*Organometallics* **1987**, *6*, 1275–1280 1275

as the distorted and uncomplexed half of the complexed naphthalene moiety in the formation of a $(\mu,\eta^6,\eta^6$-naphthalene)$(\eta^6$-arene)$(\eta^6$-naphthalene)dichromium intermediate.

**Acknowledgment.** We express our appreciation to Jim Wallin, Steve Sorey, and Dr. Ben A. Shoulders for the NMR spectra reported here and for many helpful suggestions. We also express our appreciation to Jack Measles, Dr. Ted. Pettijohn, and Dr. John Chinn for mass spectral data. We are pleased to acknowledge the generous support of the Robert A. Welch Foundation.

**Registry No.** I, 33085-81-3; IX, 108058-60-2; $(\eta^6$-naphthalene)$(\eta^6$–fluorobenzene)chromium, 108008-83-9; $(\eta^6$–naphthalene)$(\eta^6$–benzene)chromium, 99537-72-1; $(\eta^6$–naphthalene)$(\eta^6$–toluene)chromium, 108008-84-0; $(\eta^6$–napthalene)$(\eta^6$–mesitylene)chromium, 99537-74-3; $(\eta^6$–naphthalene)$(\eta^6$–hexamethylbenzene)chromium, 99537-75-4; $(\eta^6$-naphthalene)$(\eta^6$-tetralin)benzene, 108008-85-1; $(\eta^6$–naphthalene)$(\eta^6$–dimethyldiphenylsilane) chromium, 108008-82-8; $(\mu,\eta^6,\eta^6$–naphthalene)bis$(\eta^6$–fluorobenzene)dichromium, 108058-59-9; $(\mu,\eta^6,\eta^6$–naphthlene)bix$(\eta^6$–toluene)dichromium, 108081-57-8; $(\mu,\eta^6,\eta^6$–naphthalene)bis$(\eta^6$–mesitylene)dichromium, 108058-61-3; bis$(\eta^6$–dimethyldiphenylsilane)chromium, 108008-86-2; bix$(\eta^6$–tetralin)chromium, 93646-21-0; naphthalene, 91-20-3.

**Supplementary Material Available:** Tables of anisotropic thermal parameters for non-hydrogen atoms, bond lengths and angles, and least-squares planes and dihedral angles (3 pages). Ordering information is given on any current masthead page.

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# Syntheses and Structural Comparison of the $\eta^6$-Arene Complexes $Sm(C_6Me_6)(AlCl_4)_3$ and $U(C_6Me_6)(AlCl_4)_3$

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*Received December 24, 1986*

The mononuclear complexes $M(C_6Me_6)(AlCl_4)_3$ of U(III), 1, and Sm(III), 2, have been prepared and structurally characterized. Although their crystals are not isomorphous because of solvent molecules in the crystal lattice of 2, the molecular complexes are isostructural and therefore permit a meaningful comparison of the geometrical properties of an actinide and a lanthanide arene complex. $U(C_6Me_6)(AlCl_4)_3$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.816$ (5) Å, $b = 17.918$ (8) Å, $c = 9.730$ (4) Å, $\alpha = 96.09$ (3)°, $\beta = 118.91$ (3)°, $\gamma = 80.98$ (3)°, $V = 1479$ (2) Å$^3$, and $Z = 2$. Crystals of $Sm(C_6Me_6)(AlCl_4)_3\cdot 1.5C_7H_8$ belong to the monoclinic crystal class, space group $P2_1/c$, with $a = 18.696$ (4) Å, $b = 16.906$ (3) Å, $c = 12.262$ (2) Å, $\beta = 100.8$ (2)°, $V = 3807$ (2) Å$^3$, and $Z = 4$. In general, comparable M–ligand bond lengths reflect the difference in the ionic radii of uranium and samarium. This suggests that the acceptor orbitals are comparable in the actinide and the lanthanide complexes and that, consequently, f orbitals are not substantially involved in arene bonding.

## Introduction

There is now ample evidence that arene derivatives of f-block elements are surprisingly stable compounds in that structurally characterized examples of U(III),[1,2] U(IV),[3,4] and Sm(III)[5] are available. The $\eta^6$-coordination of the neutral arenes leaves no doubt that thermodynamically stable dative $\pi$-bonds can be formed with f elements, albeit, as the samarium complex would suggest, without significant participation of f orbitals.

When $Sm(hmb)(AlCl_4)_3$ (**2**) was found to be structurally related to a previously reported benzene complex of U(III), $U(C_6H_6)(AlCl_4)_3$ (**3**),[1] we decided to pursue the synthesis of the mononuclear hmb derivative of U(III) in order to evaluate the structural changes that occur upon lanthanide vs. actinide substitution in arene complexes. The abovementioned benzene complex **3** appeared unsuitable for this purpose because we had observed that steric interactions of the methyl substituents play an important role in determining the structural details of the samarium complex. More importantly, the benzene ring in compound **3** had not been included in the refinement but rather was fitted to the Fourier map with idealized geometry.

We have now prepared a homologous pair of hmb complexes of Sm(III) and U(III) which allows a meaningful comparison of the structural data.

## Experimental Section

All preparations were performed in an atmosphere of purified argon in Schlenk-type glassware. Solvents were distilled under $N_2$ from appropriate drying agents and transferred with syringes. $AlCl_3$ was sublimed prior to use. $SmCl_3$ (Alfa) and hmb (Kodak) were used as received. $UCl_4$ was prepared by published procedures.[6]

**Preparation of $M(hmb)(AlCl_4)_3$ (M = U, Sm).** In a typical experiment 1 mmol of the respective metal halide ($SmCl_3$, $UCl_4$), 405 mg (2.5 mmol) of hmb, and 1 g (7.5 mmol) of $AlCl_3$ were boiled under reflux in toluene for ca. 30 min before 100 mg of aluminum foil (in strips) was added from a side-arm flask. The foil had previously been cleaned with acetone and $CH_2Cl_2$. Reflux was continued for 5 h during which time a color change to blood red (Sm) or maroon (U) occurred. The solutions were filtered hot

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**Table I. Crystal Data for the Arene Complexes 1 and 2**

| | 1 | 2 |
|---|---|---|
| formula | $U(C_6Me_6)(AlCl_4)_3$ | $Sm(C_6Me_6)(AlCl_4)\cdot 1.5C_7H_8$ |
| fw | 906.7 | 963.2 |
| space group | $P\bar{1}$ | $P2_1/c$ |
| systematic absences | | $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$ |
| $a$, Å | 9.816 (5) | 18.696 (4) |
| $b$, Å | 17.918 (8) | 16.906 (3) |
| $c$, Å | 9.730 (4) | 12.262 (2) |
| $\alpha$, deg | 96.09 (3) | |
| $\beta$, deg | 118.91 (2) | 100.81 (2) |
| $\gamma$, deg | 80.98 (3) | |
| $V$, Å$^3$ | 1479 (2) | 3807 (2) |
| $Z$ | 2 | 4 |
| $d_{calcd}$, g/cm$^3$ | 2.04 | 1.68 |
| cryst size, mm | 0.3 × 0.2 × 0.2 | 0.3 × 0.2 × 0.2 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 63.92 | 24.83 |
| data collect instrument | Syntex P3 | Syntex P3 |
| radiatn (monochromated in incident beam) | Mo K$\alpha$ ($\lambda_{\bar{\alpha}}$ = 0.71073 Å) | |
| orientatn reflectns, no. range (2$\theta$) | 25, 16–28 | 25, 15–30 |
| temp, °C | 22 | 22 |
| scan method | $\omega$ | $\omega$ |
| data collectn range, 2$\theta$, deg | 4–45 | 4–45 |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 3785, 2630 | 3286, 2018 |
| no. of parameters refined | 253 | 287 |
| trans. factors, max, min (exptl) | 1.0, 0.64 | 1.0, 0.87 |
| cryst. decay (corrected) | 24.5 | 27% |
| $R^a$ | 0.051 | 0.053 |
| $R_w{}^b$ | 0.062 | 0.062 |
| quality-of-fit indicator$^c$ | 1.14 | 0.98 |
| largest shift/esd, final cycle | 0.02 | 0.9 (disordered solvent) |
| largest peak, e/Å$^3$ | 1.0 (near U) | 0.8 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

into preheated receiving flasks and allowed to cool slowly to room temperature.

In the case of uranium, crystals of 1 deposited upon cooling and were filtered off immediately. The mother liquor afforded more of the dark brown material, albeit contaminated with a yellowish white precipitate. The crystals, once deposited, are only sparingly soluble in hot toluene. They are exceedingly sensitive to air and moisture and seem to undergo reactions with halocarbon or donor solvents. Yield of pure 1: 310 mg (34%).

In the preparation of the samarium complex no deposition is usually observed upon cooling, although occasionally droplets of a red oil were encountered. In that case the solution is decanted once more after cooling. Compound 2 is deposited in crudely crystalline form within days. Several batches were collected by filtration. The collection was discontinued when a red tarry residue started precipitating together with crystals of 2. This tar is insoluble in all solvents which are nondestructive for compound 2 and therefore impossible to separate. The total isolated yield of 2 was 60 mg (14%). Addition of $CH_2Cl_2$ to the red solution (assumed to be a compound of Sm(II)) resulted in a color change to yellow within 3 h, but only oily residues have so far been obtained.

**X-ray Crystallography.** Since both compounds are very sensitive to air, the crystals for X-ray work were embedded in Lindemann glass capillaries and sealed under argon. All geometrical and intensity data were obtained by automated four-circle diffractometers.

**Structure 1.** The raw data in the unique half-sphere were corrected for isotropic decay (26.5% over 63 h of data collection) and absorption (semiempirical, based on the intensity variations observed during azimuthal scans of nine reflections with Eurlerian angle $\chi$ close to 90°). A model for the U position was derived from a three-dimensional Patterson map, assuming the centrosymmetric space group $P\bar{1}$. The remainder of the structure developed smoothly during the iterative application of least-squares cycles and difference Fourier maps.[7] The refinement converged at residuals $R = 0.051$ and $R_w = 0.062$. Many data pertaining to data collection and refinement are listed in Table I.

**Structure 2.** The data were corrected for decay and absorption as above. The centrosymmetric space group $P2_1/c$ was uniquely determined by the systematic absences. A model for the Sm position was derived from the Patterson map and the structure developed by consecutive least-squares procedures and difference Fourier maps. There are two toluene molecules of crystallization in the lattice. One occupies a general site without significant signs of disorder. The entire molecule was located in the difference Fourier map and refined as a rigid group.[8] A second molecule of toluene was located around a center of inversion. It had to be refined in two preferred orientations. No effort was made to refine the methyl group which is consequently disordered over at least 12 sites. The refinement converged at residuals $R = 0.053$ and $R_w = 0.063$. Fractional coordinates for compounds 1 and 2 are listed in Tables II and III, respectively.

## Results and Discussion

**Syntheses.** Our previous synthesis of a U(III)–arene complex under reducing Friedel–Crafts conditions with stoichiometric amounts of $AlCl_3$ afforded a trinuclear complex.[2] The same conditions were unsuccessfully employed in an attempt to synthesize the arene complex of a lanthanide metal, samarium, and product formation was observed only when $AlCl_3$ was added in massive molar excess. Undoubtedly it is instrumental in assisting the solubilization of the metal halide and thus promoting the arylation reaction as well as the reduction step. The blood red color of the solution is indicative for a Sm(II) compound, but the only product characterized at this time is a derivative of Sm(III), $Sm(C_6Me_6)(AlCl_4)_3$ (2). Although formally no reduction is required for the formation of 2, we have so far failed to prepare it by any other, more direct route.

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[7] The Enraf-Nonius Structure Determination Package (VAXSDP) was used for all crystallographic computation unless otherwise stated.

[8] Sheldrick, G. M. SHELX-76, a Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

**Table II. Positional Parameters and Their Estimated Standard Deviations for Compound 1**[a]

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| U(1) | 0.14920 (7) | 0.24831 (4) | 0.10896 (6) | 3.19 (1) |
| Cl(1) | 0.0821 (5) | 0.4046 (3) | 0.0174 (5) | 5.0 (1) |
| Cl(2) | 0.4336 (5) | 0.3170 (3) | 0.2188 (5) | 5.6 (1) |
| Cl(3) | 0.3836 (7) | 0.5150 (3) | 0.2480 (7) | 7.8 (2) |
| Cl(4) | 0.3622 (6) | 0.4209 (4) | −0.0962 (6) | 8.1 (2) |
| Cl(5) | 0.1575 (5) | 0.2364 (3) | −0.1889 (4) | 5.2 (1) |
| Cl(6) | −0.1654 (4) | 0.2731 (3) | −0.1439 (4) | 4.5 (1) |
| Cl(7) | −0.1924 (7) | 0.1666 (4) | −0.4720 (6) | 8.5 (2) |
| Cl(8) | −0.1566 (7) | 0.3600 (4) | −0.4452 (5) | 8.2 (2) |
| Cl(9) | 0.4167 (5) | 0.1349 (3) | 0.1800 (6) | 5.6 (1) |
| Cl(10) | 0.0504 (5) | 0.1020 (3) | −0.0190 (5) | 5.1 (1) |
| Cl(11) | 0.3335 (6) | −0.0478 (3) | 0.1785 (7) | 7.7 (2) |
| Cl(12) | 0.2963 (6) | 0.0186 (3) | −0.1690 (6) | 7.1 (2) |
| Al(1) | 0.3234 (6) | 0.4223 (3) | 0.0947 (6) | 5.0 (1) |
| Al(2) | −0.0959 (6) | 0.2589 (4) | −0.3298 (5) | 5.4 (2) |
| Al(3) | 0.2858 (6) | 0.0431 (3) | 0.0400 (6) | 4.8 (1) |
| C(1) | −0.051 (2) | 0.240 (1) | 0.245 (1) | 4.9 (5) |
| C(2) | 0.078 (2) | 0.185 (1) | 0.332 (2) | 4.8 (4) |
| C(3) | 0.222 (2) | 0.204 (1) | 0.424 (2) | 6.5 (5) |
| C(4) | 0.247 (2) | 0.281 (1) | 0.443 (2) | 5.8 (5) |
| C(5) | 0.120 (2) | 0.339 (1) | 0.366 (2) | 5.8 (5) |
| C(6) | −0.028 (2) | 0.318 (1) | 0.269 (2) | 5.2 (4) |
| C(7) | −0.214 (2) | 0.216 (2) | 0.147 (2) | 10.1 (9) |
| C(8) | 0.050 (3) | 0.103 (1) | 0.328 (2) | 10.2 (7) |
| C(9) | 0.365 (3) | 0.147 (2) | 0.522 (2) | 10.9 (8) |
| C(10) | 0.410 (3) | 0.304 (2) | 0.566 (2) | 13 (1) |
| C(11) | 0.145 (3) | 0.421 (1) | 0.407 (2) | 10.5 (9) |
| C(12) | −0.166 (2) | 0.375 (1) | 0.186 (2) | 8.2 (6) |

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{22}]$.

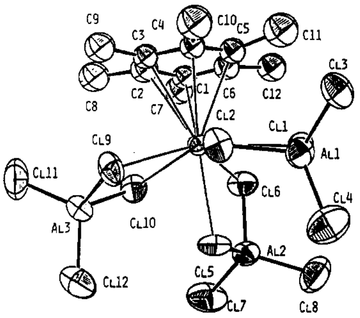

**Figure 1.** Perspective drawing of the $M(C_6Me_6)(AlCl_4)_3$ (M = U, Sm) complexes. The atom numbering scheme pertains to both structures.

We then realized that **2** was in many ways structurally related to our previously characterized trinuclear hmb complex of U(III), $[U_3(hmb)_3(AlCl_4)_3(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_3]^+$ (**4**). Specifically, a mononuclear compound akin to **2** can formally be derived from **4** by substitution of the Cl bridges by $AlCl_4$ moieties. Consequently we repeated the reductive arylation of $UCl_4$ in the presence of a large excess of $AlCl_3$ and obtained the desired mononuclear species **1**.

**Structural Results.** The molecular hmb complexes $U(C_6Me_6)(AlCl_4)_3$ and $Sm(C_6Me_6)(AlCl_4)_3$ are isostructural even though their crystals are not isomorphous because of solvent molecules in the crystal lattice of **2**. A perspective drawing of the molecular complexes is shown in Figure 1. The atom numbering scheme pertains to both complexes. Important bond lengths and angles are listed in Tables IV and V for compound **1** and **2**, respectively.

The coordination polyhedra of the metal atoms are best described as pentagonal bipyramids. Two of the three bidentate $AlCl_4$ ligands (Al1 and Al3) are located in the equatorial plane. The third $AlCl_4$ unit (Al2) spans one of the slant edges so as to complete with Cl(6) the equatorial pentagon while Cl(5) occupies an apical site. The hmb moiety occupies the second apical position. There is no crystallographic symmetry imposed on either compound though the virtual symmetry is $C_s$. The Cl–M–Cl bond angles for adjacent chlorine atoms are within the ranges

**Table III. Positional Parameters and Their Estimated Standard Deviations for Compound 2**[a]

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Sm | 0.28370 (6) | 0.07336 (6) | 0.09815 (9) | 2.84 (2) |
| Cl(1) | 0.1436 (3) | 0.0459 (3) | −0.0414 (5) | 4.4 (1) |
| Cl(2) | 0.1863 (3) | 0.1985 (3) | 0.1208 (5) | 5.0 (2) |
| Cl(3) | 0.0042 (3) | 0.1397 (4) | 0.0675 (6) | 7.4 (2) |
| Cl(4) | 0.0768 (5) | 0.2280 (5) | −0.1471 (7) | 9.0 (3) |
| Cl(5) | 0.2923 (3) | 0.1686 (3) | −0.0884 (5) | 4.8 (2) |
| Cl(6) | 0.3024 (3) | −0.0281 (3) | −0.0817 (5) | 4.7 (2) |
| Cl(7) | 0.4091 (4) | 0.0760 (5) | −0.2399 (6) | 7.8 (2) |
| Cl(8) | 0.2206 (4) | 0.0605 (5) | −0.3296 (6) | 8.3 (2) |
| Cl(9) | 0.3633 (3) | 0.2030 (3) | 0.2061 (5) | 5.0 (2) |
| Cl(10) | 0.4352 (3) | 0.0594 (3) | 0.0863 (5) | 4.6 (2) |
| Cl(11) | 0.5509 (4) | 0.1622 (4) | 0.2951 (7) | 8.0 (2) |
| Cl(12) | 0.4882 (4) | 0.2553 (4) | 0.0395 (7) | 8.1 (2) |
| Al(1) | 0.0950 (4) | 0.1574 (4) | −0.0056 (6) | 4.9 (2) |
| Al(2) | 0.3073 (4) | 0.0687 (4) | −0.1955 (5) | 4.3 (2) |
| Al(3) | 0.4677 (4) | 0.1750 (4) | 0.1578 (6) | 4.9 (2) |
| C(1) | 0.322 (1) | −0.072 (1) | 0.211 (2) | 4.3 (6) |
| C(2) | 0.350 (1) | −0.016 (2) | 0.296 (2) | 5.6 (8) |
| C(3) | 0.304 (1) | 0.039 (1) | 0.338 (2) | 4.1 (6) |
| C(4) | 0.228 (1) | 0.032 (1) | 0.297 (2) | 4.0 (6) |
| C(5) | 0.198 (1) | −0.024 (1) | 0.219 (2) | 4.4 (7) |
| C(6) | 0.245 (1) | −0.075 (1) | 0.175 (2) | 4.9 (6) |
| C(7) | 0.372 (1) | −0.130 (1) | 0.175 (2) | 6.1 (8) |
| C(8) | 0.433 (1) | −0.016 (2) | 0.349 (2) | 7.4 (9) |
| C(9) | 0.335 (2) | 0.095 (1) | 0.428 (2) | 6.7 (8) |
| C(10) | 0.175 (1) | 0.084 (2) | 0.352 (2) | 7.5 (9) |
| C(11) | 0.113 (1) | −0.039 (1) | 0.196 (2) | 6.8 (8) |
| C(12) | 0.211 (1) | −0.142 (1) | 0.094 (2) | 6.2 (8) |
| C(13) | 0.2027 (8) | 0.7483 (8) | 0.348 (1) | 8.4 (8)* |
| C(14) | 0.2751 (8) | 0.7526 (8) | 0.369 (1) | 6.8 (7)* |
| C(15) | 0.3078 (8) | 0.8091 (8) | 0.445 (1) | 7.7 (7)* |
| C(16) | 0.2678 (8) | 0.8627 (8) | 0.495 (1) | 10.0 (9)* |
| C(17) | 0.1895 (8) | 0.8590 (8) | 0.479 (1) | 9.1 (8)* |
| C(18) | 0.1557 (8) | 0.7994 (8) | 0.402 (1) | 6.5 (6)* |
| C(19) | 0.1534 (8) | 0.6918 (8) | 0.275 (1) | 12 (1)* |
| C(20) | 0.011 (3) | 0.913 (2) | 0.571 (4) | 6 (1)* |
| C(21) | −0.023 (3) | 0.904 (2) | 0.451 (4) | 6 (1)* |
| C(22) | −0.021 (3) | −0.003 (2) | 0.409 (4) | 6 (2)* |
| C(23) | 0.003 (3) | 0.052 (3) | 0.483 (5) | 5 (1)* |
| C(24) | 0.029 (4) | 0.061 (4) | 0.612 (6) | 9 (2)* |
| C(25) | 0.032 (4) | −0.034 (5) | 0.646 (6) | 10 (2)* |

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

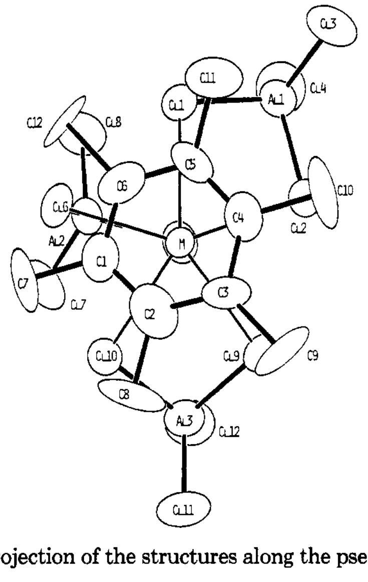

**Figure 2.** Projection of the structures along the pseudopentagonal axis.

**Table IV. Selected Bond Distances (Å) and Angles (deg) for Compound 1**[a]

| atom 1 | atom 2 | dist | atom 1 | atom 2 | dist | atom 1 | atom 2 | dist |
|---|---|---|---|---|---|---|---|---|
| U(1) | Cl(1) | 2.908 (5) | U(1) | C(3) | 2.95 (2) | Cl(6) | Al(2) | 2.201 (8) |
| U(1) | Cl(2) | 2.891 (5) | U(1) | C(4) | 2.927 (14) | Cl(7) | Al(2) | 2.070 (9) |
| U(1) | Cl(5) | 2.922 (5) | U(1) | C(5) | 2.95 (2) | Cl(8) | Al(2) | 2.084 (9) |
| U(1) | Cl(6) | 2.871 (3) | U(1) | C(6) | 2.93 (2) | Cl(9) | Al(3) | 2.169 (7) |
| U(1) | Cl(9) | 2.893 (5) | Cl(1) | Al(1) | 2.177 (8) | Cl(10) | Al(3) | 2.206 (7) |
| U(1) | Cl(10) | 2.882 (5) | Cl(2) | Al(1) | 2.185 (7) | Cl(11) | Al(3) | 2.075 (9) |
| U(1) | Al(2) | 3.762 (4) | Cl(3) | Al(1) | 2.064 (8) | Cl(12) | Al(3) | 2.083 (9) |
| U(1) | C(1) | 2.88 (2) | Cl(4) | Al(1) | 2.065 (9) | | | |
| U(1) | C(2) | 2.96 (2) | Cl(5) | Al(2) | 2.176 (6) | | | |

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cl(1) | U(1) | Cl(2) | 68.4 (1) | Cl(6) | U(1) | C(1) | 74.5 (2) | C(3) | U(1) | C(4) | 27.7 (6) |
| Cl(1) | U(1) | Cl(5) | 76.8 (1) | Cl(6) | U(1) | C(2) | 98.0 (3) | C(3) | U(1) | C(5) | 49.6 (6) |
| Cl(1) | U(1) | Cl(6) | 70.9 (1) | Cl(6) | U(1) | C(3) | 122.8 (4) | C(3) | U(1) | C(6) | 57.4 (5) |
| Cl(1) | U(1) | Cl(9) | 132.9 (2) | Cl(6) | U(1) | C(4) | 125.9 (3) | C(4) | U(1) | C(5) | 28.3 (5) |
| Cl(1) | U(1) | Cl(10) | 140.3 (1) | Cl(6) | U(1) | C(5) | 101.3 (3) | C(4) | U(1) | C(6) | 48.9 (4) |
| Cl(1) | U(1) | Al(2) | 70.0 (1) | Cl(6) | U(1) | C(6) | 77.1 (3) | C(5) | U(1) | C(6) | 27.2 (5) |
| Cl(1) | U(1) | C(1) | 103.8 (4) | Cl(9) | U(1) | Cl(10) | 6.91 (1) | U(1) | Cl(1) | Al(1) | 96.6 (2) |
| Cl(1) | U(1) | C(2) | 127.3 (4) | Cl(9) | U(1) | Al(2) | 108.9 (1) | U(1) | Cl(2) | Al(1) | 96.9 (2) |
| Cl(1) | U(1) | C(3) | 123.3 (4) | Cl(9) | U(1) | C(1) | 119.4 (4) | U(1) | Cl(5) | Al(2) | 94.0 (2) |
| Cl(1) | U(1) | C(4) | 96.8 (5) | Cl(9) | U(1) | C(2) | 91.5 (3) | U(1) | Cl(6) | Al(2) | 94.8 (2) |
| Cl(1) | U(1) | C(5) | 74.5 (4) | Cl(9) | U(1) | C(3) | 78.9 (4) | U(1) | Cl(9) | Al(3) | 96.8 (2) |
| Cl(1) | U(1) | C(6) | 78.0 (4) | Cl(9) | U(1) | C(4) | 91.7 (4) | U(1) | Cl(10) | Al(3) | 96.3 (2) |
| Cl(2) | U(1) | Cl(5) | 82.8 (1) | Cl(9) | U(1) | C(5) | 119.7 (3) | Cl(1) | Al(1) | Cl(2) | 96.7 (3) |
| Cl(2) | U(1) | Cl(6) | 135.5 (1) | Cl(9) | U(1) | C(6) | 136.3 (3) | Cl(1) | Al(1) | Cl(3) | 110.7 (4) |
| Cl(2) | U(1) | Cl(9) | 68.7 (1) | Cl(10) | U(1) | Al(2) | 71.2 (1) | Cl(1) | Al(1) | Cl(4) | 110.3 (3) |
| Cl(2) | U(1) | Cl(10) | 135.7 (1) | Cl(10) | U(1) | C(1) | 81.1 (4) | Cl(2) | Al(1) | Cl(3) | 111.1 (3) |
| Cl(2) | U(1) | Al(2) | 110.9 (2) | Cl(10) | U(1) | C(2) | 73.2 (3) | Cl(2) | Al(1) | Cl(4) | 109.7 (4) |
| Cl(2) | U(1) | C(1) | 132.5 (3) | Cl(10) | U(1) | C(3) | 89.9 (4) | Cl(3) | Al(1) | Cl(4) | 116.5 (4) |
| Cl(2) | U(1) | C(2) | 120.8 (3) | Cl(10) | U(1) | C(4) | 117.5 (5) | U(1) | Al(2) | Cl(5) | 50.8 (2) |
| Cl(2) | U(1) | C(3) | 94.8 (4) | Cl(10) | U(1) | C(5) | 128.7 (5) | U(1) | Al(2) | Cl(6) | 49.5 (1) |
| Cl(2) | U(1) | C(4) | 76.8 (4) | Cl(10) | U(1) | C(6) | 108.9 (4) | U(1) | Al(2) | Cl(7) | 122.5 (3) |
| Cl(2) | U(1) | C(5) | 84.8 (4) | Al(2) | U(1) | C(1) | 109.3 (2) | U(1) | Al(2) | Cl(8) | 122.2 (3) |
| Cl(2) | U(1) | C(6) | 110.7 (4) | Al(2) | U(1) | C(2) | 128.3 (3) | Cl(5) | Al(2) | Cl(6) | 100.3 (2) |
| Cl(5) | U(1) | Cl(6) | 70.9 (1) | Al(2) | U(1) | C(3) | 154.2 (4) | Cl(5) | Al(2) | Cl(7) | 112.2 (4) |
| Cl(5) | U(1) | Cl(9) | 79.3 (1) | Al(2) | U(1) | C(4) | 159.4 (4) | Cl(5) | Al(2) | Cl(8) | 110.3 (4) |
| Cl(5) | U(1) | Cl(10) | 76.7 (2) | Al(2) | U(1) | C(5) | 131.3 (3) | Cl(6) | Al(2) | Cl(7) | 108.0 (4) |
| Cl(5) | U(1) | Al(2) | 35.2 (1) | Al(2) | U(1) | C(6) | 111.3 (3) | Cl(6) | Al(2) | Cl(8) | 109.7 (4) |
| Cl(5) | U(1) | C(1) | 143.1 (2) | C(1) | U(1) | C(2) | 28.3 (4) | Cl(7) | Al(2) | Cl(8) | 115.2 (3) |
| Cl(5) | U(1) | C(2) | 149.8 (3) | C(1) | U(1) | C(3) | 48.7 (5) | Cl(9) | Al(3) | Cl(10) | 96.9 (3) |
| Cl(5) | U(1) | C(3) | 157.4 (4) | C(1) | U(1) | C(4) | 57.2 (4) | Cl(9) | Al(3) | Cl(11) | 110.7 (3) |
| Cl(5) | U(1) | C(4) | 159.5 (4) | C(1) | U(1) | C(5) | 49.4 (6) | Cl(9) | Al(3) | Cl(12) | 113.6 (4) |
| Cl(5) | U(1) | C(5) | 151.2 (4) | C(1) | U(1) | C(6) | 28.6 (6) | Cl(10) | Al(3) | Cl(11) | 109.4 (4) |
| Cl(5) | U(1) | C(6) | 144.2 (3) | C(2) | U(1) | C(3) | 26.1 (5) | Cl(10) | Al(3) | Cl(12) | 107.7 (3) |
| Cl(6) | U(1) | Cl(9) | 135.8 (1) | C(2) | U(1) | C(4) | 47.5 (5) | Cl(11) | Al(3) | Cl(12) | 116.5 (4) |
| Cl(6) | U(1) | Cl(10) | 72.7 (1) | C(2) | U(1) | C(5) | 56.6 (6) | | | | |
| Cl(6) | U(1) | Al(2) | 35.7 (1) | C(2) | U(1) | C(6) | 49.6 (5) | | | | |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

of 68.4–72.7° and 69.4–71.1° for U and Sm, respectively. The equatorial chlorine atoms thus define a fairly regular pentagon with deviations of individual Cl atoms from the mean plane of less than 0.08 and 0.09 Å for **1** and **2**, respectively. The metal atoms are substantially displaced from the mean plane toward the arene ring (0.641 and 0.629 Å for **1** and **2**, respectively. The major distortion from the idealized pentagonal-bipyramidal geometry is a kink in the pseudopentagonal axis. The reason for it becomes obvious from Figure 2 in which the complexes are viewed along the M–Cl(5) axis. A parallel stacking of a regular hexagon (the hmb molecule) and a regular pentagon (the equatorial Cl atoms) will always entail some eclipsed and some staggered interactions. In our examples, the most prominent steric interactions occur between the methyl substituents of the benzene ring and the equatorial chlorine atoms and manifest themselves in the displacement of the metal atom from the pentagonal plane. Some of this strain is relieved by tilting and shifting the hmb molecule toward the uncongested site of Cl(6). Note that the apparent eclipses of C(7) and Cl(7) as well of C(12) and Cl(8) do not represent a close contact as both Cl atoms in question point away from the equatorial plane. This is easily verified in Figure 1. There is no significant deviation of the hmb moiety from $D_{6h}$ symmetry in either **1** or **2**.

Compounds **1** and **2** provide the unique opportunity of a direct comparison of the structural data of a pair of isomorphous lanthanide and actinide arene complexes. The metal–ligand bonding contacts, averaged according to the virtual $C_s$ symmetry, are listed in Table VI. The Al–Cl bond lengths are also included as an internal reference. Overall, comparable metal–ligand distances are systematically shorter in the samarium complex. This is to be expected as the ionic radii of Sm(III) and U(III) are 0.964 and 1.025 Å, respectively. Focussing our attention first on the M–Cl distances we are confronted with a rather surprising variation in the differences between comparable bond lengths. In one extreme, the M–Cl(5) (the apical Cl atom) is shorter in the samarium complex by 0.096 Å ($\Delta/\sigma$ = 16). In the other extreme there is no significant difference between the two compounds as far as the M–Cl(6) distance is concerned ($\Delta$ = 0.005 Å; $\Delta/\sigma$ = 1). The differences between the remaining two M–Cl bonds involving Cl atoms of the pentagonal plane are 0.064 and 0.007 Å. That this apparently erratic behavior of the differences in the M–Cl bond lengths is not an artifact of refinement or crystal quality is evident from a comparison of the Al–Cl distances, of which there are two sets, bridging and ter-

**Table V. Selected Bond Distances (Å) and Angles (deg) for Compound 2[a]**

| atom 1 | atom 2 | dist | atom 1 | atom 2 | dist | atom 1 | atom 2 | dist |
|---|---|---|---|---|---|---|---|---|
| Sm | Cl(1) | 2.886 (5) | Sm | C(3) | 2.95 (2) | Cl(5) | Al(2) | 2.189 (9) |
| Sm | Cl(2) | 2.839 (6) | Sm | C(4) | 2.92 (2) | Cl(6) | Al(2) | 2.164 (9) |
| Sm | Cl(5) | 2.826 (6) | Sm | C(5) | 2.89 (3) | Cl(7) | Al(2) | 2.078 (10) |
| Sm | Cl(6) | 2.866 (6) | Sm | C(6) | 2.82 (2) | Cl(8) | Al(2) | 2.086 (9) |
| Sm | Cl(9) | 2.834 (5) | Cl(1) | Al(1) | 2.173 (9) | Cl(9) | Al(3) | 2.195 (10) |
| Sm | Cl(10) | 2.843 (6) | Cl(2) | Al(1) | 2.193 (9) | Cl(10) | Al(3) | 2.181 (9) |
| Sm | C(1) | 2.84 (2) | Cl(3) | Al(1) | 2.085 (11) | Cl(11) | Al(3) | 2.078 (10) |
| Sm | C(2) | 2.93 (3) | Cl(4) | Al(1) | 2.081 (11) | Cl(12) | Al(3) | 2.074 (11) |

| atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle | atom 1 | atom 2 | atom 3 | angle |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cl(1) | Sm | Cl(2) | 69.5 (2) | Cl(6) | Sm | Cl(9) | 133.9 (2) | C(3) | Sm | C(4) | 28.2 (6) |
| Cl(1) | Sm | Cl(5) | 78.2 (2) | Cl(6) | Sm | Cl(10) | 69.4 (2) | C(3) | Sm | C(5) | 50.1 (6) |
| Cl(1) | Sm | Cl(6) | 71.1 (2) | Cl(6) | Sm | C(1) | 78.7 (5) | C(3) | Sm | C(6) | 58.9 (6) |
| Cl(1) | Sm | Cl(9) | 137.8 (2) | Cl(6) | Sm | C(2) | 103.7 (5) | C(4) | Sm | C(5) | 27.8 (6) |
| Cl(1) | Sm | Cl(10) | 138.6 (2) | Cl(6) | Sm | C(3) | 129.6 (5) | C(4) | Sm | C(6) | 49.6 (6) |
| Cl(1) | Sm | C(1) | 105.5 (5) | Cl(6) | Sm | C(4) | 128.1 (4) | C(5) | Sm | C(6) | 28.4 (7) |
| Cl(1) | Sm | C(2) | 127.1 (5) | Cl(6) | Sm | C(5) | 102.3 (5) | Sm | Cl(1) | Al(1) | 96.2 (3) |
| Cl(1) | Sm | C(3) | 119.5 (5) | Cl(6) | Sm | C(6) | 78.6 (5) | Sm | Cl(2) | Al(1) | 97.1 (3) |
| Cl(1) | Sm | C(4) | 91.7 (5) | Cl(9) | Sm | Cl(10) | 69.6 (2) | Sm | Cl(5) | Al(2) | 94.6 (3) |
| Cl(1) | Sm | C(5) | 71.5 (4) | Cl(9) | Sm | C(1) | 112.2 (5) | Sm | Cl(6) | Al(2) | 94.0 (3) |
| Cl(1) | Sm | C(6) | 78.2 (5) | Cl(9) | Sm | C(2) | 84.8 (5) | Sm | Cl(9) | Al(3) | 97.1 (3) |
| Cl(2) | Sm | Cl(5) | 77.8 (2) | Cl(9) | Sm | C(3) | 74.3 (4) | Sm | Cl(10) | Al(3) | 96.3 (3) |
| Cl(2) | Sm | Cl(6) | 134.0 (2) | Cl(9) | Sm | C(4) | 91.9 (4) | Cl(1) | Al(1) | Cl(2) | 96.8 (3) |
| Cl(2) | Sm | Cl(9) | 70.6 (2) | Cl(9) | Sm | C(5) | 119.6 (5) | Cl(1) | Al(1) | Cl(3) | 111.6 (4) |
| Cl(2) | Sm | Cl(10) | 136.3 (2) | Cl(9) | Sm | C(6) | 132.5 (4) | Cl(1) | Al(1) | Cl(4) | 109.8 (4) |
| Cl(2) | Sm | C(1) | 134.5 (5) | Cl(10) | Sm | C(1) | 78.2 (5) | Cl(2) | Al(1) | Cl(3) | 109.3 (4) |
| Cl(2) | Sm | C(2) | 118.7 (6) | Cl(10) | Sm | C(2) | 74.6 (6) | Cl(2) | Al(1) | Cl(4) | 113.0 (4) |
| Cl(2) | Sm | C(3) | 90.9 (5) | Cl(10) | Sm | C(3) | 95.2 (5) | Cl(3) | Al(1) | Cl(4) | 115.0 (4) |
| Cl(2) | Sm | C(4) | 75.9 (5) | Cl(10) | Sm | C(4) | 122.4 (5) | Cl(5) | Al(2) | Cl(6) | 99.8 (3) |
| Cl(2) | Sm | C(5) | 87.0 (5) | Cl(10) | Sm | C(5) | 128.7 (5) | Cl(5) | Al(2) | Cl(7) | 109.8 (4) |
| Cl(2) | Sm | C(6) | 114.8 (6) | Cl(10) | Sm | C(6) | 105.1 (5) | Cl(5) | Al(2) | Cl(8) | 110.8 (4) |
| Cl(5) | Sm | Cl(6) | 71.6 (2) | C(1) | Sm | C(2) | 28.6 (7) | Cl(6) | Al(2) | Cl(7) | 111.4 (4) |
| Cl(5) | Sm | Cl(9) | 80.4 (2) | C(1) | Sm | C(3) | 50.9 (6) | Cl(6) | Al(2) | Cl(8) | 109.7 (4) |
| Cl(5) | Sm | Cl(10) | 78.5 (2) | C(1) | Sm | C(4) | 58.8 (7) | Cl(7) | Al(2) | Cl(8) | 114.3 (4) |
| Cl(5) | Sm | C(1) | 147.2 (5) | C(1) | Sm | C(5) | 51.0 (7) | Cl(9) | Al(3) | Cl(10) | 96.1 (4) |
| Cl(5) | Sm | C(2) | 152.4 (5) | C(1) | Sm | C(6) | 29.1 (7) | Cl(9) | Al(3) | Cl(11) | 111.8 (5) |
| Cl(5) | Sm | C(3) | 154.5 (4) | C(2) | Sm | C(3) | 27.8 (7) | Cl(9) | Al(3) | Cl(12) | 109.7 (4) |
| Cl(5) | Sm | C(4) | 153.8 (5) | C(2) | Sm | C(4) | 49.0 (7) | Cl(10) | Al(3) | Cl(11) | 110.0 (4) |
| Cl(5) | Sm | C(5) | 149.3 (4) | C(2) | Sm | C(5) | 57.9 (7) | Cl(10) | Al(3) | Cl(12) | 112.3 (4) |
| Cl(5) | Sm | C(6) | 146.6 (4) | C(2) | Sm | C(6) | 50.0 (7) | Cl(11) | Al(3) | Cl(12) | 115.3 (4) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

**Table VI. Comparison of Bond Lengths in 1 and 2**

| | M = Sm | M = U | Δ |
|---|---|---|---|
| M–C(1),C(6) | 2.83 [1] | 2.90 [2] | 0.07 |
| M–C(2),C(5) | 2.91 [3] | 2.96 [1] | 0.05 |
| M–C(3),C(4) | 2.94 [2] | 2.95 [2] | 0.01 |
| M–Cl(5) | 2.826 (6) | 2.922 (4) | 0.096 |
| M–Cl(6) | 2.866 (6) | 2.871 (4) | 0.005 |
| M–Cl(1),Cl(10) | 2.880 [9] | 2.887 [6] | 0.007 |
| M–Cl(2),Cl(9) | 2.837 [4] | 2.901 [11] | 0.064 |
| M(III) radius (ionic) | 0.964 | 1.025 | 0.061 |
| Al–Cl(bridging) | 2.183 [12] | 2.185 [15] | |
| Al–Cl(terminal) | 2.080 [5] | 2.074 [9] | |

minal ones. As would be expected, there is no statistically significant difference between comparable Al–Cl distances within each compound nor between compounds 1 and 2.

What, then is the reason for the substantial variation of M–Cl bond lengths? It seems unlikely that a change of the electronic structure between Sm and U would give raise to the observed pattern, especially the unsystematic variation of the M–Cl(equatorial) distances. We therefore propose that it is caused by steric factors, possibly including packing forces. Due to the smaller size of the samarium atom its entire coordination shell is contracted, thereby accentuating the steric congestion at the chlorine and methyl sites. Consequently it is altered so as to minimize the *totality* of interactions, and it is thus impossible to predict qualitatively where the most significant changes will materialize. The relatively wide range spanned by the differences of comparable bond length, viz., 0.005–0.096 Å, can be rationalized by the fact that very long bonds (ca. 2.95 Å) are involved for which rather shallow minima in the total energy hypersurface are expected.

With this in mind the differenes between the equally long M–C distances must not be overinterpreted. Since they cover about the same range as the M–Cl bonds (0.01–0.06 Å), we can conclude that the nature of the arene bonding in 1 and 2 is very similar. This implies that f orbitals do not play an important role in the $\pi$-bonding since the 4f orbitals in lanthanides are not assumed to extend radially beyond the closed $5s^25p^6$ shells.

Finally, Raymond and Eigenbrot have proposed a formalism within which the nature of the ligand bonding (covalent vs. ionic) is discussed in terms of structural criteria.[9] Their conclusion, based on the comparison of a large number of actinide, lanthanide, and d-transition-metal organometallics, is that the f-block derivatives show structural trends characteristic for the ionic bonding mode. The main basis of their argument is the plausible assumption that the geometries of ionic compounds tend to be irregular and depend on the steric bulk, and number, and charge of the ligands as a result of a balance between ionic attractive forces and nonbonded repulsions. Covalent bonds, on the other hand, are typified by regular geometries and directional bonds.

While the above definition certainly provides a reasonably good model for strong metal–ligand interactions, our

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(9) Raymond, K. N.; Eigenbrot, C. W., Jr. *Acc. Chem. Res.* **1980**, *13*, 283.

results indicate that the picture becomes blurry in the domain of long, weak bonds as encountered in f-metal complexes. The orientation of the hmb ligand, obviously not an anionic ligand, is clearly determined by steric interactions. Moreover, reducing the size of the central atom entails a rearrangement which affects the entire coordination sphere. The resulting differences in the lengths of equivalent bonds span a range comparable to the difference in ionic radii, the $\pi$-bonds of the neutral arene and the $\sigma$-bonds of the ionic $AlCl_4$ ligands being affected equally. We therefore conclude that the small structural changes in complexes with weakly bonded ligands are not suitable criteria for the evaluation of the nature of the bonds.

**Acknowledgment.** This work was supported by The Robert A. Welch Foundation (Grant No. A-494).

**Supplementary Material Available:** A full list of bond distances and angles and tables of anisotropic thermal parameters (9 pages); listings of observed and calculated structure factors (26 pages). Ordering information is given on current masthead page.

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# Metal Alkoxides—Models for Metal Oxides. 12.[1] The First Molecular Carbido Cluster of Tungsten $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ and $^{13}C$ NMR Spectroscopic Evidence for a Related Oxo–Carbido Cluster, $W_4(C)(O)(O\text{-}i\text{-}Pr)_{12}$, Formed in the Stepwise Reductive Cleavage of Carbon Monoxide by Lower Valent Tungsten Alkoxides

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The first molecular carbido tungsten cluster compound $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ is formed as a minor component in the reaction between $W_2(NMe_2)_6$ and $i$-PrOH ($\gg$6 equiv). The black crystalline compound has been characterized by elemental analysis, mass spectroscopy, $^1H$ and $^{13}C$ NMR spectroscopy, cyclic voltammetry, and a single-crystal X-ray study. There is a butterfly of tungsten atoms with five W–W edge distances of ca. 2.80 Å supported by bridging O-$i$-Pr ligands. The unique NMe ligand bridges a backbone–wingtip edge such that the molecule has no virtual element of symmetry. The $W_4(\mu\text{-}C)$ distances fall into two categories: backbone–W–C = 2.25 Å and wingtip–W–C = 1.93 Å (av). The bonding in this carbido cluster has been investigated by calculations employing the Fenske–Hall method on the $W_4(C)(OH)_{13}^+$ model cation constrained to $C_{2v}$ symmetry. The results of this calculation are compared with those recently reported for "iron-butterfly" carbido clusters, $Fe_4(\mu_4\text{-}C)$, supported by carbonyl ligands. The high-valent early-transition-metal and low-valent later transition-metal $M_4(\mu_4\text{-}C)$ clusters are related by an isolobal $d^3$–$d^9$ "hole formalism". In both the $W_4(\mu_4\text{-}C)$ and $Fe_4(\mu_4\text{-}C)$ clusters the stronger carbon-to-metal bonding to the wingtip metal atoms is reflected by (i) the shorter M–C distances and (ii) the atomic overlap population between the metal and carbon orbitals. The tungsten cluster shows a significant bonding interaction with the C 2s atomic orbital; this situation is not found in the $Fe_4(\mu_4\text{-}C)$ clusters. Spectroscopic evidence, based solely on $^{13}C$ NMR data, is presented for the formation of an isoelectronic and isostructural carbido–oxide cluster, $W_4(C)(O)(O\text{-}i\text{-}Pr)_{12}$, in the reaction between carbon monoxide and $W_2(O\text{-}t\text{-}Bu)_6$ (2 equiv) followed by addition of $i$-PrOH ($\gg$12 equiv). The stepwise sequence of C—O and W—W bond order reduction provides an extension to earlier studies of the reaction $W{\equiv}W + C{\equiv}O \rightarrow (W{=}W)(\mu\text{-}C{=}O) \rightarrow [(W\text{-}W)(\mu\text{-}C\text{-}O)]_2$: *Organometallics* **1986**, *5*, 2125. Crystal data for $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ at −165 °C: $a = 19.379$ (1) Å, $b = 12.516$ (1) Å, $c = 11.883$ (1) Å, $\alpha = 119.37$ (6)°, $\beta = 84.98$ (5)°, $\gamma = 98.79$ (5)°, $Z = 2$, $d_{calcd} = 1.988$ g cm$^{-3}$, and space group $P\bar{1}$.

## Introduction

Central to the theme of this research is the compatibility of ligands such as hydride, alkyl, aryl, alkylidene, alkylidyne, carbide ($C_2$ or $C_1$), etc. with cluster fragments of molybdenum and tungsten supported exclusively by alkoxide and/or oxide/alkoxide ligands. We have suggested that compounds formed from these ligands and the cluster fragments may provide models for the organometallic chemistry which occurs on the surfaces of the reduced oxides of these elements.[2] Irrespective of the validity of this suggestion, the organometallic chemistry of alkoxide-supported clusters is of fundamental interest and represents a totally new area of organometallic cluster chemistry. For these compounds to act as models for the reduced oxides, the ratio of alkoxide ligands (representing oxo ligands, either terminal or bridging) to hydrocarbyl ligands (or other ligands of interest, e.g. H or N) must be relatively large. Furthermore, the "organometallic" ligand to metal ratio should be small, in general less than one, although cluster compounds in which one metal atom is

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(1) Part 11: Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Tatz, R. J. *Organometallics* **1986**, *5*, 1599.

(2) (a) Chisholm, M. H. *ACS Symp. Ser.* **1983**, *No. 211*, 243. (b) Chisholm, M. H. *J. Solid State Chem.* **1985**, *57*, 120.