Communications to the Editor

Syntheses of Heterotetranuclear Metallacarboranes Containing a Planar M_2Cu_2 (M = Mo, W) Rhomb and B–H–Cu Bridges: Structure of $[Mo_2Cu_2(\mu\text{-}CO)_4(CO)_2(\mu\text{-}H)_2(C_2B_9H_{10})_2]^{2-}$

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The nido ion $[7,8\text{-}C_2B_9H_{11}]^{2-}$,[1] which is isolobal[2] with the η^5-cyclopentadienyl ligand, has formed a class of metallacarborane complexes[3] which lack stable counterparts in cyclopentadienyl chemistry.[4] Later, metallacarboranes which involved metal–hydride–boron bridge bonds began to emerge.[5] In both cases, the striking feature of carboranyl complexes is perhaps best ascribed to the excellent electron donor ability of the open pentagonal C_2B_3 face and/or the terminal hydrogen atoms of the dicarbollide anion. The presence of this intrinsic dualism in the electron donor properties of the dicarbollide anion raises the engaging question as to the potential role of $[7,8\text{-}C_2B_9H_{11}]^{2-}$ in the synthesis of polynuclear metal clusters. Consequently, a search for "clustered clusters"[6] was undertaken using rational methods of chemical synthesis. The work described here includes the syntheses of $[M_2Cu_2(\mu\text{-}CO)_4(CO)_2(\mu\text{-}H)_2(C_2B_9H_{10})_2]^{2-}$ (M = Mo, **1**; W, **2**) as well as the molecular structure of $(PPN)_2\cdot$**1**.[7]

A slurry of (Tl)[*closo*-3,1,2-$TlC_2B_9H_{11}$][8] (1.12 mmol) and equimolar PPN^+Cl^- in 40 mL of acetonitrile was allowed to react anaerobically with 1.12 mmol of $[M(CO)_3(CH_3CN)_3]$ (M = Mo; W)[9] at ambient temperature, developing an orange–red slurry within 1 h. The addition of anhydrous CuCl (1.12 mmol) to the foregoing reaction mixture was followed by stirring for a period of 20 h and filtration. Two recrystallizations (THF–ether and then DMK–ether)[7] of the solids obtained by removing solvent from the yellow filtrate afforded analytically pure crystalline

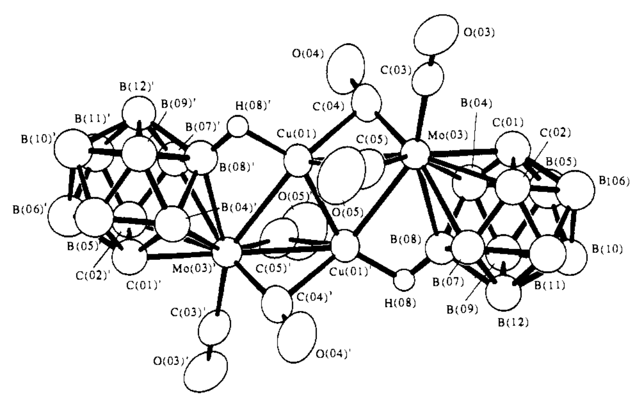

Figure 1. Structure of $[Mo_2Cu_2(\mu\text{-}CO)_4(CO)_2(\mu\text{-}H)_2(C_2B_9H_{10})_2]^{2-}$ showing the atom labeling scheme. All hydrogen atoms except the B–H–Cu bridges have been omitted for clarity. Selected values or ranges of interatomic distances (Å) are Cu(01)–Cu(01)′, 2.403 (1); Mo(03)–Cu(01), 2.656 (1); Mo(03)–Cu(01)′, 2.834 (1); Cu(01)–H(08)′, 1.69 (6); Mo(03)–μ-CO, 1.947 (7), 1.940 (7); Cu(01)–μ-CO, 2.247 (7), 2.251 (5); Cu(01)–B(08), 2.186 (6); Mo(01)–C(C_2B_3 face), 2.343 (6), 2.362 (5); Mo(01)–B (C_2B_3 face), 2.430 (7), 2.425 (6), 2.496 (6). Selected values or ranges of interatomic angles (deg) are Cu(01)–Mo(3)–Cu(01)′, 51.78 (2); Mo(03)–C–O (bridging CO), 168.8 (6), 170.8 (6); Cu(01)–C–O (bridging CO), 112.9 (5), 110.9 (5); Cu(01)–H(08)′–B(08)′, 97 (3).

$(PPN)_2\cdot$**1**$\cdot$(DMK)[10a] (brownish yellow; 61%) or $(PPN)_2\cdot$**2**$\cdot$(DMK)[10b] (greenish yellow; 18%). Spectroscopic data[10a] for **1** revealed the presence of bridging and terminal CO groups as well as ligated [*nido*-7,8-$C_2B_9H_{11}$]$^{2-}$. The composition and crystal structure of the anion of **1** were established by single-crystal X-ray analysis.[11] Elemental analysis[10b] of **2** and the comparison of spectroscopic data[10] for **1** and **2** indicate that the anion **2** has the same configurational core as **1**.

The crystal structure consists of well-separated **1** anion and PPN^+ cations. The anion has crystallographically imposed C_i symmetry. The structure of **1** (Figure 1) contains a planar $MoCu_2Mo$ rhomb incorporated in two 12-vertex molybdacarboranes whose overall symmetry approaches C_{2h}. Two scalene

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(6) The term "clustered clusters" was introduced to describe metallacarborane aggregates containing a regular array of mutually bonded metal centers, some or all of which may serve as one vertex of a metallacarborane cage.

(7) PPN^+ = bis(triphenylphosphoranylidene)ammonium cation, THF = tetrahydrofuran, DMK = acetone.

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(10) (a) Data for $(PPN)_2\cdot$**1**$\cdot$(DMK): IR (KBr) ν_{BH} = 2540, ν_{CO} = 1898, 1811, ν_{DMK} = 1707 cm^{-1}; $^{11}B\{^1H\}$ NMR (in acetone; chemical shifts, referenced to external $BF_3\cdot OEt_2$ in C_6D_6, upfield of the reference are designated as negative) −11.4, −13.7, −18.0, −21.8 ppm; ^1H NMR (in CD_3CN; referenced to residual solvent protons = 1.93 ppm) 2.73 (carborane CH), 2.07 (DMK), −3.85 (B–H–Cu, weak and very broad). Anal. Calcd (found): C, 54.10 (54.19); H, 4.70 (4.91); B, 10.31 (9.53); Cu, 6.73 (6.37); Mo, 10.17 (10.04); N, 1.48 (1.41); P, 6.57 (6.64). (b) Data for $(PPN)_2\cdot$**2**$\cdot$(DMK): IR (KBr) ν_{BH} = 2547, ν_{CO} = 1887, 1805, ν_{DMK} = 1706 cm^{-1}; $^{11}B\{^1H\}$ NMR (in acetone) −9.8, −11.2, −14.1, −18.5, −21.9 ppm; ^1H NMR (in CD_3CN) 3.04 (carborane CH), 2.07 (DMK), −3.74 ppm (B–H–Cu, weak and very broad). Anal. Calcd (found): C, 49.49 (49.28); H, 4.30 (4.60); B, 9.43 (10.18); Cu, 6.16 (5.71); N, 1.36 (1.11); P, 6.01 (6.18); W, 17.82 (17.95).

(11) (a) The anion **1** was originally isolated as the PPN salt from the reaction mixture of equimolar $Tl_2C_2B_9H_{11}/PPN^+Cl^-/Mo(CO)_3(MeCN)_3/CuCl(PPh_3)_2$ in CH_3CN/CH_2Cl_2. The structural work on crystals obtained by vapor diffusion of ether into an acetone solution revealed the nature of this product as $(PPN)_2\cdot$**1**. The absence of a solvate was further supported by spectroscopic means. Use of anhydrous CuCl and CH_3CN as a copper source and solvent, respectively, also led to the isolation of $(PPN)_2\cdot$**1**. In both cases, the purification of the product by recrystallization was hampered by coprecipitation of unidentified component(s). As noted in the text, the adoption of a THF–ether solvent pair followed by a DMK–ether pair afforded a convenient route to an analytically pure salt of **1** in the solvated form, $(PPN)_2\cdot$**1**$\cdot$(DMK).[10a] (b) Diffraction data were collected at 25 °C on an automated diffractometer equipped with a larger Huber circle, Mo Kα radiation. Absorption corrections were applied. The structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. (c) $(PPN)_2\cdot$**1**: a = 11.722 (2) Å, b = 13.431 (3) Å, c = 14.744 (3) Å, α = 109.59 (1)°, β = 97.40 (1)°, γ = 92.67 (1)°, space group $P\bar{1}$, unique data ($I > 3\sigma(I)$) 5482, $R(R_w)$ = 5.23 (6.49)%.

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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, $[closo\text{-}3,3,3\text{-}(CO)_3\text{-}3\text{-}Tl\text{-}3,1,2\text{-}MC_2B_9H_{11}]^{1-}$ (**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] $[closo\text{-}3\text{-}(\mu\text{-}CO)\text{-}8\text{-}PPh_3\text{-}3,1,2\text{-}NiC_2B_9H_{10}]_2$,[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 $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ and **3** in cluster synthesis as well as the reactivity of **1** and **2** are under investigation.

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

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

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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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(25) In this paper the periodic group notation in parentheses in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the numbering: e.g., III → 3 and 13.)

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

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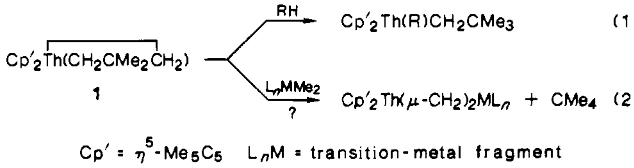
The facility with which strained thoracyclobutane **1** undergoes C–H activating[1] reactions with hydrocarbons (eq 1)[2] suggests routes to new types of actinide–organotransition metal molecules, e.g., heterobimetallic μ-methylene[3,4] complexes as in eq 2. We communicate here an implementation of this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



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