triangular $MoCu_2$ subunits share the Cu–Cu edge, forming a heteronuclear raft with a center of symmetry in the middle of the Cu–Cu edge. A planar tetrametallic framework constitutes a relatively new and expanding class of metallic cores in cluster chemistry.[12–14]

The Cu_2 unit, whose interatomic distance of 2.403 (1) Å is among the shortest yet observed in Cu(I) complexes,[15] also links two carborane cages via two Cu–H–B bridges. The Cu–(μ)-H distance of 1.69 (6) Å falls into the range (~1.70–2.08 Å) observed in copper hydroborate complexes.[16] The Mo–Cu distances (2.656 (1) and 2.834 (1) Å) represent the first values of heteronuclear Mo(0)–Cu(I) interatomic separation while values of Mo(VI)–Cu(I) distances (~2.611–2.775 Å) are available from the series of complexes of $[MoS_{4-n}O_n]^{2-}$ (n = 0, 1) with group Ib (group 11)[25] d^{10} metal ion.[17] The shorter Mo–Cu bond is associated with two CO groups which show semibridging (μ_2)[18] interactions with a copper atom. The Cu–C distances of 2.247 (7) and 2.251 (6) Å are similar to those observed in the mixed copper/iron/carbonyl clusters.[15g]

Assembly of clustered clusters **1** and **2**, which is a direct manifestation of the versatile electron-donor ability of the dicarbollide anion, proceeds via a mononuclear group VIa (group 6)[25] metallacarborane, [*closo*-3,3,3-$(CO)_3$-3-Tl-3,1,2-$MC_2B_9H_{11}]^{1-}$ (**3**),[19] according to eq 1 and 2. The present work provides the synthetic route to clustered metallacarboranes with the highest known nuclearity. The species **1**, **2**, $[Fe_2(CO)_4(C_2B_9H_{11})_2]^{2-}$,[20] [*closo*-3-($\mu$-CO)-8-$PPh_3$-3,1,2-$NiC_2B_9H_{10}]_2$,[21] and $[(PPh_3)Rh(C_2B_9H_{10}L)]_2$ (L = H;[5c,g] C_6H_5[5g]) along with bimetallic carborane complexes with W–M (M = Mo;[5h] W;[5h] Pt;[22] Rh;[23] Au[23]) interactions constitute the current set of characterized polynuclear transition metal complexes of the dicarbollide anion.[24] The further applications of [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ and **3** in cluster synthesis as well as the reactivity of **1** and **2** are under investigation.

$$\mathrm{Tl}[closo\text{-}3,1,2\text{-}\mathrm{TlC_2B_9H_{11}}] + \mathrm{(PPN)^+Cl^-} + \mathrm{[M(CO)_3(CH_3CN)_3]} \xrightarrow[\text{room temp}]{\mathrm{CH_3CN}} \mathrm{(PPN)}[closo\text{-}3,3,3\text{-}\mathrm{(CO)_3}\text{-}3\text{-}\mathrm{Tl}\text{-}3,1,2\text{-}\mathrm{MC_2B_9H_{11}}] + \mathrm{TlCl} + 3\ \mathrm{CH_3CN} \quad (1)$$

$$2\mathrm{(PPN)}[closo\text{-}3,3,3\text{-}\mathrm{(CO)_3}\text{-}3\text{-}\mathrm{Tl}\text{-}3,1,2\text{-}\mathrm{MC_2B_9H_{11}}] + 2\mathrm{CuCl} \xrightarrow{\mathrm{CH_3CN}} \mathrm{(PPN)_2[M_2Cu_2(\mu\text{-}CO)_4(CO)_2(\mu\text{-}H)_2(C_2B_9H_{10})_2]} + 2\ \mathrm{TlCl} \quad (2)$$

Acknowledgment. This work was supported by the Office of Naval Research.

Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles (9 pages); listing of observed and calculated structural factors (25 pages). Ordering information is given on any current masthead page.

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C–H Activating Reactions of Thoracyclobutanes. Routes to Unusual Actinide–Transition Metal μ-Methylene Complexes

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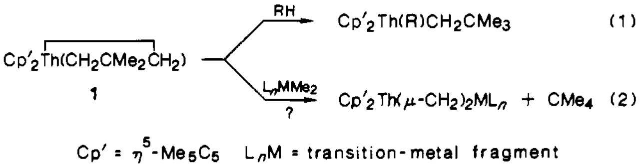
The facility with which strained thoracyclobutane **1** undergoes C–H activating[1] reactions with hydrocarbons (eq 1)[2] suggests routes to new types of actinide–organotransition metal molecules, e.g., heterobimetallic μ-methylene[3,4] complexes as in eq 2. We communicate here an implementation of this strategy and some of the interesting structural/dynamic characteristics of the products.



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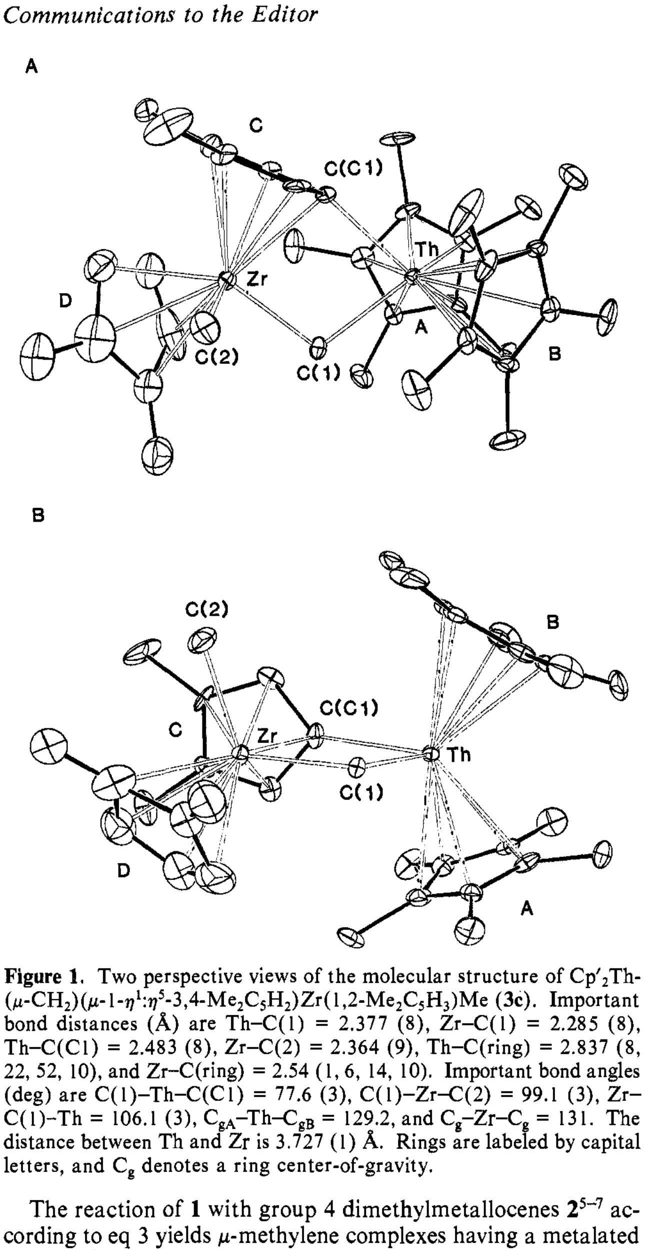


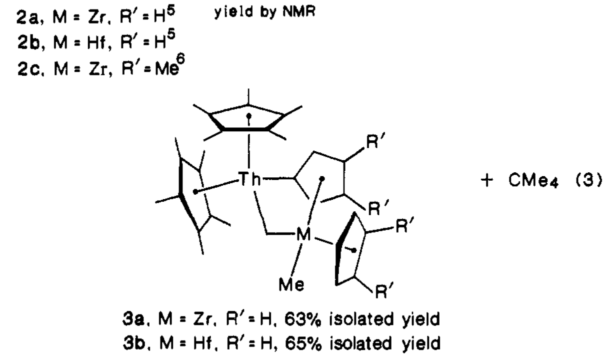
Figure 1. Two perspective views of the molecular structure of $Cp'_2Th(\mu\text{-}CH_2)(\mu\text{-}1\text{-}\eta^1{:}\eta^5\text{-}3,4\text{-}Me_2C_5H_2)Zr(1,2\text{-}Me_2C_5H_3)Me$ (**3c**). Important bond distances (Å) are Th–C(1) = 2.377 (8), Zr–C(1) = 2.285 (8), Th–C(C1) = 2.483 (8), Zr–C(2) = 2.364 (9), Th–C(ring) = 2.837 (8, 22, 52, 10), and Zr–C(ring) = 2.54 (1, 6, 14, 10). Important bond angles (deg) are C(1)–Th–C(C1) = 77.6 (3), C(1)–Zr–C(2) = 99.1 (3), Zr–C(1)–Th = 106.1 (3), C_{gA}–Th–C_{gB} = 129.2, and C_g–Zr–C_g = 131. The distance between Th and Zr is 3.727 (1) Å. Rings are labeled by capital letters, and C_g denotes a ring center-of-gravity.

Table I. NMR Spectral Parameters for μ-CH_2 Groups of Complexes **3a**, **3b**, and **3c**

solvent	**3a** (Zr) toluene-d_8	**3a** (Zr) THF-d_8	**3b** (Hf) toluene-d_8	**3c** (Zr) toluene-d_8
δ H_a, 213 K	6.10	5.88	4.75	5.69
δ H_b, 213 K	0.68	0.07	2.32	0.78
$^2J_{H\text{-}H}$	10.0	10.0	~10.0^b	10.0
T_c, K^a	277	287	268	282
$\Delta G^\ddagger$ at T_c, kcal mol^{-1}	11.2 (3)	11.5 (2)	11.5 (2)	11.8 (2)
δ $^{13}C_{298}$	177.2	177.0	163.3	174.3
$^1J_{C\text{-}H_a}$, 213 K	124		124	124
$^1J_{C\text{-}H_b}$, 213 K	89		84	95

^{a}400-MHz ^{1}H NMR. ^{b}Poorly resolved.

The reaction of **1** with group 4 dimethylmetallocenes **2**[5-7] according to eq 3 yields μ-methylene complexes having a metalated Cp ring.[8] Reaction is rapid (≤8 h) for **2a** and **2b** at room temperature, while that for **2c** is more sluggish (≈96 h/60 °C). Although transient intermediates are apparent in the ^{1}H NMR during the course of eq 3, they account for ≤5% of the total signal intensity. Structural formulation **3** is supported by elemental analysis/cryoscopy,[9] $^1H/^{13}C$[9] (vide infra) and 2D NOE[9,10] ^{1}H NMR spectroscopies, mass spectroscopy,[9] and single-crystal X-ray diffraction.



$$1 + (1,2\text{-}R'_2C_5H_3)_2MMe_2 \xrightarrow[\text{quantitative yield by NMR}]{\text{hexane}}$$

2a, M = Zr, R' = H[5]
2b, M = Hf, R' = H[5]
2c, M = Zr, R' = Me[6]

3a, M = Zr, R' = H, 63% isolated yield
3b, M = Hf, R' = H, 65% isolated yield
3c, M = Zr, R' = Me, 82% isolated yield

Crystals of **3c** suitable for diffraction were grown by slow cooling of a saturated toluene solution, followed by vapor diffusion of pentane.[11] The molecule consists of two "bent metallocene" units connected via shared methylene and cyclopentadienyl ligands (Figure 1). Except for the μ-methylene group, the metrical parameters associated with the Cp'_2Th[12] and $(Me_2C_5H_3)(Me_2C_5H_2)Zr$[13] fragments are unexceptional. The Zr–C(1) contact of 2.285 (8) Å is in the usual range for Zr(IV)–C(alkyl) distances, while Zr–C(2) (2.364 (9) Å) may be slightly long.[13,14] The Zr–C(1)–Th angle of 106.1 (3)° is reasonable for a μ-CH_2 group bridging nonbonded metal atoms[3] and is commensurate with the long (nonbonding) Th–Zr distance of 3.727 (1) Å—0.23 Å longer than the sum of the metallic radii.[15] While Th–C(C1) = 2.483 (8) Å is normal for a thorium aryl (2.449 (12) Å in $Cp'_2\overline{ThCH_2SiMe_2\text{-}o\text{-}C_6H_4}$),[16a,b] the Th–C(1) distance of 2.377 (8) Å is by far the shortest ever observed in a Cp'_2Th alkyl[16a] (cf.

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(5) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 155–161.

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(11) **3c** crystallizes in the orthorhombic space group $Pbcn$-D_{2h}^{14} (No. 60), with a = 30.171 (6) Å, b = 9.991 (2) Å, c = 21.587 (7) Å, and Z = 8 at 150 (5) K. The structure was refined (full-matrix least squares) to agreement factors R and R_w on F_o of 0.035 and 0.053, respectively, with 344 parameters and 2787 reflections having $F_o^2 > 3\sigma(F_o^2)$ out of the 4788 unique data measured with an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, λ = 0.71069 Å; $2\theta_{max}$ = 45°). A full description of the structure determination is included in the supplementary material.

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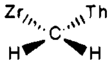
(14) (a) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics*, in press. (b) Zr–C_{alkyl} = 2.273 (5), 2.280 (5) Å (Cp_2ZrMe_2);[13a] 2.294 (8) Å ($Cp_2Zr(neopentyl)_2$);[13c] 2.379 (6), 2.396 (6) Å ($Cp_2Zr(CHPh_2)_2$).[13b]

(15) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; pp 1286–1288.

2.446 (4) and 2.543 (4) Å in $Cp'_2Th(neopentyl)_2$,[16b] 2.493 (11) Å in $Cp'_2\overline{ThCH_2SiMe_2\text{-}o\text{-}C_6H_4}$,[16b] and 2.55 (3) Å in $Cp'_2Th(\eta^4\text{-}C_4H_6)$[16a]). Correcting for differences in Th(IV) and U(IV) ionic radii[17] yields a hypothetical U–C distance of 2.32 (1) Å, which compares favorably with the U–C "multiple bond" distance of 2.29 (3) Å in $Cp_3U(CHPMe_2Ph)$.[18,19]

Unusual aspects of the μ-CH_2 bonding are also revealed by variable-temperature NMR. At room temperature, the formally nonequivalent methylene protons are undergoing rapid exchange (T_c = 268–287 K, Table I). Low-temperature spectroscopy reveals AB pairs with *very large* chemical shift dispersions (2.4–5.8 ppm) and distinctive $^1J_{C-H}$ parameters (Table I). The low-field methylene resonance having $^1J_{C-H}$ = 124 Hz is typical of a μ-CH_2 group involving an early transition metal center.[3,4] On the other hand, the upfield displacement and small $^1J_{C-H}$ (85–95 Hz) of the second methylene resonance suggests an "agostic interaction."[16b,20] The sensitivity of these latter parameters to the identity of the group 4 metal (Zr vs. Hf) implies that the interaction is with that metal.

In regard to molecular dynamics, it is noteworthy that the μ-CH_2 hydrogen interchange process *does not* time-average other aspects of the instantaneous C_1 molecular symmetry (nonequivalent Cp′, nonequivalent halves of the metalated Cp, unaffected Zr–CH_3). Moreover, $\Delta G_c^{\ddagger}$ values for the three complexes are low, virtually identical, and insensitive to toluene vs. THF (Table I). Although further information on the methylene interchange process awaits precise determination of H atom positions, it is noteworthy that any mechanism involving $Zr(CH_2)Th$ bridge breaking must occur in such a manner that the resulting charge separation/coordination unsaturation is insensitive to the presence of THF and that "spinning" of the transitory terminal CH_2 prior to bridge closure must occur with a lower barrier than commonly observed in d^0 methylidene complexes.[21] More intriguing is the possibility, supported by preliminary EHMO calculations,[22] that hydrogen exchange occurs via a "planar" "anti van't Hoff" intermediate, possibly stabilized by agostic interactions (e.g., A–C). Of particular relevance here are the small calculated energy differences between tetrahedral and planar CH_2Li_2 structures,[23] as well as the similarity in polar metal–ligand bonding and the availability of empty metal acceptor orbitals.



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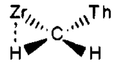

B

C

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Supplementary Material Available: Spectroscopic and analytical data, X-ray experimental details (including positional and anisotropic displacement parameters), and tables of bond lengths and angles (19 pages); listing of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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Synthesis of 9-Acetyl-9-azatricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene, a Valence Isomer of 1-Acetyl-2,7-methanoaza[9]annulene

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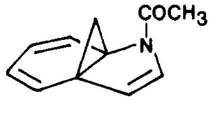
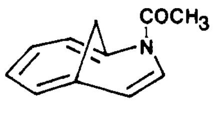
We report here the synthesis of 9-acetyl-9-azatricyclo[4.3.1.$0^{1,6}$]deca-2,4,7-triene (**1**), a valence isomer of 1-acetyl-2,7-methanoaza[9]annulene (**2**).

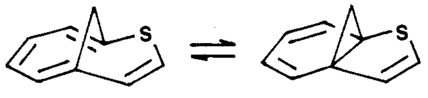


1



2

Although there has been much current interest in bridged annulenes and heteroannulenes,[1] only a few examples have been reported for the latter.[2] It is probably due to the limited availability of useful synthetic methods for such heterocycles. Recently we have reported the synthesis of 2,7-methanothia[9]annulene (**3**) starting from 1,6-diiodo-1,3,5-cycloheptatriene (**4**) and the existence of an equilibrium between **3** and its valence isomer **3′**.[3] The diiodide (**4**) is a very useful starting material for this type of heterocycle,[4,5] and the title compound (**1**), a nitrogen analogue of bridged thia[9]annulene **3**, has now been synthesized from **4** by a route as shown in Scheme I.[6] One of the iodines was converted into a 2-hydroxyethyl group by selective monovinylation followed by hydroboration to give alcohol **6**. After introduction of a carboxyl group by halogen–metal exchange and subsequent carboxylation, the resulting carboxylic acid **7** was



3 3′

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(6) All the new compounds (**1**, **7**, **9–15**, and **17**) were identified by spectral (^1H, ^{13}C NMR, IR, and MS) and analytical (exact mass and/or elemental analyses) data. See supplementary material for the details.

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