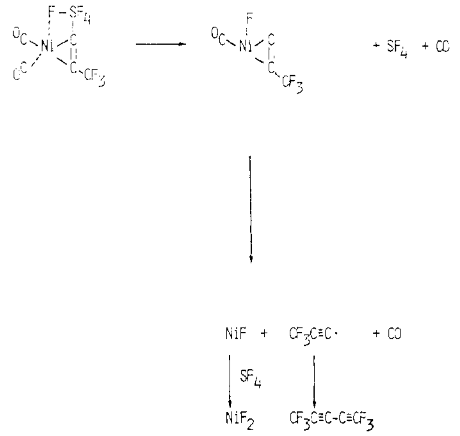

Figure 2. Proposed decomposition path for $Ni(CO)_2(SF_5C_2CF_3)$.

$J_{F_A-F_B}$ = 126 Hz. In the CF region, a multiplet (sextet, δ = 53.2, J = 6.4 Hz) is observed.

Our results show that $SF_5C{\equiv}CCF_3$ reacts with $Ni(CO)_4$ to form a product whose spectroscopic and chemical properties are consistent with the formulation $Ni(CO)_2(SF_5C_2CF_3)$ as shown in Figure 1. This is analogous to the reaction of hexafluorobutyne with $Ni(CO)_4$ at 50-60 °C to form $Ni(CO)_2(\eta^2\text{-}CF_3C_2CF_3)$ (**3**).[3] Although both compounds are moderately stable at room temperature in the presence of either excess CO for **1** or hexafluorobutyne for **3**, they decompose to give very different products. For example, **1** eliminates CO, SF_4, and $CF_3{\equiv}C{-}C{\equiv}CCF_3$, suggesting an interaction between the nickel atom and the SF_5 group as shown in Figure 2, whereas $Ni(CO)_2(\eta^2\text{-}CF_3C_2CF_3)$ forms the cluster complex $Ni_4(CO)_4\{\mu_3\text{-}(\eta^2\text{-}CF_3C_2CF_3)\}_3$. The triphenylphosphine derivative of **1** is stable at ambient conditions, showing no tendency to decompose in this fashion. This could be attributed to the nickel atom being a comparatively weaker Lewis acid toward the fluorine lone pairs as a result of its bonding to the more basic triphenylphosphine groups in **2**. In neither system do we find evidence for the cyclization or polymerization of $SF_5{\equiv}CCF_3$, which was our primary objective.

Experimental Section

Vacuum-system operations were carried out in a Pyrex system equipped with greaseless Kontes glass/Teflon stopcocks. Routine infrared spectra were recorded on a Perkin-Elmer 467 spectrophotometer using a 10-cm glass cell equipped with 25-mm KBr windows. NMR spectra were obtained by using a JEOL JNM-FX60Q spectrometer operating at 59.75 MHz for ^1H and 56.20 MHz for ^{19}F. Chemical shifts are reported relative to $(CH_3)_4Si$ and $CFCl_3$ for proton and fluorine spectra, respectively. Mass spectra were recorded with a CVC time-of-flight spectrometer operating at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Pentafluoro[(trifluoromethyl)acetylenyl]sulfur was prepared according to published procedures.[4]

Infrared Study of $Ni(CO)_4 + SF_5C{\equiv}CCF_3$. Nickel tetracarbonyl (0.10 mmol) and $SF_5C{\equiv}CCF_3$ (0.11 mmol) were condensed into the cold finger of a gas-phase infrared cell. The mixture was subjected to several freeze-thaw cycles, which resulted in the formation of a yellow liquid in the cell. The gas-phase spectrum of the vapor above the liquid contained the following bands: 2360 (br, w), 2180 (br, w), 2140 (vs), 2100 (vs), 2060 (vs), 1890 (m), 1865 (s), 1260 (vs), 1245 (vs), 1200 (vs), 940 (vs), 910 (vs), 885 (vs), 840 (vs), 765 (s), 735 (PQR, w), 720 (m), 675 (s), 650 (m), 610 (vs), 590 (m), 515 (w), 490 (m), 455 (m), 425 (w) cm^{-1}. Noncondensable gases were removed, and a second spectrum was run, which revealed a considerable decrease in the intensities of bands at 2360, 2180, 2060, and 425 cm^{-1} and a moderate increase in the PQR band at 735 cm^{-1}. The mass spectrum of these materials in the gas phase contained peaks arising from $SF_5C{\equiv}CCF_3$, CO, CO_2, $CF_3C{\equiv}C{-}C{\equiv}CCF_3$, and possibly SF_4 (a strong peak at 89 amu for SF_3^+ suggested the presence of SF_4; this would be consistent with assigning the PQR band at 735 cm^{-1} in the infrared spectrum to SF_4[5]). The materials that were volatile at −78 °C were removed, leaving a yellow liquid whose gas-phase spectrum contained bands at 2140 (vs), 2100 (vs), 2060 (m), 1890 (m), 1865 (s), 1255 (vs), 1240 (vs), 1180 (vs), 945 (s), 910 (s), 885 (vs), 850 (vs), 765 (s), (740, 730, 720) (s), 675 (s), 645 (m), 610 (s), 585 (m), 575 (m), 520 (w), 490 (m), and 455 (m) cm^{-1}.

NMR Study of $Ni(CO)_4 + SF_5C{\equiv}CCF_3$. Nickel tetracarbonyl (0.48 mmol) and $SF_5C{\equiv}CCF_3$ (0.71 mmol) were condensed into an NMR tube and warmed to room temperature. The mixture was subjected to several freeze-thaw cycles at −196 °C to remove noncondensable gases (presumably CO) produced in the formation of a yellow liquid. Fluorotrichloromethane (0.98 mmol) was added to the mixture, and the tube was sealed off. The spectra are discussed in the text.

Synthesis of $Ni(P(C_6H_5)_3)_2(SF_5C_2CF_3)$. Nickel tetracarbonyl (0.74 mmol) and $SF_5C{\equiv}CCF_3$ (0.97 mmol) were condensed into one part of a two-sided reactor connected by the side arm of a glass/Teflon stopcock. The second part of the reactor contained an evacuated solution of $P(C_6H_5)_3$ (2.11 mmol in 1 mL of dry diethyl ether). After removal of the noncondensable gases from the $Ni(CO)_4$-$SF_5C_2CF_3$ mixture with several freeze-thaw cycles at −196 °C, the mixture was cooled to −78 °C, and excess $SF_5C_2CF_3$ (0.27 mmol) was removed, leaving a yellow liquid. The triphenylphosphine-ether solution was then transferred into the section containing the yellow liquid, and a yellow solid formed immediately. The noncondensable gases were removed, and the ether was distilled out of the reactor upon warming. The solid was dissolved in CH_2Cl_2, followed by precipitation at −78 °C and washing with hexane to yield 136.4 mg (23%) of a yellow powder identified as $Ni(P(C_6H_5)_3)_2(SF_5C_2CF_3)$ (**2**). The compound melted at 137 °C with decomposition. Anal. Calcd for $Ni(P(C_6H_5)_3)_2(SF_5C_2CF_3)$: C, 58.31; H, 3.76; Ni, 7.31. Found: C, 59.65; H, 3.97; Ni, 7.50. Molecular weight: calcd, 803; found (in CH_2Cl_2), 828. The infrared spectrum of **2** in a KBr pellet contained the following bands: 3060 (w), 1750 (m), 1480 (m), 1430 (m), 1310 (w), 1245 (m), 1215 (vs), 1110 (vs), 1025 (w), 1000 (w), 900 (m), 825 (vs), 745 (s), 690 (s), 655 (w), 630 (w), 590 (w), 510 (s), 495 (s), 455 (w), 420 (w) cm^{-1}. The NMR spectra in methylene-d_2 chloride are discussed in the text.

Registry No. **1**, 79681-89-3; **2**, 79681-90-6; $Ni(CO)_4$, 13463-39-3; $SF_5C{\equiv}CCF_3$, 69923-35-9.

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Crystal and Molecular Structure of Dimethyl-μ-cyclopentadienyl-aluminum Polymer

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The chemistry, structures, and bonding associated with cyclopentadienylmetal derivatives are of major interest because of the ability of this organic moiety to form derivatives with η^1-, η^2-, η^3-, and η^5-bound cyclopentadienyl groups and often include two or more types of cyclopentadienyl groups bound

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Table I. Experimental Data from X-ray Diffraction Study on $[Al(\mu\text{-}C_5H_5)(CH_3)_2]_n$

mol formula: $C_7H_{11}Al$
mol wt: 122.15/monomer unit
cryst system: monoclinic
space group: $P2_1/n$[a]
cell dimensions:[b] $a = 6.554$ (2) Å, $b = 9.156$ (2) Å, $c = 12.134$ (8) Å, $\beta = 96.89$ (4)°
$V = 723$ Å
$Z = 4$
$D_{calcd} = 1.12$ g/cm³
radiation: Mo $K\bar{\alpha}$ ($\lambda = 0.71069$ Å)
monochromator: graphite crystal
rflctns measd: $+h,+k,\pm l$
2θ range: 2–55°
scan type: θ–2θ; moving crystal–moving counter
scan speed: 2.0°/min (in 2θ)
scan width: $[2\theta(\text{Mo } K\alpha_1) - 1.3]° \rightarrow [2\theta(\text{Mo } K\alpha_2) + 1.3]°$
bkgd measmt: stationary crystal–stationary counter at beginning and end of 2θ, each for one-fourth the time taken for the 2θ scan
std rflctns: 3 measured every 97 reflections; maximum deviation in intensity for the standards less than 2% and no decay correction applied
unique data: 1941
unique data with $F^2 > 2.5\sigma(F_o^2)$: 1179
abs coeff: $\mu = 1.79$ cm^{-1}
F_{000}: 264 electrons
R_F: 0.034
R_{wF}: 0.045

[a] The space group $P2_1/n$ with equivalent positions $\pm y$, $\pm y$, $\pm z$ and $(^1/_2 + x)$, $\pm(^1/_2 - y)$, $\pm(^1/_2 + z)$. This nonstandard form of space group $P2_1/c$, No. 14 in the "International Tables of Crystallography", was chosen so that the β angle could be close to 90°. [b] Lattice parameters were obtained by using an autoindexing program and a least-squares fit to the setting angles at the unresolved Mo $K\bar{\alpha}$ components of 15 reflections with 2θ values between 8 and 27°.

Table II. Atomic Coordinates for $[Al(\mu\text{-}C_5H_5)(CH_3)_2]_n$

atom	x	y	z
Al	0.21503 (8)	0.21642 (6)	0.13886 (4)
C(1)	0.3880 (3)	0.0410 (2)	0.2407 (2)
C(2)	0.2449 (3)	−0.0648 (2)	0.1996 (2)
C(3)	0.1178 (3)	−0.0950 (2)	0.2819 (2)
C(4)	0.1858 (4)	−0.0025 (2)	0.3740 (2)
C(5)	0.3520 (4)	0.0746 (2)	0.3508 (2)
C(6)	0.3184 (5)	0.1847 (3)	−0.0042 (2)
C(7)	−0.0779 (3)	0.2208 (3)	0.1524 (2)
H(1)	0.511 (4)	0.063 (2)	0.212 (2)
H(2)	0.238 (3)	−0.111 (2)	0.128 (2)
H(3)	−0.020 (4)	−0.140 (3)	0.263 (2)
H(4)	0.132 (4)	0.001 (3)	0.440 (2)
H(5)	0.432 (4)	0.142 (3)	0.399 (2)
H(61)	0.283 (5)	0.259 (3)	−0.058 (3)
H(62)	0.264 (5)	0.097 (3)	−0.038 (3)
H(63)	0.452 (8)	0.186 (4)	0.005 (4)
H(71)	−0.148 (5)	0.154 (4)	0.101 (3)
H(72)	−0.099 (5)	0.202 (3)	0.225 (3)
H(73)	−0.140 (6)	0.310 (4)	0.135 (3)

to a given metal or two types of bonding interaction between metal atoms and a single ring. Further, the main-group-metal cyclopentadienyl derivatives are widely used in chemical synthesis, and for this reason, it is of importance to understand the way in which metal atoms interact with the cyclopentadienyl groups since these interactions will influence the properties and reactions of the specific derivative. For these reasons, and the results reported in several papers[1-9] that indicated complex behavior including partial association for cyclopentadienylaluminum derivatives, we have determined the crystal and molecular structure of dimethyl-μ-cyclopentadienyl-aluminum and have compared it with the known structures of the boron,[10] gallium,[11] and indium derivatives.[12]

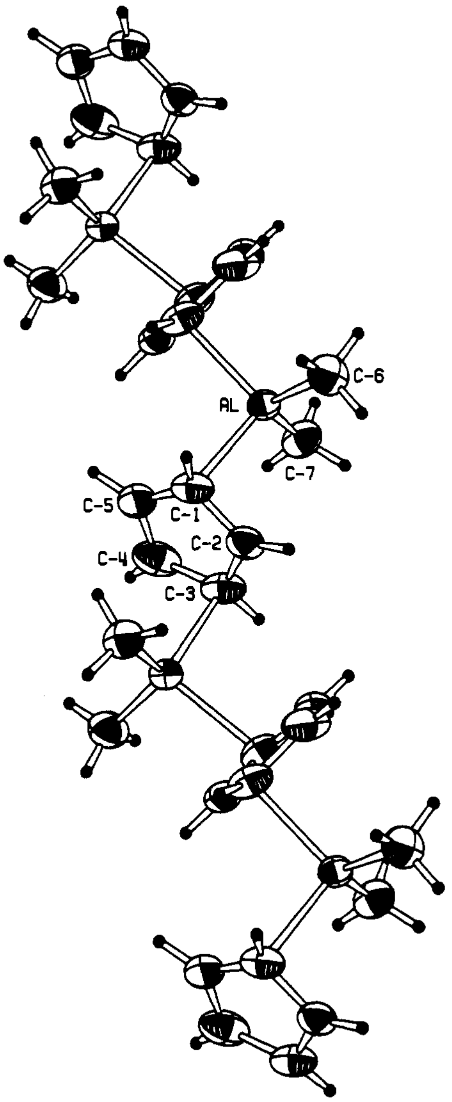

Figure 1. Perspective view of a portion of the $Al(\mu\text{-}C_5H_5)(CH_3)_2$ chain with the atoms labeled.

Experimental Section

Synthesis and Crystal Selection of $[Al(\mu\text{-}C_5H_5)(CH_3)_2]_n$. Dimethyl-μ-cyclopentadienyl-aluminum polymer was prepared by the direct reaction of Al_2Me_6 and excess cyclopentadiene in a manner similar to that used by Kroll and Hudson.[8] The reactants were distilled into a reaction vessel on the vacuum line, which was then sealed off and placed in an oil bath at 130 °C. After 24 h, well-defined white crystals were sublimed from the reactions mixture and deposited on the walls of the vessel. These were removed in an argon-filled drybox and were used without further purification. Several crystals that appeared suitable for X-ray diffraction studies from a microscopic examination were placed in thin-walled capillaries in the drybox, plugged with silicon grease, and flame sealed when they were removed from the drybox.

Data Collection. The crystal selected for data collection was 0.40

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Table III. Isotropic Thermal Factors of Hydrogens and Anisotropic Thermal Factors of Nonhydrogen Atoms in $[\mathrm{Al}(\mu\text{-}C_5H_5)(CH_3)_2]_n$[a]

atoms	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	2.74 (0)	2.43 (2)	3.13 (2)	0.04 (2)	0.59 (2)	−0.11 (2)
C(1)	3.5 (1)	2.8 (1)	5.1 (1)	0.1 (1)	0.9 (1)	0.9 (1)
C(2)	4.4 (1)	2.4 (1)	3.7 (1)	0.5 (1)	0.6 (1)	0.2 (1)
C(3)	3.5 (1)	2.6 (1)	5.9 (1)	0.3 (1)	1.1 (1)	0.8 (1)
C(4)	7.1 (1)	2.9 (1)	4.7 (1)	1.1 (1)	2.6 (1)	0.4 (1)
C(5)	6.5 (1)	2.5 (1)	4.4 (1)	−0.2 (1)	−0.4 (1)	0.0 (1)
C(6)	5.4 (1)	4.1 (1)	3.7 (1)	0.4 (1)	1.2 (1)	−0.3 (1)
C(7)	2.9 (1)	3.7 (1)	5.3 (1)	−0.1 (1)	0.4 (1)	−0.2 (1)

atoms	B, Å^2	atoms	B, Å^2	atoms	B, Å^2
H(1)	5.2 (5)	H(5)	6.3 (6)	H(71)	6.9 (7)
H(2)	4.7 (5)	H(61)	6.5 (7)	H(72)	6.9 (7)
H(3)	5.4 (6)	H(62)	7.9 (8)	H(73)	9.1 (10)
H(4)	6.0 (6)	H(63)	11.7 (14)		

[a] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Interatomic Distances (Å) and Angles (Deg) for $[\mathrm{Al}(\mu\text{-}C_5H_5)(CH_3)_2]_n$

Al–C(1)	2.248 (2)	C(1)–Al–C(6)	100.1 (1)
Al–C(2′)	2.793 (2)	C(1)–Al–C(3′)	97.4 (1)
Al–C(3′)	2.203 (2)	C(1)–Al–C(7)	113.9 (1)
Al–C(4′)	2.664 (2)	C(6)–Al–C(7)	121.8 (1)
Al–(C-2)	2.679 (2)	C(6)–Al–C(3′)	107.2 (1)
Al–(C-5)	2.924 (2)	C(7)–Al–C(3′)	113.0 (1)
Al–(C-6)	1.959 (2)	Al–C(1)–C(2)	91.5 (1)
Al–(C-7)	1.947 (2)	Al–C(1)–C(5)	103.5 (1)
C(1)–C(2)	1.398 (3)	Al–C(1)–H(1)	92
C(2)–C(3)	1.403 (3)	C(2)–C(1)–C(5)	107.8 (1)
C(3)–C(4)	1.430 (3)	C(1)–C(2)–C(3)	108.3 (2)
C(4)–C(5)	1.356 (3)	C(2)–C(3)–C(4)	106.5 (2)
C(5)–C(1)	1.418 (3)	C(3)–C(4)–C(5)	109.2 (2)
C(1)–H(1)	0.94 (2)	C(4)–C(5)–C(1)	108.2 (2)
C(2)–H(2)	0.96 (2)	Al–C(3′)–C(2′)	99.1 (1)
C(3)–H(3)	1.00 (3)	Al–C(3′)–C(4′)	91.8 (1)
C(4)–H(4)	0.92 (3)	Al–C(3′)–H(3′)	100 (1)
C(5)–H(5)	0.96 (3)	Al–C(6)–H(61)	115 (2)
		Al–C(6)–H(62)	111 (2)
C(6)–H(61)	0.95 (3)	Al–C(6)–H(63)	110 (2)
C(6)–H(62)	0.95 (3)	Al–C(7)–H(71)	109 (2)
C(6)–H(63)	0.87 (5)	Al–C(7)–H(72)	110 (2)
C(7)–H(71)	0.95 (3)	Al–C(7)–H(73)	114 (2)
C(7)–H(72)	0.93 (3)	C(2)–C(1)–C(5)	107.8 (2)
C(7)–H(73)	0.93 (3)	C(1)–C(2)–C(3)	108.3 (2)
		C(2)–C(3)–C(4)	106.5 (2)
		C(3)–C(4)–C(5)	109.2 (2)
		C(1)–C(5)–C(4)	108.2 (2)

× 0.19 × 0.08 mm and was mounted in a thin-walled capillary tube, 0.2 mm in diameter. Data were collected on a Syntex $P2_1$ automated diffractometer with Mo K$\bar{\alpha}$ radiation diffracted from a highly oriented graphite crystal in the parallel mode with a θ–2θ scan in the bisecting mode. The specific conditions, unit cell, and unit cell dimensions are given in Table I. The final data were corrected for background, Lorentz, and polarization effects.

Solution and Refinement of the Structure. The location of the aluminum atom was determined from a Patterson synthesis.[13] All other atoms including nine of the eleven hydrogen atoms (the H atoms appeared as well-defined peaks with intensities ranging from 0.4 to 0.6 e/Å^3) in the asymmetric unit were placed by using a series of least-squares calculations and ΔF maps. The remaining two hydrogen atoms, located one each on the two methyl groups, were placed in idealized position with the use of HFINDER. Positional and anisotropic thermal parameters for the aluminum and carbon atoms were refined by using our usual weighting scheme.[14] Hydrogen atoms were refined for x, y, z isotropically. Neutral-atom scattering factors for aluminum,[15] carbon,[15] and hydrogen[16] were used. The final refinement gave R values[17] of $R_F = 3.4\%$ and $R_{wF} = 4.5\%$. In the final cycle of least squares the maximum shift was 0.02σ with 117 variables. The highest peak on a final ΔF map represented 0.34 e/Å^3.

Final positional and thermal parameters are presented in Tables II and III. Observed and calculated structure amplitudes are available.[18]

Results and Discussion

The structure of $\mathrm{Al}(\mu\text{-}C_5H_5)(CH_3)_2$ consists of infinite chains in the solid state as seen in Figure 1. There is no appreciable interaction between chains, with the closest approach occurring between hydrogens on adjacent chains. The chains are composed of dimethylaluminum groups bridged by C_5H_5 rings. The bonding in the $\mathrm{Al}(CH_3)_2$ unit is normal, with a C–Al–C angle of 121.8° and Al–C distances of 1.95 Å, which are typical for terminal alkyl groups bound to aluminum.[19] The bridging units in the isomorphous gallium derivative and the related indium compound are unsymmetrically bound to the metal atoms and show significant distortion within the ring. Table V presents a comparison of selected bond distances in these three derivatives as well as some parameters obtained for several other main-group cyclopentadienylmetal compounds. These data show for the bridged group 3 derivatives that the same atoms are involved in bonding, that the metal–carbon distances are unsymmetrical, and that one bridge bond distance is the length anticipated for an electron-deficient bridged bond while the other is significantly longer. These results may be interpreted as indicating essentially molecular units, which are then held together by the secondary interactions.

Examination of the C–C distances in the cyclopentadienyl ring (Table II) shows that there are two pairs of essentially equivalent distances, C(1)–C(2) $\simeq$ C(2)–C(3) and C(1)–C(5) $\simeq$ C(3)–C(4), with the remaining distance, C(4)–C(5), appearing significantly shorter. A similar pattern is observed for the indium and gallium compounds and also occurs for the σ-bonded groups. Thus, it would appear that the short M–C(1) interaction leads to the distortions observed in these rings. Similar, although less pronounced, distortions occur in the (pentamethylcyclopentadienyl)aluminum derivative[20] and in

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(13) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reductions; (2) FORDAP, A. Zalkin's Fourier program; (3) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models.

(14) The weighting scheme is defined as $w = F_o^2/(\sigma(F_o^2))^2$.

(15) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 73–74.

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(17) Values for the R factors are defined as $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(18) See the paragraph at the end of the paper regarding supplementary material.

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Table V. Selected Metal–Carbon and C–C Bond Distances (Å) in Group 3 Cyclopentadienyl–Metal Derivatives

compd	metal-bridging carbon distances: ring A	ring A′	other M–C distances	C–C distances in the C_5 rings: C_1–C_2	C_2–C_3	C_3–C_4	C_4–C_5	C_5–C_1	av
Al(μ-C_5H_5)Me_2	2.203 (2)	2.248 (2)	1.959 (2) 1.947 (2)	1.397 (3)	1.402 (3)	1.430 (3)	1.355 (3)	1.418 (3)	1.400
Ga(μ-C_5H_5)Me_2[b]	2.215 (2)	2.314 (2)	1.972 (2) 1.962 (1)	1.415 (2)	1.415 (2)	1.415 (2)	1.365 (2)	1.426 (3)	1.407
In(μ-C_5H_5)(C_5H_5)$_2$[c]	2.374 (7)	2.466 (8)		1.395 (13)	1.381 (13)	1.443 (13)	1.358 (15)	1.412 (14)	1.398
ring B			2.243 (9)	1.405 (14)	1.344 (14)	1.412 (13)	1.340 (13)	1.426 (13)	1.385
ring C			2.237 (9)	1.425 (14)	1.370 (14)	1.411 (15)	1.337 (16)	1.430 (14)	1.395
Al(C_5H_5)Me_2[d]	Al–C(1) = Al–C(2) = 2.21 (2)			1.422 (2)					
AlCl(C_5Me_5)(Me)[e]				1.43 (1)	1.39 (1)	1.37 (11)	1.38 (1)	1.44 (1)	
Mg(C_5H_5)$_2$[f]	2.304 (8) av			1.39 (2) av, range 1.35 (2)–1.41 (2)					
Na(C_5H_5)·TMEDA[g]	2.283 (7)–2.324 (7)			1.381 av, range 1.366–1.402 (18)					

[a] This work. [b] Reference 11. [c] Reference 12; rings B and C are σ bonded to the In atom. [d] Reference 19; monomer, gas phase Al(C_5H_5)(CH_3)$_2$; all C–C distances assumed to be equivalent in the cyclopentadienyl ring. [e] Reference 20. [f] Reference 21. [g] Reference 22.

the magnesium[21] and sodium[22] cyclopentadienides cited in Table V.

These differences have been assumed to be averaged or nonexistent for the monomeric aluminum in the gas phase, with subsequent molecular orbital calculations[23] providing support for an η^2-C_5H_5–metal interaction. The present work, as noted above, supports a more localized interaction for the compound in the solid state.

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Registry No. [Al(μ-C_5H_5)(CH_3)$_2$]$_n$, 79255-65-5.

Supplementary Material Available: Listings of observed and calculated structure amplitudes (×10) (6 pages). Ordering information is given on any current masthead page.

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Correspondence

Closo Clusters with Unusual Electron Numbers: Molecular Orbital Considerations and Localized Bonding Schemes

Sir:

Most known closo borane clusters with *n* skeletal atoms, like the anions $B_nH_n^{2-}$ (n = 6–12) and carboranes $C_2B_{n-2}H_n$ (n = 5–12) are held together by (n + 1) skeletal bond pairs.[1-6] However, there is an increasing number of closo systems now known, including neutral boron halides such as B_8Cl_8[7] and B_9Cl_9,[8] the cationic bismuth cluster Bi_9^{5+},[9] and the interesting pair of metallaboranes (η^5-C_5H_5)$_4Co_4B_4H_4$[10] and (η^5-C_5H_5)$_4Ni_4B_4H_4$,[11] which are diamagnetic species with closed electronic shells even though they contain either *n* or (n + 2) skeletal bond pairs, for which capped closo or nido structures, respectively, might have appeared more appropriate. The existence of these apparent anomalies has been variously attributed either to the compatibility of individual structures with particularly apt localized bond schemes or to the effect of substituents, particularly to π back-bonding from halogen substituents.[12,13] Here we draw attention to some commonly overlooked molecular orbital considerations that allow one to establish which closo structures may be compatible with *n* or (n + 2) bond pairs. We also point out that, although localized bond schemes have certain advantages (some of which we illustrate) in describing the bonding in clusters of known structure, they cannot be regarded as explanations of these structures, since equally plausible localized bond networks can be devised for the whole range of hypothetical closo *n*-atom clusters (n = 6–12) with *n* or (n + 2) bond pairs, most of which, on the basis of molecular orbital (MO) considerations, are not expected to exist.

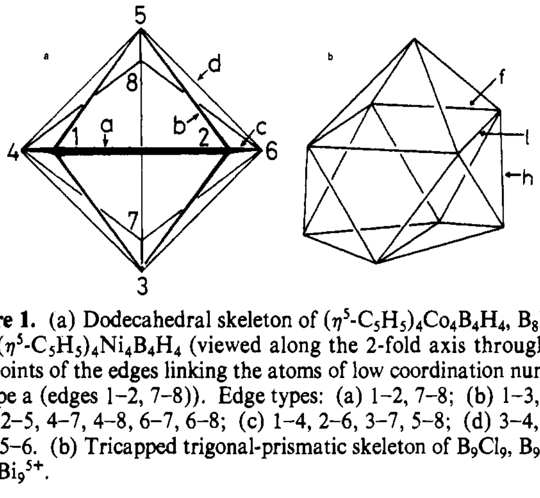

Figure 1. (a) Dodecahedral skeleton of (η^5-C_5H_5)$_4Co_4B_4H_4$, $B_8H_8^{2-}$, and (η^5-C_5H_5)$_4Ni_4B_4H_4$ (viewed along the 2-fold axis through the midpoints of the edges linking the atoms of low coordination number, of type a (edges 1–2, 7–8)). Edge types: (a) 1–2, 7–8; (b) 1–3, 1–5, 2–3, 2–5, 4–7, 4–8, 6–7, 6–8; (c) 1–4, 2–6, 3–7, 5–8; (d) 3–4, 3–6, 4–5, 5–6. (b) Tricapped trigonal-prismatic skeleton of B_9Cl_9, $B_9H_9^{2-}$, and Bi_9^{5+}.

MO Considerations. It is convenient to consider first why the 8-vertex D_{2d} dodecahedron and the 9-vertex D_{3h} tricapped trigonal prism (Figure 1) can accommodate n, (n + 1), or (n + 2) skeletal bond pairs, as represented by B_8Cl_8[7] (eight pairs), (η^5-C_5H_5)$_4Co_4B_4H_4$[10] (eight pairs), $B_8H_8^{2-}$[14] (nine pairs),

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