of these compounds. The other principal fragments obtained are the following. VII: 324 ($CF_2CF_2NNCF_2CF_2S_3^+$, 6.1), 260 ($(CF_2CF_2)_2N_2S^+$, 9.2), 229 ($CF_3NNCF_2CF_2S^+$, 30.3), 119 ($CF_3CF_2^+$, 15.1), 69 (CF_3^+, 100), 64 (S_2^+, 2.4). VIII: 259 ($CF_2ClNNCF_2S_3^+$, 3.1), 227 ($CF_2ClNNCF_2S_2^+$, 2.3), 195 ($CF_2ClNNCF_2S^+$, 1.6), 163 ($CF_2ClNNCF_2^+$, 4.6), 128 ($CF_2NNCF_2^+$, 7.4), 85 (CF_2Cl^+, 11), 64 (S_2^+, 0.9), 61 ($NCCl^+$, 100). The ^{19}F NMR spectrum of VII shows two singlets at ϕ −87.3 (CF_3) and −113.0 (CF_2) in the ratio of 3:2. A singlet at ϕ −62.3 is obtained in ^{19}F NMR spectrum of VIII.

Anal. Calcd for $(CF_3CF_2N)_2S_3$: S, 26.52. Found: S, 25.67. Calcd for $(CF_2ClN)_2S_3$: S, 32.65. Found: S, 31.8.

Preparation of IX and X. $R_fN{=}NR_f$ (R_f = CF_3CF_2 or CF_2Cl) (1 mmol) and S_2Cl_2 (4 mmol) were photolyzed in a quartz vessel for 12 h. Both the compounds were obtained in 9–11% yield. The infrared spectra are as follows. IX: 1290 s, 1235 s, 1170 br, 1130 m, 1100 w, 1030 m, 715 w cm^{-1}. X: 1280 s, 1220 m, 1180 s, 1140 m, 1050 br, 580 m cm^{-1}. Vapor pressures of IX and X at room temperatures are 4 and 7 torr, respectively. The molecular weight of IX is found to be 390 (thoretical 394). The molecular ion peak was observed in IX at *m*/*e* 394. The other principal peaks obtained follow. IX: 356 ($(CF_2CF_2N)_2S_4^+$, 3.1), 324 ($(CF_2CF_2)_2N_2S_3^+$, 3.1), 292 ($(CF_2CF_2)_2N_2S_2^+$, 7.8), 260 ($(CF_2CF_2)_2N_2S^+$, 6.25), 229 ($CF_3CF_2NNCF_2S^+$, 68.7), 160 ($CF_2CF_2N_2S^+$, 21.8), 146 ($CF_2CF_2NS^+$, 100), 119 ($CF_3CF_2^+$, 18.7), 69 (CF_3^+, 93.8), 64 (S_2^+, 3.5). X: 291 ($CF_2ClNNCF_2S_4^+$, 4.1), 259 ($CF_2ClNNCF_2S_3^+$, 5.2), 227 ($CF_2ClNNCF_2^+$, 2.6), 195 ($CF_2ClNNCF_2S^+$, 1.1), 163 ($CF_2ClNNCF_2^+$, 5.8), 128 ($CF_2NNCF_2^+$, 8.6), 85 (CF_2Cl^+, 12.6), 64 (S_2^+, 0.6), 61 ($NCCl^+$, 100). The ^{19}F NMR spectrum of IX showed two singlets at ϕ −88.4 (CF_3) and −116.3 (CF_2) in the ratio of 3:2. A singlet at ϕ −64.6 was obtained in ^{19}F NMR spectrum of $(CF_2ClN)_2S_4$. Anal. Calcd. for $(CF_3CF_2N)_2S_4$: S, 32.48. Found: s, 31.41. Calcd for $(CF_2ClN)_2S_4$: S, 39.14. Found: 40.91.

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η^5 Bonding between Main-Group Elements and Cyclopentadiene Rings: An Xα–Scattered-Wave Study

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SCF-Xα–scattered wave (Xα–SW) calculations have been performed on (η^5-C_5H_5)Li, (η^5-C_5H_5)In, (η^5-C_5H_5)BeH, and (η^5-C_5H_5)BeCl. For each molecule, the HOMO is computed to be a doubly degenerate orbital that is located primarily on the C_5H_5 ring. Lone-pair and σ_{BeX} MO's participate to only a minor extent in interstitial bonding. It is suggested that the electronic structures of these simple molecules are more consistent with a six- than an eight-electron counting procedure. Several ionization energies (IE's) have been computed for all four molecules by using the transition-state method. The computed IE's for (η^5-C_5H_5)In agree with experimental ultraviolet photoelectron spectroscopic (UV PES) data but are in disagreement with previous MO calculations on (η^5-C_5H_5)In and (η^5-C_5H_5)Tl. Likewise, our Xα–SW study of (η^5-C_5H_5)BeCl suggests that the UV PES assignments for this molecule should be revised.

Introduction

Following the discoveries of ferrocene, bis(benzene)chromium, and uranocene, there has been an intense interest in annulene π complexes of the d- and f-block elements. As a consequence, significant progress has been made toward understanding the electronic structures and patterns of stability of these fascinating compounds.[2] Much less, however, is known about the perhapto interaction of main-group elements with carbocyclic ligands. Minkin and Minyaev[3] have suggested that annulene-cap perhapto bonding will be favored when the total number of ring π plus main-group moiety electrons is 8. On the other hand, Schleyer et al.[4] have emphasized the "three-dimensional aromaticity" concept and suggested that the optimum number of interstitial electrons[5] is six. Other important attempts to understand the bonding in such main-group nido compounds include ab initio MO calculations on C_5H_5Li[6] and C_5H_5BeH.[7] At the semiempirical level of theory, Dewar and Rzepa[8] have explored the interaction of BeX moieties with cyclopentadienyl, indenyl, and fluorenyl groups, and Bews and Glidewell[9] have investigated beryllium derivatives of various $(CH)_n$ carbocycles. Beryllium derivatives of the type C_5H_5BeR have also been investigated by the PRDDO method.[10] Some polyhedral carbocations bear a close resemblance to multihapto-bonded main-group systems (vide infra); hence, mention should be made of the ab initio calculations[4,11] on $(C_5H_5)CH^{2+}$. Other carbocations such as $C_6H_5^+$ and the heavier congener $C_5H_5Si^+$ have been investigated by ab initio methods.[4c,12] The EHMO method has been employed to study the analogous tin cation $C_5H_5Sn^+$ and the motion of a CH_2^{2+} fragment across a $C_5H_5^-$ ring.[13,14]

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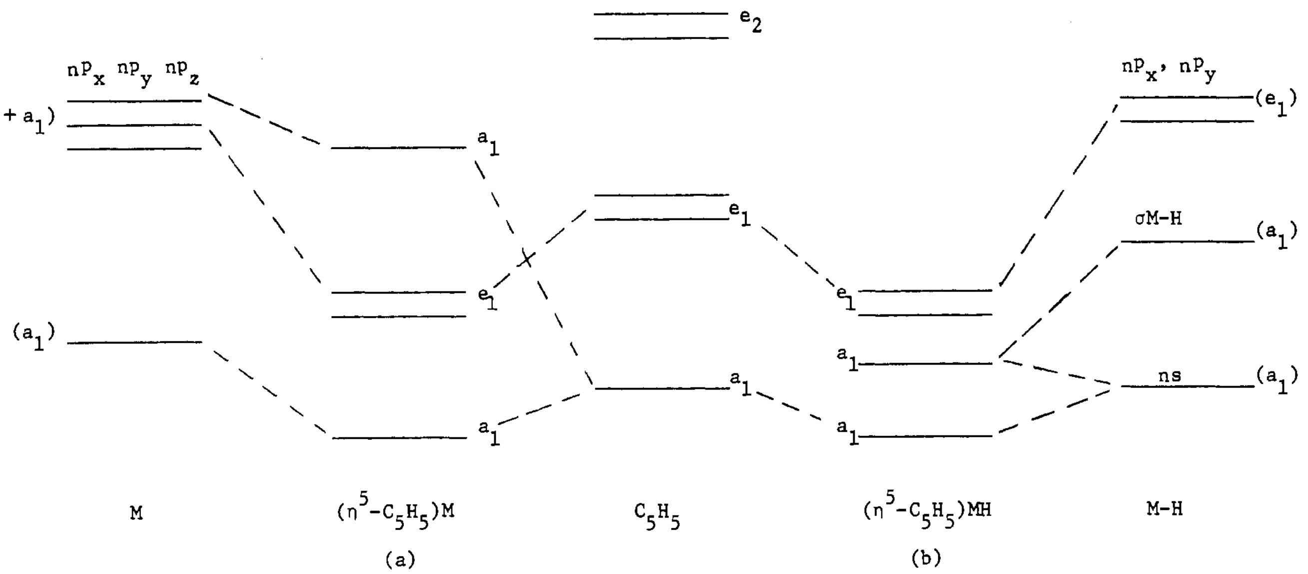

Figure 1. Qualitative scheme for the η^5 interaction of C_5H_5 π orbitals with a main-group element, M (left), or an M–H σ bond (right).

Table I. Xα–SW Sphere Radii,[a] α_{int}, and α_{outer} Values

	$(\eta^5\text{-}C_5H_5)Li$	$(\eta^5\text{-}C_5H_5)In$	$(\eta^5\text{-}C_5H_5)BeH$	$(\eta^5\text{-}C_5H_5)BeCl$
r_M[b]	2.201	3.180	1.778	1.931
r_C	1.712	1.773	1.850	1.688
r_H	1.329	1.375	1.436	1.311
other r			1.875[c]	2.607[d]
r_{outer}	5.687	6.052	5.954	6.344
α_{int}	0.76359	0.756	0.76377	0.74921
α_{outer}	0.77795	0.749	0.77225	0.74575

[a] In atomic units. [b] M = metal. [c] Radius of H sphere of H σ bonded to Be. [d] r_{Cl}.

Normally, a symbiotic relationship exists between molecular orbital calculations and photoelectron spectroscopy. Ultraviolet photoelectron spectra (UV PES) have been reported[15] for $(\eta^5\text{-}C_5H_5)In$ and $(\eta^5\text{-}C_5H_5)Tl$. However, the spectroscopically assigned levels are not in agreement with those computed by NOCOR[16] or CNDO[17] methods. UV PES data are also available for several $(\eta^5\text{-}C_5H_5)BeX$ derivatives.[18]

The present paper is concerned with an attempt to develop further a model for η^5 bonding between the cyclopentadiene ring and main-group moieties by using the Xα–SW approach. The molecules studied viz. C_5H_5Li, C_5H_5BeH, C_5H_5BeCl, and C_5H_5In feature η^5 bonding of caps from groups 1A, 2A, and 3A. The focal point of the work, which represents the first Xα–SW study of these molecules, is to delineate whether a six- or eight-electron interstitial electron[5] counting procedure is more appropriate. A secondary objective was to determine whether the Xα–SW method could resolve disagreements regarding the interpretation of UV PES data of these compounds. We have previously used the Xα–SW method to investigate the electronic structures of bent-sandwich molecules of the group 4A elements.[19]

Theoretical Methods

The Xα–SW calculations were made by employing the spin-restricted procedure of Johnson and Slater.[20] The requisite bond distances and angles were taken from electron diffraction data for $(\eta^5\text{-}C_5H_5)In$[21] and $(\eta^5\text{-}C_5H_5)BeCl$.[22] Microwave data were used for $(\eta^5\text{-}C_5H_5)BeH$,[23] and the geometry from an ab initio calculation was used for $(\eta^5\text{-}C_5H_5)Li$.[6a] Because of the large metal to carbon distances, overlapping the metal and carbon spheres to any substantial degree leads to carbon spheres that are almost touching or even beyond the hydrogen nuclei. Thus, the normal method of choosing absolute atomic sphere radii by optimizing the virial ratio[24] leads to an unrealisitic approximation. It was decided to choose (as is usual), from the initial Xα charge distribution derived from the superposition of free atom charge densities, a ratio of radii from the values of the radius of each atom that just enclosed the number of electrons assigned from atomic structures.[24] The absolute radii were chosen at a point where the carbon and metal spheres were tangential, while the carbon and hydrogen spheres were overlapping. A similar criterion was successfully emplloyed for an Xα calculation on $(\eta^5\text{-}C_5H_5)_2Sn$.[19] The outer-sphere radius was chosen to be tangential to the outermost atomic spheres in all cases. Schwartz's exchange parameters,[25] α_{HF}, were used for all atoms except hydrogen, where Slater's value[26] was employed. The α value for indium, 0.701, was estimated by extrapolation of Schwartz's values.[25] α_{outer} was obtained by averaging the atomic values (of the spheres touching the outer sphere) according to the number of valence electrons. α_{int} was obtained by averaging the α values for all atomic spheres according to the number of valence electrons. These data are summarized in Table I. Spherical harmonics through $l = 3$ were employed for In and the outer sphere on $(\eta^5\text{-}C_5H_5)In$, through $l = 2$ for Cl and all other outer spheres, through $l = 1$ for C, and through $l = 0$ for H. All SCF calculations converged to better than 0.01 eV while keeping all cores (except in In 4d) fixed. Ionization energies were computed by the transition-state method.[27]

Qualitative Considerations

The discussion can start advantageously by qualitative consideration of the interactions between a main-group element, M, and the familiar π-bond orbitals of a C_5H_5 ring.[28]

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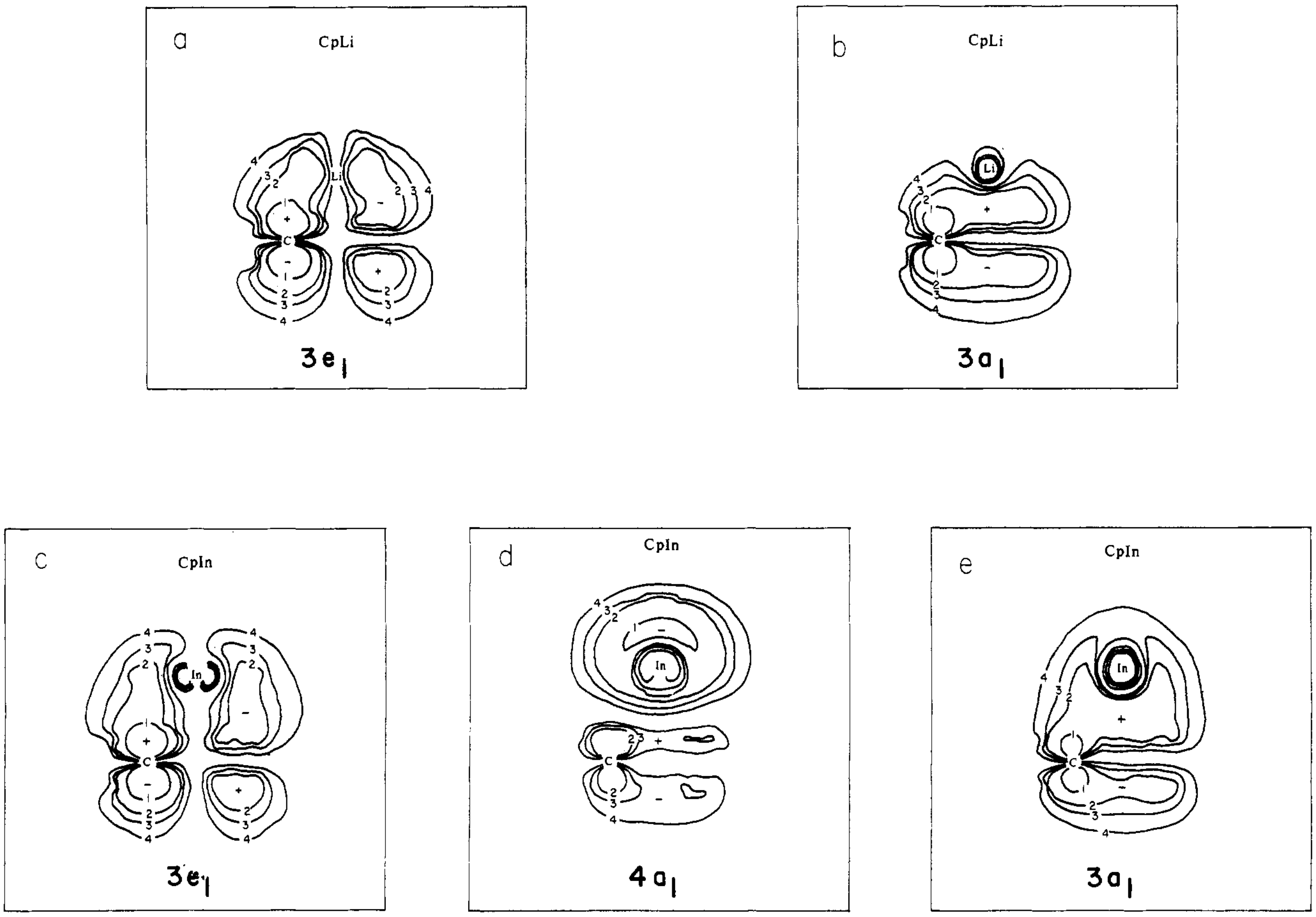

Figure 2. Xα–SW contour plots for (a) $3e_1$ MO of CpLi, (b) $3a_1$ MO of CpLi, (c) $3e_1$ MO of CpIn, (d) $4a_1$ MO of CpIn, and (e) $3a_1$ MO of CpIn.

As shown in figure 1a, bonding interactions take place between the valence s AO of M and the ring a_1 MO and between the degenerate n_{p_x} and n_{p_y} AO's of M and the e_1 MO. The higher lying a_1 MO is a consequence of mixing between the antibonding component of the lower lying a_1 MO and a bonding interaction between the valence p_z AO and the a_1 ring MO. The relative energies of the e_1 and the higher lying a_1 MO's will depend inter alia on the energy differences between the M and C_5H_5 π orbitals and also on the degree of overlap. A comparable orbital synthesis can be effected for the interaction between a C_5H_5 ring and an M–H moiety (Figure 1b). Here, of course, one expects the higher lying a_1 MO to be more stable than the e_1. Clearly, eight electrons can be accommodated in either the (η^5-C_5H_5)M or (η^5-C_5H_5)MH bonding schemes. However, the question of whether the six- or eight-electron interstitial electron count is more valid will depend on (a) whether the higher lying a_1 MO is occupied and (b) if the higher lying a_1 MO is occupied, whether it involves significant ring–M interaction.

Cyclopentadienyllithium. To the best of our knowledge, no structural data are available for cyclopentadienyllithium. It was therefore necessary to use the optimized geometry computed by an ab initio method[6a] for the present Xα–SW calculation. Support for the η^5 geometry for C_5H_5Li is provided by NMR data and by the fact that X-ray crystallographic studies show that the closely related molecules indenyllithium[30] and cyclopentadienylsodium[31] adopt this geometry.

The HOMO of η^5-C_5H_5Li is doubly degenerate ($3e_1$) and is separated by over 3.5 eV from the next bonding MO ($3a_1$) (Table II). In general the Xα–SW result is in conformity with Figure 1a with the assumption of an electron occupancy of six. Both occupied valence MO's are localized predominantly on the C_5H_5 ring. However, the contribution of the Li($2p_x$) and Li($2p_y$) AO's to the $3e_1$ MO is evident from the charge densities (Table II) and the orbital contour plot (Figure 2a). Likewise the $3a_1$ MO feature a small but significant contribution from the Li(2s) and Li($2p_z$) AO's (Figure 2b). Interestingly, the Li(2s) contribution exceeds the Li($2p_z$) contribution slightly.

The question of the ionic or covalent character of the group 1A cyclopentadienides is a recurrent one. Our Xα–SW results are consistent with a modicum of covalency in the C_5H_5Li molecule.[32]

Even though no experimental UV PES data are available for C_5H_5Li, we have computed the ionization energies for this molecule by the transition-state method[27] (Table III).

Cyclopentadienylindium. Both C_5H_5In and C_5H_5Tl exhibit polymeric structures in the solid state.[33] In the vapor phase, however, these compounds are monomeric and adopt C_{5v} geometries.[21,34] The metric parameters from the electron dif-

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Table II. Xα–SW "Ground-State" Eigenvalues and Charge Densities[a]

$(\eta^5\text{-}C_5H_5)Li$

MO	ϵ[b]	metal		C		H (s)	outer[c]	int[d]
		s	p	s	p		total	total
$3e_1$	−4.35		0.07	0.00	0.55	0.00	0.01	0.37
$3a_1$	−8.07	0.04	0.03	0.00	0.55	0.00	0.00	0.38
$2e_2$	−9.25			0.00	0.75	0.20	0.00	0.05
$2e_1$	−9.77		0.00	0.00	0.65	0.35	0.01	0.00
$2a_1$	−13.17	0.00	0.00	0.00	0.55	0.40	0.01	0.04
$1e_2$	−13.58			0.30	0.35	0.30	0.01	0.04
$1e_1$	−17.47		0.01	0.65	0.15	0.15	0.00	0.04
$1a_1$	−21.68	0.01	0.02	0.80	0.15	0.05	0.00	0.00

$(\eta^5\text{-}C_5H_5)In$

MO	ϵ[b]	In				C		H (s)	outer[c]	int[d]
		s	p	d	f	s	p		total	total
$3e_1$	−4.41		0.11	0.02	0.01	0.00	0.50	0.00	0.01	0.35
$4a_1$	−5.26	0.48	0.08	0.01	0.00	0.00	0.15	0.00	0.05	0.23
$3a_1$	−8.91	0.25	0.03	0.00	0.00	0.00	0.45	0.00	0.01	0.26
$2e_2$	−9.56			0.00	0.00	0.00	0.75	0.20	0.01	0.04
$2e_1$	−10.08		0.00	0.00	0.00	0.00	0.65	0.35	0.01	0.00
$2a_1$	−13.47	0.00	0.00	0.00	0.00	0.05	0.55	0.40	0.01	0.00
$1e_2$	−13.85			0.00	0.00	0.30	0.40	0.30	0.00	0.00
$1e_1$	−17.72		0.00	0.10	0.00	0.60	0.15	0.15	0.00	0.00
e	−18.61	0.00	0.00	0.98	0.00	0.00	0.00	0.00	0.00	0.02
e	−18.66			0.99	0.00	0.00	0.00	0.00	0.00	0.01
e	−18.77		0.00	0.89	0.00	0.05	0.00	0.00	0.00	0.06
$1a_1$	−22.27	0.01	0.01	0.02	0.00	0.80	0.15	0.00	0.00	0.01

[a] Charge densities are the percentage of electron densities within the atomic spheres. [b] Eigenvalues in eV. [c] Charge density outside outer sphere. [d] Intersphere charge density inside outer sphere and not accounted for by atomic spheres. [e] In(4d) AO.

fraction structure[21] were used in the present Xα–SW calculation on C_5H_5In. NOCOR[16] and CNDO[17] MO calculations on C_5H_5Tl and C_5H_5In, respectively, indicate that the HOMO is of a_1 symmetry and the sequence of MO's is $a_1 > e_1 > a_1$. However, the sequence of ionic states deduced from UV PES data[15] is $^2E_1 < {}^2A_1 < {}^2A_1$; hence, assuming the validity of Koopman's theorem,[35] the orbital sequence is $e_1 > a_1 > a_1$. Our Xα–SW results indicate that the HOMO of C_5H_5In is doubly degenerate ($3e_1$) (Table II) and that the next two MO's are of a_1 symmetry ($4a_1$ and $3a_1$). To circumvent the use of Koopmans' theorem, we have performed transition-state calculations for the various ionizations of C_5H_5In. The computed IE's (Table III) are in very satisfactory agreement with the experimental values. The major disagreement between our Xα–SW calculation on C_5H_5In and previous calculations on C_5H_5In and C_5H_5Tl is that the order of the $3e_1$ and $4a_1$ (our numbering system) is reversed. Note also that the ordering of the e_1 and a_1 MO's in C_5H_5In is the reverse of that in C_5H_5Li and of that shown in Figure 1a. If this were not so, C_5H_5Li would presumably be a paramagnetic molecule.

The HOMO of C_5H_5In resembles that of C_5H_5Li in the sense that it originates mainly from the interaction of the e_1 C_5H_5 π MO with valence p_x and p_y AO's. The extent of the interaction is, however, more pronounced in C_5H_5In than in C_5H_5Li. This is clear from a comparison of charge densities and also from a comparison of the orbital contours for the HOMO's of these molecues (Figures 1a and 2c).

That the $4a_1$ MO corresponds to the In lone pair is apparent from Figure 2d. The charge densities indicate that the major contribution to the $4a_1$ MO comes from the In(5s) AO. The contributions from the In(5p), In(5d), and the a_1 C_5H_5 π MO are much less important. The fact that the $4a_1$ is not an interstitial MO will be of significance with respect to a subsequent section on electron-counting rules. Presumably it is the $4a_1$ MO that is responsible for the reported Lewis base behavior of C_5H_5In toward boron trihalides.[36] Vibrational spectroscopic data for these $C_5H_5In\cdot BX_3$ complexes have been interpreted as implying η^1 coordination of the C_5H_5 ring. On the other hand, boron cations of the type $[C_5H_5BX]^+$ (which can be regarded as the product of addition of X^+ to the congeneric but as yet unknown carborane $\eta^5\text{-}C_5H_5B$) adopt η^5 geometries.[37]

As in other Xα–SW calculations,[38] the lone-pair character is not confined to one particular orbital but tends to be distributed among other MO's of the same symmetry. Thus, the $3a_1$ MO, even though it is localized predominantly on the C_5H_5 ring, still possesses a distinct lone-pair appearance (Figure 2e).

Cyclopentadienylberyllium Hydride. Experimentally, $(C_5H_5)BeH$ has been shown to possess an η^5 structure by microwave spectroscopy.[23] These structural data were employed in the present work. The sequence of valence MO's (Table IV) is in conformity with qualitative expectations (Figure 1b) and other MO calculations. The $3e_1$ HOMO of $(C_5H_5)BeH$ resembles that of C_5H_5Li (cf. Figures 2a and 3a) and is of approximately the same orbital composition, viz. mostly ring π with a small amount of Be(2p) character. That the next MO ($4a_1$) is the Be–H σ bond is obvious from the orbital contour plot in Figure 3b. The charge densities demonstrate only a very small contribution from the a_1 ring π orbital; hence, like the ($4a_1$) lone-pair orbital of C_5H_5In, the ($4a_1$) σ_{BeH} orbital of C_5H_5BeH does not participate in interstitial bonding. The $3a_1$ MO derives principally from the interaction of the Be(2s) AO with the totally symmetric ring π MO. There is, however, a small but significant contribution from the Be–H σ bond—a point that is obvious from the orbital contour diagram (Figure 3c).

Unfortunately, it was not possible to record the UV PES data of C_5H_5BeH because of disproportionation to $(C_5H_5)_2Be$ in the vapor phase.[18] Because of this we have performed an Xα–SW calculation on the more stable chloride, C_5H_5BeCl, for which UV PES data are available.[18]

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Table III. Computed and Experimental Ionization Energies (eV)

MO	computed IE	exptl IE
	$(\eta^5\text{-}C_5H_5)Li$[a]	
$3e_1$	7.25	
$3a_1$	11.02	
$2e_2$	12.60	
$2e_1$	13.09	
$2a_1$	16.43	
$1e_2$	16.85	
$1e_1$	20.83	
$1a_1$	25.16	
	$(\eta^5\text{-}C_5H_5)In$[b]	
$3e_1$	7.22	8.28
$4a_1$	8.30	9.23
$3a_1$	11.79	12.89
$2e_2$	12.89	
$2e_1$	13.37	
$2a_1$	16.69	16.26
$1e_2$	17.13	16.95
$1e_1$	21.06	21.09
d	24.32	23.69 24.54
d	25.15	
d	25.25	
$1a_1$	25.76	
	$(\eta^5\text{-}C_5H_5)BeH$[a]	
$3e_1$	8.70	
$4a_1$	12.02	
$3a_1$	12.91	
$2e_2$	15.26	
$2e_1$	15.75	
$2a_1$	19.17	
$1e_2$	19.52	
$1e_1$	23.74	
$1a_1$	28.94	
	$(\eta^5\text{-}C_5H_5)BeCl$[c]	
$4e_1$	8.25	9.60
$3e_1$	10.97	11.15
$5a_1$	11.93	12.45
$4a_1$	13.09	13–15
$2e_2$	14.04	
$2e_1$	14.63	

[a] No experimental IE data available. [b] Experimental IE data from ref 15b. [c] Experimental IE data from ref 18; see text for discussion of assignments. [d] In(4d) AO.

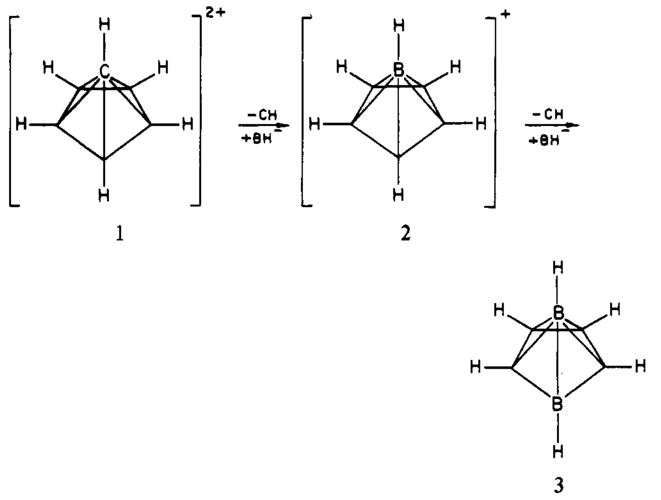
Cyclopentadienylberyllium Chloride. Like the corresponding hydride, C_5H_5BeCl has been shown to adopt an η^5 geometry in the vapor phase.[22] These electron diffraction data were used in the Xα–SW calculation.

In general, the MO's of C_5H_5BeCl are expected to resemble those of C_5H_5BeH with the exception that it is now necessary to consider the chlorine lone-pair orbitals that transform as e_1 in the requisite C_{5v} symmetry.

The Xα–SW calculation reveals that, as with the other nido molecules studied, the HOMO is doubly degenerate ($4e_1$) and principally a Cp ring π orbital with minor contribution from the main-group element moiety. Interestingly, the contribution of the Cl(3p) AO's to this MO exceeds that of the Be(2p) AO's (Table IV and Figure 3d). That the second MO corresponds to the chlorine lone pairs is obvious from the contour plot in Figure 3e and also from the charge densities. There is only a minor contribution from the Be(2p) AO and the e_1 ring π MO. The $5a_1$ MO, shown in Figure 3f, corresponds clearly to the Be–Cl σ bond, the Cl(3p) AO contribution exceeding that of the Be(2p) AO's. The contribution of the a_1 ring π MO is larger than that for corresponding $\sigma_{BeH}(3a_1)$ MO in C_5H_5BeH. Nevertheless, it is more convenient to regard the $5a_1$ MO of C_5H_5BeCl as being noninterstitial.

Transition-state calculations have been carried out for the first six MO's of C_5H_5BeCl, and the IE's thus computed have been assembled in Table III and compared with the experimental data from UV PES. Our Xα–SW MO sequence and the computed IE's are not in agreement with CNDO calculations and UV PES assignments of Böhm, Gleiter, et al.[18] The principal difference in the results is that the ring π ($4e_1$) and chlorine lone-pair ($3e_1$) MO's are reversed. MNDO calculations on C_5H_5BeCl produce the same orbital sequence as the Xα–SW calculations (Tables III and IV).

Scheme I



A Six- or Eight-Electron Count?

As pointed out in the Introduction, Minkin and Minyaev[3] have suggested that nido structures will be formed when the total of ring plus main-group fragment electrons is eight. Schleyer et al.,[4a] on the other hand, have suggested that the optimum number of electrons is six. The difference between these approaches is that the Minkin and Minyaev model counts all electrons while the approach of Schleyer et al. counts only the electrons in orbitals that are involved in interstitial bonding. For the specific molecules considered here, all eight electrons would be counted for C_5H_5In and C_5H_5BeX by using the Minkin and Minyaev approach, while in the Schleyer et al. model the lone pair of C_5H_5In and the Be–X σ-bonding electrons of C_5H_5BeX would be excluded on the basis of their being noninterstitial.

The present calculations support the views of Schleyer et al.[4a] Thus, although the indium lone pair of C_5H_5In is not confined to the $4a_1$ MO, it is predominantly this MO that is of lone-pair character. Of particular significance is the fact that only minor participation of the ring π MO is observed in the $4a_1$ lone-pair MO. Note that the $4a_1$ MO of C_5H_5In is not the HOMO. The salient point then in deciding between the two sets of rules is not the relative MO energies but of excluding MO's from the count which are not involved in interstitital bonding. The case of C_5H_5BeH is similar to that of C_5H_5In. The second occupied MO ($4a_1$) is highly Be–H σ bonding in character, and the participation of the C_5H_5 π MO is even less than that of the lone-pair MO of C_5H_5In. Clearly the $4a_1$ MO of C_5H_5BeH should be excluded from the electron count. Similar arguments can be made regarding the third occupied MO of C_5H_5BeCl, which is identifiable as the Be–Cl σ bond. Granted, there is more delocalization here; however, it remains predominantly a noninterstitial orbital.

A further reason for preferring a six-electron rule is that it affords conformity with Wade's rules.[39] According to Wade's rules, nido structures are predicted with $n + 2$ skeletal electron pairs, where n is the number of atoms in the cluster. Each CH group contributes three skeletal electrons; hence, in C_5H_5In and C_5H_5BeX, only one valence electron from In

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[39] (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

Table IV. Xα-SW "Ground-State" Eigenvalues and Charge Densities[a]

$(\eta^5\text{-}C_5H_5)BeH$

MO	ϵ[b]	Be		H_{Be} (s)	C		H_C (s)	outer[c] total	int[d] total
		s	p		s	p			
$3e_1$	−5.58		0.06		0.00	0.60	0.00	0.01	0.33
$4a_1$	−8.08	0.06	0.14	0.61	0.00	0.10	0.00	0.03	0.06
$3a_1$	−9.77	0.09	0.00	0.05	0.00	0.60	0.00	0.01	0.25
$2e_2$	−11.51				0.00	0.75	0.25	0.00	0.00
$2e_1$	−12.04		0.00		0.00	0.65	0.35	0.01	0.00
$2a_1$	−15.55	0.00	0.00	0.00	0.05	0.55	0.40	0.00	0.00
$1e_2$	−15.78				0.30	0.45	0.25	0.00	0.00
$1e_1$	−19.88		0.00		0.70	0.20	0.15	0.00	0.00
$1a_1$	−24.86	0.01	0.01	0.00	0.75	0.20	0.00	0.00	0.03

$(\eta^5\text{-}C_5H_5)BeCl$

MO	ϵ[b]	Be		Cl			C		H (s)	outer[c] total	int[d] total
		s	p	s	p	d	s	p			
$4e_1$	−5.51		0.06		0.12	0.00	0.00	0.50	0.00	0.01	0.31
$3e_1$	−7.45		0.04		0.68	0.00	0.00	0.05	0.00	0.01	0.22
$5a_1$	−8.92	0.01	0.14	0.01	0.53	0.02	0.00	0.20	0.00	0.02	0.07
$4a_1$	−9.90	0.15	0.00	0.01	0.21	0.01	0.00	0.35	0.00	0.01	0.26
$2e_2$	−10.84					0.00	0.00	0.75	0.20	0.00	0.05
$2e_1$	−11.46		0.01		0.00	0.00	0.00	0.65	0.35	0.01	0.00
$3a_1$	−14.77	0.00	0.01	0.00	0.00	0.00	0.05	0.55	0.40	0.01	0.00
$1e_2$	−15.15					0.00	0.30	0.35	0.30	0.00	0.05
$1e_1$	−19.10		0.01		0.00	0.00	0.65	0.15	0.15	0.00	0.04
$2a_1$	−19.21	0.03	0.03	0.91	0.01	0.00	0.00	0.00	0.00	0.00	0.02
$1a_1$	−23.56	0.02	0.02	0.00	0.00	0.00	0.75	0.15	0.00	0.00	0.06

[a] Charge densities are the percentage of electron densities within the atomic spheres. [b] Eigenvalues in eV. [c] Charge density outside the outer sphere. [d] Intersphere charge density inside outer sphere and not accounted for by atomic spheres.

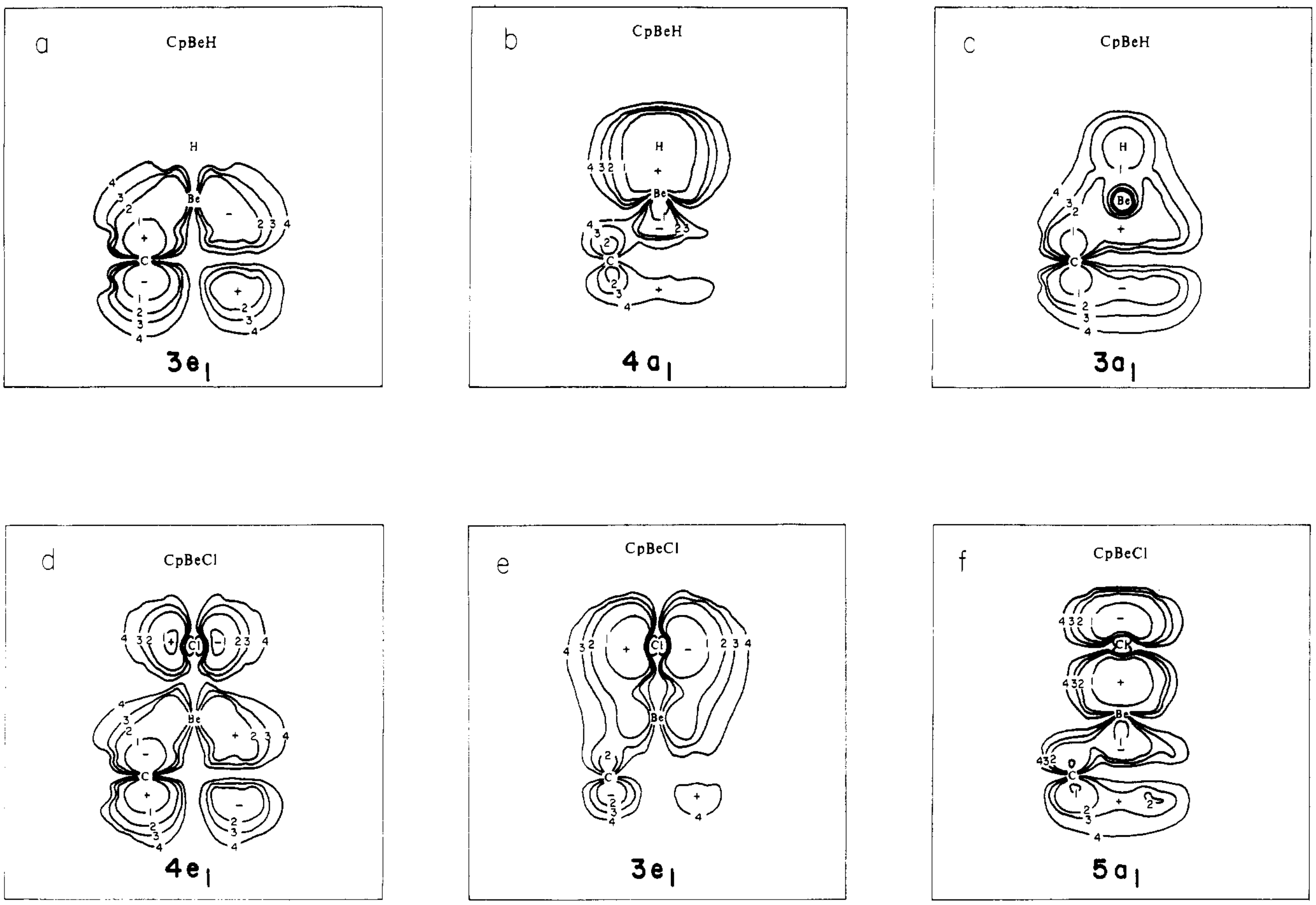

Figure 3. Xα-SW contour plots for (a) $3e_1$ MO of CpBeH, (b) $4a_1$ MO of CpBeH, (c) $3a_1$ MO of CpBeH, (d) $4e_1$ MO of CpBeCl, (e) $3e_1$ MO of CpBeCl, and (f) $5a_1$ MO of CpBeCl.

or BeX is needed to achieve the required total of 16 electrons.

It should be emphasized, however, that the molecule studied so far are relatively simple and involve one noninterstitial lone pair or bond that is directed along the C_5 axis. Systems with two σ bonds (e.g. $C_5H_5BH_2$), two lone pairs (e.g. $C_5H_5S^+$), or a lone pair and a σ bond (e.g. $C_5H_5PH^+$) are liable to be considerably more complicated. These "intermediate hapticity" systems will be the subject of a separate manuscript.

Relationship of Main-Group Annulene Complexes to Polyhedral Carbocations, Carboranes, and Boranes

Finally, we comment that annulene complexes of the main-group elements are related conceptually to polyhedral carbocations[40] and hence to familiar main-group clusters such as the carboranes and boranes.[41] These interrelationships can be illustrated by starting with the polyhedral carbocation $[C_6H_6]^{2+}$ (**1**) (Scheme I). This dication is unknown; however, the corresponding permethylated cation $[C_6Me_6]^{2+}$ is known and believed to possess a nido (η^5) structure on the basis of NMR spectroscopic data.[42]

If the capping group of **1** is regarded as CH^{2+}, then this moiety contributes one electron to interstitital bonding and obeys the six-electron rule like the isoelectronic molecule $(\eta^5\text{-}C_5H_5)BeH$. Replacement of the apical CH by an isoelectronic BH^- group generates the carborane cation **2**. As mentioned earlier, some B–halogen analogues of **2** are known[37] and believed to possess η^5 structures on the basis of NMR spectroscopic data. Like **1**, **2** also conforms to the six-electron rule. A further CH/BH^- replacement produces the known neutral carborane **3**.[43] In order to maintain neutrality, it is necessary to replace further basal CH groups with H–B–H– moieties. Such replacements generate sequentially the carboranes $C_3B_3H_7$, $C_2B_4H_8$, and CB_5H_9 and finally the polyhedral borane B_6H_{10}. Relationships to a host organometallic system are made possible by use of the isolobal concept.[44]

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Registry No. CpLi, 16733-97-4; CpIn, 34822-89-4; CpBeH, 50293-77-1; CpBeCl, 36346-97-1.

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(40) For reviews of polyhedral carbocation chemistry, see: (a) Hogveen, K.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413. (b) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 991. (c) Balaban, A. T.; Rouvvay, D. H. *Tetrahedron* **1980**, *36*, 1851.

(41) Several authors have discussed the morphological and electronic similarities of polyhedral carbocations, boranes, and carboranes. Examples include Lipscomb's Nobel Prize address (Lipscomb, W. N. *Science (Washington, D.C.)* **1977**, *196*, 1046. *Angew. Chem.* **1977**, *89*, 685), Dewar's theoretical work (Dewar, M. J. S.; McKee, M. L. *Inorg. Chem.* **1980**, *19*, 2662), and Schleyer's comments in Brown's book on nonclassical ions (Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; p 16).

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Electronic Structure of Metal Carbonyl Clusters. 2. An INDO Investigation of Tetra-, Penta-, and Hexanuclear Nickel Complexes

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Tetra-, penta-, and hexanuclear nickel carbonyl clusters have been theoretically investigated by means of a MO–LCAO INDO method. Qualitative correlations have been found between the molecular stability and the electron density on metal atoms and ligand groups. The electronic density on the carbonyls has been described by means of the occupation numbers of the MO's of the free CO molecule, thereby giving a systematic description of the variations in donor–acceptor properties of the coordinated carbonyls. The cluster stability has been analyzed in terms of two-atom interaction energies for evaluating the separate contributions of metal–metal, metal–ligand, and ligand–ligand interactions. The main contribution is the direct interaction between a nickel atom and its ligand groups, but significant bonding interactions occur also between a metal atom and the ligand groups not directly bonded and between different ligand groups. All these intramolecular interactions are even more important than the direct metal–metal ones. These latter interactions do not give the most important contribution to the cluster stability.

1. Introduction

In a previous paper,[1] hereafter referred to as part 1, the electronic structure of carbonyl clusters having up to three nickel atoms was investigated by means of semiempirical MO–LCAO INDO calculations. The most important result of part 1 is that the INDO method suggests that the stability of the metal clusters cannot be accounted for by simplified electron-count models.[2]

In this paper, the theoretical approach outlined in part 1 is applied to the nickel carbonyl clusters of higher nuclearity, with the aim of obtaining more detailed information on the different electronic contributions to the overall cluster stability. As pointed out in a recent review paper,[3] the cluster stability problem is still far from being solved, mainly because the rigorous quantum-chemical methods cannot be applied to molecular clusters of high nuclearity. On the other hand, the results of different semiempirical methods are difficult to compare because of their basic approximations.

A widely discussed aspect of the cluster stability is the contribution of the metal–metal bond, which according to the classic definition of a metal cluster compound is supposed to play an important role.[4] However, the problematic nature

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