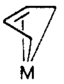
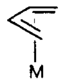
studies to date have thus far only revealed diene units coordinated in the usual cis fashion, whereas a diffraction study for Nb(C_5H_5)(η^8-$C_{14}H_{22}$) has revealed that one of the diene units is present in the trans form (Figure 1).[8,14] Such coordination had previously been observed only for Zr(C_5H_5)$_2$(η^4-diene) and Mo(C_5H_5)(NO)(η^4-diene) complexes,[9] although we have also found trans-diene coordination in Ru(η^4-diene)(acac)$_2$ complexes.[15] The niobium complex now provides the first opportunity to compare simultaneous η^4-*cis*- and η^4-*trans*-diene coordination modes to a single metal center. While the complex might appear to be a Nb(I) compound, it is quite common for diene coordination in "low valent" early metal complexes to possess significant butenediyl character (IV), as opposed to the normal diene form (V).[8] Such coordination (IV) is generally manifested by a long–short–long carbon backbone and a short–long–long–short series of metal–carbon distances. In Nb(C_5H_5)(η^8-$C_{14}H_{22}$), it is the η^4-*cis*-diene portion which engages in butenediyl coordination (having C–C distances of 1.55 (3), 1.32 (2), and 1.52 (2) Å, and Nb–C distances of 2.317 (14), 2.590 (20), 2.570 (15), and 2.366 (18) Å), while the trans form engages in more of a diene coordination (having C–C distances of 1.37 (2), 1.47 (2), and 1.41 (2) Å and Nb–C distances of 2.630 (15), 2.349 (16), 2.304 (15), and 2.363 (12) Å).[16] The greater favorability for the *cis*-diene to engage in butenediyl coordination is in accord with results on the zirconium and molybdenum species and agrees with theoretical studies indicating that the η^4-*trans*-diene coordination is favored when the ligand → metal donor interaction is dominant.[17]



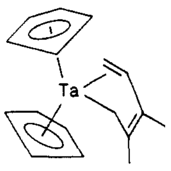
IV



V

In marked contrast, related reactions for Ta(C_5H_5)Cl_4 lead to Ta(C_5H_5)$_2$(pentadienyl) (pentadienyl = 2,3-C_7H_{11}, 2,4-C_7H_{11}) complexes. While the existence of M(C_5H_5)$_2$(η^3-allyl) compounds[18] suggests that analogous M(C_5H_5)$_2$(η^3-pentadienyl) complexes should exist (M = Nb, Ta), spectroscopic features of the Ta(C_5H_5)$_2$(pentadienyl) complexes were not in accord with such a formulation. Notably, a low value of $J_{^{13}C-H}$ (123 Hz) was observed for a terminal dienyl carbon atom, although a reasonable C–C stretching frequency for the free double bond was observed, 1607 cm^{-1}.

A single crystal diffraction study for Ta(C_5H_5)$_2$(2,3-C_7H_{11}) revealed that η^3 coordination by the dienyl fragment was indeed present[14] but involved localized tantalum-alkyl and tantalum-olefin coordination,[19] as in VI, which is an entirely new mode of η^3-dienyl coordination. As a significant input of energy should be needed to convert a delocalized allyl anion to localized alkyl anion and olefin units, the avoidance of η^3-allyl coordination suggests that the Ta(C_5H_5)$_2$ coordination sphere has a strong preference for the more localized, in-plane interactions. Interestingly, however, variable temperature NMR studies for Ta(C_5H_5)$_2$(2,4-C_7H_{11}) reveal that the two ends of the C_7H_{11} ligand may become equivalent, with $\Delta G^\ddagger = 10.7 \pm 0.2$ kcal/mol. Similarly the two C_5H_5 ligands may become equivalent, with $\Delta G^\ddagger = 10.4 \pm 0.2$ kcal/mol. For Ta(C_5H_5)$_2$(2,3-C_7H_{11}), the two C_5H_5 ligand resonances were not observed to undergo coalescence, perhaps an indication that the 2,4-C_7H_{11} group adopts more of a U than S (sickle) conformation. For the former complex, it is not clear whether the intermediate in the equilibration is a 16-electron species such as Ta(C_5H_5)$_2$(η^1-2,4-C_7H_{11}) (bound through the central pentadienyl carbon atom) or an 18-electron Ta(η^5-C_5H_5)(η^3-C_5H_5)(η^5-2,4-C_7H_{11}) species.



VI

The above results reveal some unexpected and subtle differences in favorabilities for niobium- and tantalum-dienyl bonding. The products observed in both reactions are each unusual in themselves. It is first clear that *trans*-η^4-diene coordination should be significantly more common than previously expected, even occurring for late metals. Additionally, the pentadienyl ligands have now revealed a new mode of η^3-coordination, one which demonstrates that η^3-dienyl bonding has available to it a dimension and versatility unknown for its η^3-allyl analogues.

Acknowledgment. R.D.E. is grateful to the NSF for support of this work through grants and a creativity award.

Supplementary Material Available: Synthetic and characterization details for the complexes described herein as well as tables of X-ray data collection parameters and atomic and bonding parameters (24 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of *closo*-$Sn_9Cr(CO)_3{}^{4-}$: The First Member in a New Class of Polyhedral Clusters

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The development of metallaborane and metallacarborane chemistry during the past 20 years has provided the chemical community with some of the most interesting and diverse molecular clusters known.[1] Incorporation of transition metals into the later main-group clusters, such as the stannides [$Sn_9{}^{4-}$, $Sn_5{}^{2-}$],[2,3] plumbides [$Pb_5{}^{2-}$],[3] antimonides [$Sb_7{}^{3-}$],[4] and arsenides [$As_7{}^{3-}$, $As_{11}{}^{3-}$, $As_{22}{}^{4-}$],[5-7] has received much less attention but should prove

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[14] Crystals of Nb(C_5H_5)($C_{14}H_{22}$) are orthorhombic, space group *Pcc*2, with $Z = 4$ and $a = 14.061$ (3) Å, $b = 14.273$ (3) Å, $c = 8.045$ (1) Å. Departures from mirror plane symmetry eliminate the space group *Pccm*. Data were collected at the University of Delaware out to 55° in 2θ, leading to 1621 unique, observed ($F_o > 3\sigma(F_o)$) reflections. Problems were encountered in the structure refinement, possibly due to the pseudo-mirror plane symmetry. Final discrepancy indices of $R = 0.073$ and $R_w = 0.088$ were obtained. For Ta(C_5H_5)$_2$(2,3-C_7H_{11}), a monoclinic space group ($P2_1/c$) was found, with $a = 7.887$ (2) Å, $b = 14.433$ (3) Å, $c = 12.645$ (3) Å, and $\beta = 97.93$ (2)°, for $Z = 4$. Data were collected at the University of Utah out to $2\theta = 51°$, leading to 2034 unique, observed ($I > 3\sigma(I)$) reflections. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in the positions indicated by a difference Fourier map. Final discrepancy indices of $R = 0.034$ and $R_w = 0.038$ were obtained.

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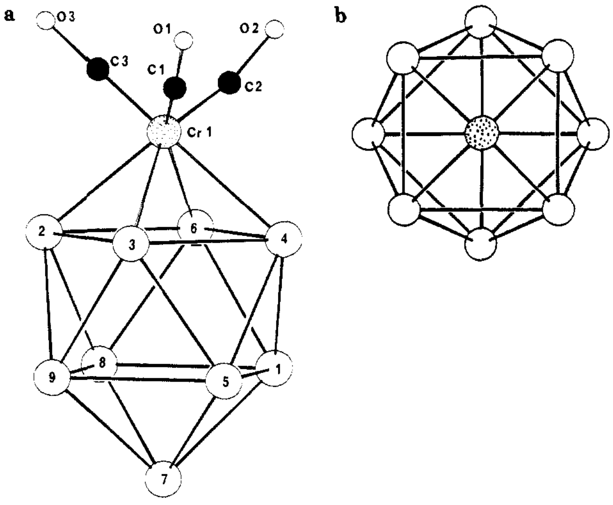

Figure 1. Chem-X[24] ball-and-stick representations of the $Sn_9Cr(CO)_3^{4-}$ ion as viewed (a) side-on and (b) down the Cr–Sn(7) vector showing the highly regular cluster geometry (carbonyl ligands omitted for clarity). Pertinent distances (Å) and angles (deg) [averaged where appropriate]: Cr(1)–Sn(3) = 2.890 (6), Cr(1)–Sn(6) = 2.859 (6), Cr(1)–Sn(2) = 2.867 (6), Cr(1)–Sn(4) = 2.869 (6), Cr(1)–C(1) = 1.71 (3), Cr(1)–C(2) = 1.66 (4), Cr(1)–C(3) = 1.71 (4), C(1)–O(1) = 1.27 (4), C(2)–O(2) = 1.26 (4), C(3)–O(3) = 1.29 (5), Sn(7)–Sn(1,5,8,9) = 2.94 (2), Sn(3)–Sn(6) = 4.35 (2), Sn(2)–Sn(4) = 4.33 (2), Sn(8)–Sn(5) = 4.43 (2), Sn(9)–Sn(1) = 4.49 (2), Cr(1)–C(1)–O(1) = 173 (3), Cr(1)–C(2)–O(2) = 170 (3), Cr(1)–C(3)–O(3) = 176 (3).

to be equally interesting. Recently, some mixed d-block main-group compounds have been prepared, namely $NbTe_{10}^{3-}$,[8] $Mo_4Te_{16}(en)_4^{2-}$,[9] $^1_\infty[Hg_2Te_5^{2-}]$,[10] $^1_\infty[K_2Au_4Te_4^{2-}\cdot 4\text{solvent}]$,[11] $KAu_9Te_7^{4-}$,[11] and $^1_\infty[Rb\cdot NbAs_8^{2-}]$.[12] These compounds have unprecedented structures and are potentially useful precursors to metastable solids.[13] Although no clusters containing transition metals and tin or lead have previously been isolated, Rudolph and co-workers[14] described NMR experiments in 1983 involving reactions between $Pt(PPh_3)_4$ and M_9^{4-} ions [where M = Sn or Pb] in ethylenediamine (en), but the resulting products were highly fluxional and the lack of single crystals prevented compositional analysis or structure determination. We report here the synthesis and characterization of *closo*-$Sn_9Cr(CO)_3^{4-}$ (**1**)—the first boron-free transition-metal main-group deltahedral cluster structurally characterized to date.

The title compound was prepared by slowly adding a toluene solution of excess $Cr(CO)_3(mes)$ [mes = η^6-1,3,5-$C_6Me_3H_3$] to a deep-red en extract of K_4Sn_9. After mixing, 4 equiv of crypt[15] were added causing a rapid color change from red to green to brown (total reaction time ≈ 5 s). No apparent reaction occurred before the addition of crypt. The tetrapotassium cryptate salt of **1** was isolated as extremely air-sensitive, well-formed brown needles in ca. 25% yield (based on Sn) according to the equation below.[16] The compound has been characterized by microprobe analysis, elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The ^{119}Sn NMR data will be discussed in a future publication.

$$Cr(CO)_3(mes) + K_4Sn_9 + 4\text{crypt} \xrightarrow{\text{en/toluene}} (K\cdot\text{crypt})_4Sn_9Cr(CO)_3 + \text{mes}$$

The X-ray structure[17] of $(K\cdot\text{crypt})_4Sn_9Cr(CO)_3$ reveals the virtually undistorted bicapped square antiprismatic cluster, Figure 1, which is isoelectronic and isostructural with $B_{10}H_{10}^{2-}$ [18] and $[(C_5H_5)NiB_9H_9]^{1-}$.[19] There are two crystallographically independent anions in the unit cell that are structurally identical within experimental error. The formation of **1** can be viewed as the insertion of a neutral $Cr(CO)_3$ fragment into the open square face of a *nido*-Sn_9^{4-} ion producing a *closo*-10-atom 22-electron deltahedral complex. The cluster has virtual C_s symmetry in solution but no crystallographic symmetry (C_1) in the solid state. The $Cr(CO)_3$ fragment of **1** occupies a capping position in the bicapped square antiprism with Cr–Sn contacts of 2.88 (2) Å (av). The Sn–Sn distances within the square plane defined by Sn(2), Sn(3), Sn(4), and Sn(6) average 3.06 (2) Å, whereas the Sn–Sn contacts within the other square plane average 3.16 (3) Å. The contacts between the two square planes average 2.99 (2) Å. Structurally, the Sn_9 core of **1** is locally distorted by the addition of the $Cr(CO)_3$ fragment as illustrated by the following: The Sn–Sn distances within the Sn capped square faces of (**1**) [3.16 (3) Å (av)] and *nido*-Sn_9^{4-} [3.24 (6) Å (av)] are equivalent, whereas the Sn–Sn distances within the $Cr(CO)_3$ capped square face of **1** [3.06 (2) Å (av)] are slightly elongated from those in the open square face of *nido*-Sn_9^{4-} [2.96 (2) Å (av)].[2] The carbonyl ligands of **1** have short Cr–C bonds [1.65 (7) Å], long C–O bonds [1.29 (4) Å] and low-energy CO bands in the IR spectrum [1809 and 1703 cm^{-1} (KI pellet)] relative to the $Cr(CO)_3(\eta^6\text{-arene})$ precursors. For comparison, $Cr(CO)_3(\eta^6\text{-}C_6Me_6)$ and $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ have Cr–C (carbonyl) distances of 1.814 and 1.842 Å (av) and C–O distances of 1.163 Å (av) and 1.145 Å (av), respectively.[20] These data indicate a significant buildup of negative charge on the Cr atom in **1** that, in turn, is stabilized by metal-to-CO π^* back-bonding.

The $Cr(CO)_3$ fragment in **1** contributes zero electrons to cluster bonding thus transforming the 22-electron *nido*-Sn_9^{4-} cluster into a 22-electron *closo*-$Sn_9Cr(CO)_3^{4-}$ polyhedron in accord with Wade's rules.[21] It is not clear whether reactions of *nido*-Sn_9^{4-} with metal-ligand fragments that donate two electrons to cluster

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(15) Crypt is an abbreviation for 4,7,13,16,21,24-hexaoxa-1,10-diazatricyclo[8.8.8]hexacosane.

(16) Experimental procedure: $Cr(CO)_3(mes)$ (30 mg, 0.12 mmol) was dissolved in toluene (ca. 1.0 mL). The resulting pale yellow solution was added dropwise to a dark red en extract (ca. 2 mL) of a melt of nominal composition K_4Sn_9 (ca. 100 mg). No apparent color change occurred. Crypt (4 equiv, 120 mg, 0.32 mmol) was added as a solid. A rapid color change from red to green to brown occurred as the crypt dissolved. The brown mixture was filtered twice and left at 25 °C. After 48 h, 55 mg of brown needles were isolated by filtration. Anal. Calcd for $K_4Sn_9Cr_1C_{75}H_{144}N_8O_{27}$: C, 31.42; H, 5.06; N, 3.91. Found C, 30.92; H, 6.36; N, 3.52.

(17) Crystallographic data for $(K\cdot\text{crypt})_4Sn_9Cr(CO)_3$: black needles, monoclinic space group $P2_1/c$, $a = 20.398$ (4) Å, $b = 49.705$ (11) Å, $c = 24.108$ (4) Å, $\beta = 91.55$ (2)°, $V = 24433$ (10) $Å^3$, $Z = 8$, $M_r = 2866.88$, $d_{calcd} = 1.56$ g/cm^3, μ(Mo Kα) = 20.89 cm^{-1} (correction factors: 0.82/1.00). Of the 20 763 reflections measured (Nicolet R3mV, ambient temperature), using ω-scans (1.4°) and a fixed scanning speed (7.32°/min), 19 646 were unique ($R_{int} = 0.069$) and 11 003 with $I > 3\sigma(I)$ were used for solution and refinement (SHELXTL). Final refinement, carried out in blocks, with hydrocarbon atoms isotropic and other atoms anisotropic, resulted in final residuals of $R = 0.0732$, $R_w = 0.1016$, and $S = 2.48$. Due to the extremely long b axis, an ω scanning mode was used to take advantage of the greater resolution available by holding the detector stationary. Scans were made over the narrowest range possible to avoid overlap. A profile analysis of the measured reflections was performed, and corrections were applied. The final difference Fourier showed a few peaks of 1.94 $e^-/Å^3$ or less that were not within bonding distance of the anions. These peaks may be due to disordered solvent molecules in the lattice.

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bonding, such as $Fe(CO)_3$ or $Pt(PPh_3)_2$, will yield the predicted[14] *nido*-$Sn_9ML_x^{4-}$ structures. Main-group polyhedral clusters, such as the 22-electron *closo*-Bi_9^{5+} ion, clearly violate traditional cluster electron counting rules,[22] and distortions to alternate geometries are known to be low-energy processes.[23] Our attempts to isolate Rudolph's proposed *nido*-$Sn_9Pt(PPh_3)_2^{4-}$ have been unsuccessful thus far.[14]

Supplementary Material Available: Experimental data and tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, and anisotropic thermal parameters (23 pages); table of observed and calculated structure factors (70 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Silyliron Porphyrin Complexes

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Several alkyliron porphyrin complexes have been synthesized and well characterized,[1,2] but we are aware of no reported preparation of silyliron porphyrin species. Two possible reasons can be offered for the absence of silyliron porphyrin studies. The first is the lack of a general method for preparation of transition-metal silyl complexes. Each metal silyl complex requires a different synthetic route. Secondly, as is described here, the silyliron porphyrin products tend to be much less stable than their alkyl analogues.

The first silyliron porphyrin complexes, paramagnetic trimethylsilyliron(III) tetraphenylporphyrin, and the corresponding diamagnetic silyliron(II) porphyrin anion are reported. Interest in silyliron porphyrins is not limited to porphyrin chemistry, but the synthesis of these derivatives provides a new class of paramagnetic organometallic compounds. The highly reactive silyliron porphyrin complexes are generated in situ along with other products and are characterized by proton and deuterium NMR spectroscopy. It is also shown that propylene oxide is inserted into the iron–silicon bond of the silyliron(III) porphyrin derivative, as is the case with other transition-metal silyl complexes.[3]

The lithium silyl reagent was generated in hexamethylphosphoramide (HMPA) solution by cleavage of hexamethyldisilane by lithium methyl at 0 °C.[4] All reactions were performed in an inert argon atmosphere. The silyliron(III) tetraphenylporphyrin complex was prepared by combination at room temperature of a stoichiometric amount of the lithium silyl in HMPA with a toluene solution of chloroiron(III) tetraphenylporphyrin (TPPFeCl) at a concentration of 1.0–5.0 mM. In order to identify the various products, it was most convenient to utilize TPPFeCl deuteriated at the pyrrole position. Formation of the silyl complex was monitored by deuterium NMR spectroscopy, in which case the pyrrole deuterium signal at 79.5 ppm for high-spin TPPFeCl was converted to a unique new signal at −21.7 ppm. A relatively sharp pyrrole deuteron (proton) signal in this region is characteristic of a low spin iron(III) porphyrin complex.[5] Pyrrole deuteron signals for other byproducts and decomposition products could be associated with the following species: 43.0 ppm, high-spin iron(II) HMPA complex;[6] 13.5 ppm, oxoiron(III) porphyrin dimer; and −16.5 ppm, methyliron(III) porphyrin complex (from lithium methyl).[7] These additional products varied in quatity as a function of mixing procedure and time after mixing. The putative silyliron(III) pyrrole signal at −21.7 ppm was converted to the iron(II) HMPA signal with a half-life of approximately 30 min at 25 °C (The silyliron(III) porphyrin was not particularly stabilized at lower temperature.). An analogous proton NMR spectrum for a toluene-d_8 solution recorded shortly after generation of the trimethylsilyliron(III) porphyrin is shown in Figure 1.

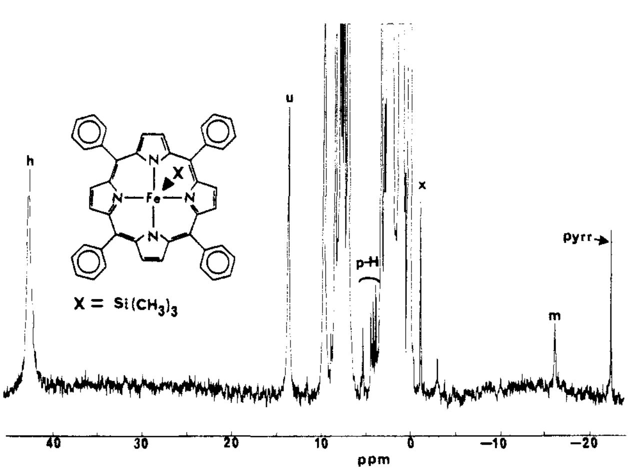

Figure 1. Proton NMR spectrum of trimethylsilyliron(III) tetraphenylporphyrin, 360 MHz, 24 °C, toluene solution, TMS reference. The pyrrole signals of silyliron(III) porphyrin are denoted "pyrr", silyl group "x", and phenyl ring hydrogens "p-H". Pyrrole signals of the high-spin iron(II) porphyrin HMPA complex are labeled "h", μ-oxo-dimeric iron(III) porphyrin "u", and methyliron(III) porphyrin complex "m".

In order to assign the proton NMR signal for the coordinated trimethylsilyl group, deuterium labeling of hexamethyldisilane was carried out by the reaction of hexachlorodisilane and methyl-d_3 magnesium iodide which was prepared from methyl-d_3 iodide and magnesium in ether solution. The trimethylsilyliron(III) porphyrin product prepared from this deuteriated material exhibited a deuterium NMR signal at −1.2 ppm. This resonance is also seen in the proton NMR spectrum in Figure 1, and integration with the −21.7 ppm pyrrole signal yields the expected 9:8 proton intensity pattern. The −1.2 ppm coordinated trimethylsilyl signal vanishes in concert with the disappearance of the −21.7 ppm signal from homolytic decomposition. The coordinated trimethylsilyl proton signal at −1.2 ppm shows a surprisingly small paramagnetic shift when compared to the corresponding β-CH_2-butyliron(III) porphyrin resonance at −64 ppm. Hence, unpaired spin transfer through the silicon atom is much less efficient as compared with the carbon analogue.

The deuterium spectrum of pyrrole-deuteriated trimethylsilyliron(III) tetraphenylporphyrin was recorded from 218 to 313 K. A plot of chemical shift vs $1/T$ was linear with an intercept of 12.4 ± 1.5 ppm and a slope of −10 400 ± 390 ppm (K). This result confirms that the −21.7 ppm signal represents a single species

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(7) Reaction of the toluene solution of TPPFeCl-d_8 with lithium methyl in HMPA yielded a low-spin methyliron(III) porphyrin complex which had only one pyrrole deuterium resonance at −16.5 ppm.