]^{-}$ **9**.[239] Nonparallel conformations are observed, consistent with the presence of a lone pair at the thallium center(s), the environment of the element being isovalent with neutral bis(π-cyclopentadienyl) complexes for elements of group 14 and cationic bis(π-cyclopentadienyl) complexes for elements of group 15. However, the analogous nonparallel triple-decker complex observed for $[Cp_3Cs_2]^{-}$, which is obtained in a similar fashion,[221] is not easily rationalized in these terms.

Tin and lead exhibit the unique ability to accommodate three π-bound Cp ligands in molecular species. The fundamental complexes $[Cp_3E]^{-}$ **10** are obtained by nucleophilic addition of $[Cp]^{-}$ (CpNa or CpLi, or Cp_2Mg) to Cp_2Sn[242,244] or Cp_2Pb,[244] and isolation of the salts $[Mg(THF)_6][Cp_3E]_2$ (E = Sn, Pb) reveals an unassociated (cation contact free) anion with a "paddle-wheel" structure and a geometry for tin described as a shallow pyramid.[243] Although the same anion is present in the $[Na{\cdot}PMDETA]^{+}$ salt, one of the Cp ligands behaves as a bridging ligand (μ-Cp), which distorts the anion.The $[Li{\cdot}PMDETA]^{+}$ salt of the aminostannyl anion $[Cp_2SnN(SiMe_3)_2]^{-}$ also shows the presence of both terminal and μ-bridging Cp ligands.[241]



Reaction of $[Cp]^{-}$ with Cp_2Pb accounts for two chainlike multinuclear anions $[Cp_5Pb_2]^{-}$ **21** and $[Cp_9Pb_4]^{-}$ **22**, in the same $[Li(12\text{-crown-}4)_2]^{+}$ salt.[245] Although, at first glance, their structures are related to the solid-state structure of Cp_2Pb (see below), they exhibit a disruption of the polymer planarity featured in the neutral parent bis(π-cyclopentadienyl) complex. Nevertheless, similar variations in the

$Cp_{centroid}-Pb$ distances (terminal $Cp_{centroid}-Pb$, are significantly shorter than those involving the μ-Cp ligands) imply models involving the Cp_2Pb unit.

Bis(cyclopentadienyl)element Complexes

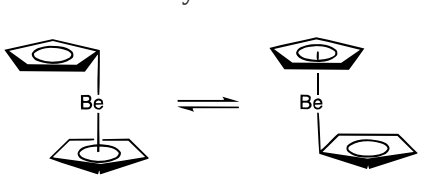
The presence of two Cp ligands, one on either side of the element, prompts the terminology "sandwich complexes", consistent with the transition metal analogues. Within each periodic group of elements, there are examples of sandwich complexes with the two ligand planes parallel **11** (usually staggered D_{5d}, but eclipsed D_{5h} conformations are often close in energy), as well as examples of nonparallel **12** (often referred to as "bent" sandwich structures) complexes. Although one or more additional (auxiliary, alternative to Cp) ligands is often observed with a nonparallel arrangement of Cp ligands, they are not necessarily responsible for the nonparallel structure. Table 5 presents a comprehensive listing of bis(cyclopentadienyl)element complexes and the pertinent characterization and structural data available for each.

The exothermicity for the association of alkalimetal ions with cyclopentadienide is calculated[38,335] to be substantially greater for lithium ($\Delta H = -703$ kJ mol^{-1},[335] -761 kJ mol^{-1})[38] than for sodium ($\Delta H = -531$ kJ mol^{-1},[335] -607 kJ mol^{-1}).[38] However, formation of the bis(cyclopentadienyl) anions from the corresponding cyclopentadienyl complexes is more exothermic for sodium ($\Delta H = -184$ kJ mol^{-1} [335]) than for lithium ($\Delta H = -163$ kJ mol^{-1} [335]) because of the electrostatic repulsive interactions between the $[Cp]^-$ anions, which are closer in the lithocene anion.

Consistent with this and the discussion of polymer−monomer relationships for neutral π-cyclopentadienyl alkali metal complexes, donor solvents such as THF dramatically influence coordination of the second (anionic) Cp ligand, so that the following equilibrium is envisaged:

$$CpEL_n + [Cp]^- \rightleftharpoons [Cp_2E]^- + nL$$

The isolation and structural confirmation of [Li-(12-crown-4)$_2$][^{iso}Cp$_2$Li][73] as well as tetraphenylphosphonium[245] and trisdimethylaminosulfonium[246] salts of the parent lithocene $[Cp_2Li]^-$ was made possible by the presence of complex cations, and the sodocene salts required the addition of excess NaCp.[245,246] Both anions exhibit a D_{5d} structure **11**. The equilibrium can also be modified by tethering the Cp ligands together to give the *ansa*-sodocene compound, which has a bent sandwich structure, opening a coordination site for an auxiliary THF molecule.[335]



23

The solid-state structure of beryllocene has been determined a number of times because of the unique asymmetric arrangement of the parallel planar Cp ligands, which is also observed in the gas phase.[250] In the solid state, the beryllium atom is disordered equally over two sites modeled as **23**. The beryllium atom is 150.5 pm from one Cp plane and 151.3 pm from the other, and the structural parameters, Raman data, and PE data[336] imply that it is bound to an sp^2 hybridized carbon center with minor perturbation of the π-bonding in the ligand. A similar structure has been observed for the isovalent Cp*$_2$Zn.[337] This "slip sandwich" structure accounts for the microwave spectroscopic data, the large dipole moment ($\mu_{25\,°C}$ in benzene, 2.46 D; in cyclohexane, 2.24 D), and the fluxionality of the complex in solution, which is clearly demonstrated by a sharp singlet observed in the ^{1}H NMR spectrum at -135 °C. The estimated rate of 10^{10} s^{-1} at 300 K corresponds to an activation energy of 5.2 kJ mol^{-1}, and the process is proposed to occur via two isomerization mechanisms with barriers of 5 ("gear wheel") and 8 kJ mol^{-1} ("molecular inversion"), respectively. The unusual structure of Cp_2Be has been modeled with one σ-bonded ligand invoking disruption of the parallel relationship of the ligands.[44,338] However, a variety of models have been developed,[250,339] and the structure can be rationalized in terms of the short Cp−Cp distance for the hypothetical D_{5d} structure (3.02 Å), which is substantially less than the van der Waals distance for two aromatic molecules (3.70 Å), and the interligand distance in bis(π-cyclopentadienyl) transition metal complexes (e.g., ferrocene 3.32 Å).[340] The term "steric oversaturation" has been used to account for such a phenomenon in which the molecule distorts to accommodate the ligands.

Essentially all magnesocene derivatives adopt D_{5d} structures **11** that are theoretically modeled as close analogues of ferrocene, and although the charge separation is larger the classification of ionic bonding is not justified.[341] In contrast, calcocene exhibits a unique nonparallel polymeric structure in the solid state (α = 57°) involving four inequivalent Cp interactions for each calcium site and μ-coordination for each ligand.[260] It can be considered in terms of optimal packing of two cyclopentadienide anions with Ca^{2+}, although the sandwich bis(π-cyclopentadienyl) complex molecular ion is observed in the mass spectrum.

A nonparallel monomeric structure **12** is generally observed in the solid state and in the gas phase for the heavier bis(π-cyclopentadienyl) alkaline earth complexes. The conformation of the Cp ligands seems dependent upon the degree of substitution around the Cp frame, so that smaller α angles and larger β angles are observed for complexes possessing more sterically imposing substituents on the Cp ring. Derivatives such as Cp$^{4I}{}_2$Ca are described in terms of the ligands "encapsulating" the element center,[267] which is responsible for the air stability of this complex in contrast to Cp*$_2$Ca and likely prevents formation of adducts. In addition, the solubility and volatility of these heavily substituted derivatives is enhanced, and DNMR studies indicate hindered rotation of the Cp rings. Introduction of auxiliary ligands has only a minor effect on the α angle and is essentially independent of the number of ligands (one or two). A decrease in the β angle defines a with-

drawal of the element center from the $Cp_{centroid}-Cp_{centroid}$ vector upon auxiliary coordination, but the geometries of the element centers are remarkably independent of element, number of ligands, or $Cp_{centroid}-E$ distance.

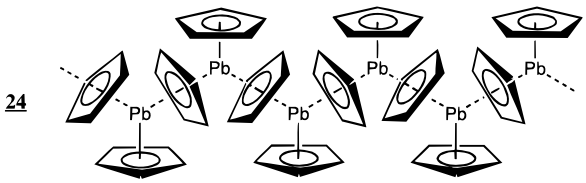
Molecular orbital calculations in general reveal small energy differences between parallel **11** and nonparallel **12** structures.[342] For example, the linearization of Cp_2Ba ($\beta = 147°$) is calculated at 1.5 kJ mol^{-1},[343] and the nonparallel structures for the decamethyl-bis(π-cyclopentadienyl) complexes of Ca, Sr, and Ba are 2−3.5 kJ mol^{-1} more stable than the corresponding parallel structures.

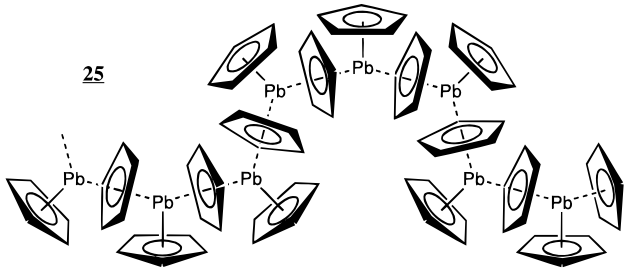
A number of novel calcocene derivatives have been reported, including an "open-calcocene",[282] complexes involving chelates,[281] or bifunctional ligands that link between two bis(π-cyclopentadienyl)element units,[274] an optically active complex,[276] and mixed metal complexes.[286,278]

Cationic bis(π-cyclopentadienyl) complexes of the general formula $[Cp'_2E]^+$ have been identified only for boron and aluminum. Cp^*_2BCl (^{11}B, −74.2 ppm) reacts with BCl_3 to give the tetrachloroborate salt of $[Cp^*_2B]^+$ as a microcrystalline precipitate (^{11}B, +44.1 ppm).[288] ^1H NMR spectroscopic studies show the cation to be structurally analogous to the isoelectronic slip-sandwich Cp_2Be complex. The D_{5d} symmetry decamethylaluminocenium cation has been confirmed in the salts $[Cp^*_2Al][Cp^*AlCl_3]$,[290] and $[Cp^*_2Al][Cp^{5Bz}_2Li]$,[237] but the parent cation $[Cp_2Al]^+$ has not yet been isolated, although it has been shown to be an effective olefin polymerization initiator.[289]

Silicocene derivatives are less accessible than germanocenes, stannocenes, and plumbocenes, perhaps because of the difficulties associated with the stabilization of a divalent silicon center, and Cp^*_2Si is the only isolated derivative.[54] It is most conveniently prepared by the reduction of dibromobis(pentamethylcyclopentadienyl)silane using potassium anthracenide, and melts without decomposition. Two geometrical isomers are observed in the solid state, one with the Cp* ligand planes parallel **11** and the other with $\alpha = 25°$ ($\beta = 155°$) **12**. The solid state (CP-MAS) ^{29}Si NMR spectrum contains two signals, at −403.2 ppm (nonparallel) and −423.4 ppm (parallel), and the solution shift (−398 ppm) indicates that the nonparallel isomer predominates.[292]

The parent plumbocene exists as a bent monomer **12** in the gas phase,[304] but is observed as a hexameric **20** or one of two polymeric arrays in the solid state depending on how the crystals are grown. The polymeric forms involve zigzag chains of lead atoms linked by π-coordinated -μ-Cp ligands and with each lead atom bearing a third terminal Cp ligand, as illustrated in **24**[236,325] and **25** (which incorporate toluene as a solvate).[199] The larger atomic radius of the heavier elements allows for greater structural flexibility, so that interplane angles (α) are sensitive to the steric encumberances of the Cp ligands. In some cases, the substitution pattern is so sterically demanding that a parallel planar structure is observed, as for Cp^{5I}_2Sn[311] and Cp^{5Ph}_2Sn.[312] However, the structural impact of the substituents is often difficult to predict. For example, Cp^{4I}_2Sn adopts a





nonparallel structure,[310] while the apparently less sterically loaded Cp^{3I}_2Pb is parallel,[7] despite having a larger $Cp_{centroid}-E$ distance. Cp^{4MBS}_2Sn[314] and Cp^{4MBS}_2Pb[329] ($Cp^{4MBS} = C_5Me_4[SiMe_2(^tBu)]$) also exhibit parallel structures with relatively limited substitution, which has led to the conclusion that the lone pair at the element center is stereochemically inactive.

While X-ray crystallographic studies of Cp_3Sb[344] and Cp_3Bi[345] clearly show a σ-interaction, π-coordination is evident in compounds with Cp ligands bearing bulky substituents or with fewer cyclopentadienyl ligands (Cp'_2ECl or $Cp'ECl_2$). The solid-state structure of Cp^{3B}_2BiCl shows an almost parallel ($\alpha = 18°$) sandwich arrangement, but with the bismuth center withdrawn from the $Cp_{centroid}-Cp_{centroid}$ axis ($\beta = 145°$).[333] The ionic materials $[Cp^*_2As][BF_4]$,[331] $[Cp^{3B}_2Sb][AlCl_4]$,[332] $[Cp^*_2Sb][AlI_4]$,[332] and $[Cp^{3B}_2Bi][AlCl_4]$[334] contain bis(π-cyclopentadienyl) complex cations which exhibit varying degrees of distortion from a parallel planar arrangement. Consistent with observations for the more extensive series of group 14 bis(π-cyclopentadienyl) complexes, Cp ligands with bulky substituents enforce a close to parallel planar structure as in the case of $[Cp^{3B}_2Sb]^+$ ($\alpha = 12°$) and $[Cp^{3B}_2Bi]^+$ ($\alpha = 10°$), while the structures of $[Cp^*_2As]^+$ ($\alpha = 36°$) and $[Cp^*_2Sb]^+$ ($\alpha = 36°$) are substantially nonparallel and the element is distorted from the centroid normal.

As for phosphorus,[346] biscyclopentadienyl derivatives of sulfur are definitively σ-complexes, with Cp^*_2S as the classic representative.[347] Nevertheless, the solid-state structure of the ionic [TAS-Cp-TAS][Cp] reveals a distinct interaction between the two sulfur centers and the centroid of the cyclopentadienide anion, which may be considered the first example of a π-interaction with sulfur.[248]

Summary and Conclusions

Extensive series of complexes involving one, two, or three π-bound cyclopentadienyl ligands are now known for most main group elements, enabling interesting comparisons and revealing some distinct steric trends. Although a local C_{5v} symmetry interaction is observed for most elements, the interactions

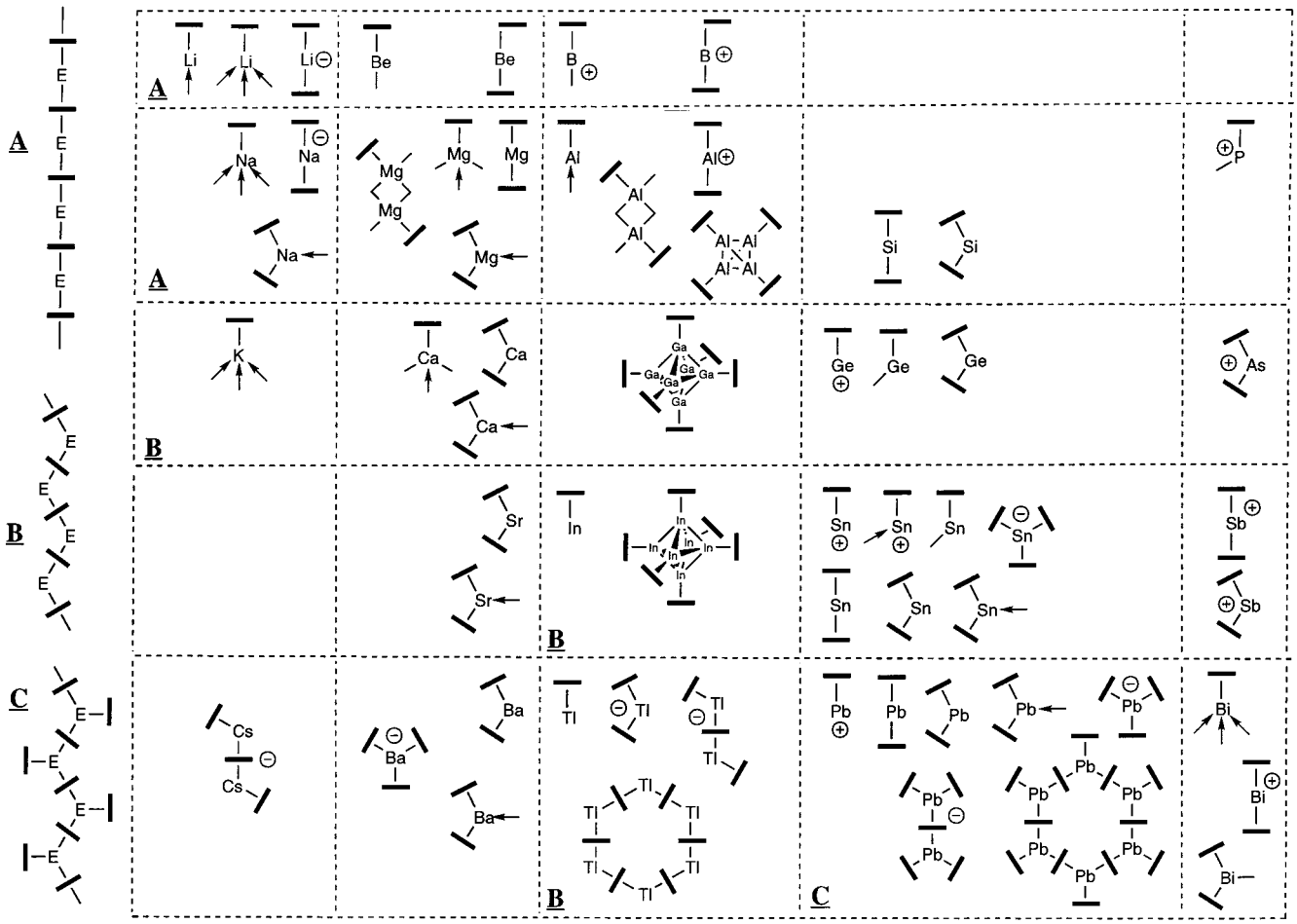


Figure 3. Structural classifications for main group π-cyclopentadienyl complexes according to the element position in the periodic table. The Cp ligands are generalized as a side-on view, three generalized polymeric types are labeled **A**, **B**, and **C**, and arrows refer to ligands of other types.

are considered flexible, allowing for fluxionality. Solid-state structures often involve intermolecular interactions, which are responsible for polymeric arrays usually involving μ-Cp ligands. The $Cp_{centroid}-Cp_{centroid}$ distances are relatively large in comparison to bis(π-cyclopentadienyl) transition metal complexes (e.g., ferrocene 3.32 Å) as would be expected on the basis of a comparison of the orbital overlap model (availability of d orbitals). In fact, most $Cp_{centroid}-Cp_{centroid}$ distances in bis(π-cyclopentadienyl) main group element complexes exceed the van der Waals contact for two aromatic systems (3.40 Å). An increase in $Cp_{centroid}-E$ distance down each group and a general decrease across each period are consistent with the trends in atomic size and effective nuclear charge. The nonsterically loaded parallel sandwich bis(π-cyclopentadienyl) complexes of lithium, magnesium, and aluminum predictably adopt the shortest $Cp_{centroid}-E$ interaction, and a slightly larger separation in Cp^*_2Si allows for both a parallel and nonparallel ($\alpha = 25°$) form in the same crystal structure, illustrating the minimal energy difference between the two conformations. The short $Cp_{centroid}-Cp_{centroid}$ distance prevents beryllocene from adopting a typical sandwich arrangement, and a distortion to slip-sandwich is observed with one of the ligands η^1-bound. However, for most elements, the $Cp_{centroid}-Cp_{centroid}$ distances are substantially greater than the standard interligand distance (4.10 Å), so that distortion from the parallel conformation is possible until this distance is achieved. The inability of electronic models to rationalize the nonparallel structures observed for the other 12 electron bis(π-cyclopentadienyl) complexes of the heavier group 2 elements (without steric loading), despite the absence of a nonbonding electron pair at the element center, highlights the importance of other factors such as the degree of ionic character in the Cp−E interaction, crystal packing forces, and interligand nonbonded interactions.

Therefore, noncovalent factors that are normally of minor structural consequence are expected to impose considerable conformational control. In this context, molecular mechanics force field calculations reveal that nonbonded attractive interactions between the Cp ligands are significant in bis(π-cyclopentadienyl) complexes of the alkaline earth metals and likely impose the nonparallel arrangements. Crystal packing forces influence the structures to some extent, but are considered less significant.

Realization of the close structural similarity for identically substituted sandwich bis(π-cyclopentadienyl) complexes of elements from groups 2 and 14 (the structure of Cp^{4I}_2Ca can be superimposed on Cp^{4I}_2Sn, and Cp^*_2Ca on Cp^*_2Sn) has also prompted the conclusion that the steric factors play a more dominant role in the control of molecular geometry than do electronic factors.[8] These arguments can be

extended to rationalize other bis(π-cyclopentadienyl) main group element complex structures. At first glance, the dimers $\{Cp^{5Bz}E\}_2$ of indium and thallium are defined by element−element interactions; however, the similarity of the bond lengths and angles in these isostructural complexes implicates the importance of interligand interactions, and a close similarity of structural features is observed in the $\{Cp^*E\}_6$ octahedral clusters of gallium and indium. The importance of interligand interactions is perhaps more apparent in these complexes than in their transition metal analogues because of the relatively weak Cp−element coordination. The result is a diverse array of structural arrangements, which are illustrated in Figure 3, and is perhaps the most distinguishing feature of this distinct new area of coordination chemistry.

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