^{13}C NMR spectroscopic analysis of the products **13** and **14** showed them to be single regio- and stereoisomers. The stereochemistry is assigned based upon analogy to cuprate substitutions of allylic carboxylates.[13] The sequence of diastereocontrolled formation of the γ-hydroxysulfones[15] followed by diastereocontrolled substitution of sulfone illustrates the use of the phenylsulfonyl group as a diastereochemical control element in the alkylation step and as a diastereochemical relay element in the substitution step. In this process, 1,3- and 1,2,3-stereochemistry is first controlled and ultimately transferred into 1,5- or 1,2,5-stereochemistry. The use of epoxides, which are available in highly enantiomerically pure form from achiral allylic alcohols,[16] as the electrophilic partner that gives rise to high diastereocontrol translates this sequence into both an enantio- as well as diastereocontrolled construction of acyclic units.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health, General Medical Sciences Institute, for their generous support of our programs. We thank the Fannie and John Hertz Foundation for a fellowship for C.A.M.

Supplementary Material Available: Spectroscopic and analytical data for **3a**, **3b**, **6**, **8**, **9**, **11a**, **11c**, **12b**, **12c**, **13**, and **14** and X-ray data for **12b**; general procedure for alkylation of sulfone dianions and procedure for equilibration illustrated by preparation of **12a** (11 pages). Ordering information is given on any current masthead page.

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[14] Cf. ref 5. To our knowledge, these are the first examples of demonstrating the stereochemistry of copper-mediated substitution of allylic sulfones. The high regioselectivity of these examples contrasts with the earlier results.

[15] For diastereoselectivity in conjugate additions that produce γ-hydroxysulfones, see: Auvray, P.; Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1985**, *26*, 2329.

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A Folded Metallacyclopentatriene and a Bicapped-Tetrahedral M_2C_4 Cluster Obtained from Coupling of Alkyne Ligands. Structures of $CpMoCl(C_4Ph_4)$ and $(CpMoCl)_2(\mu,\eta^4\text{-}C_4Ar_4)$ (Ar = *p*-Tolyl)

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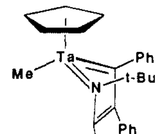
We recently reported[1] the synthesis and structure of **1**, a derivative of a new class of metallacycles, the metallacyclopenta*tri*enes. Our EHMO calculations[1,2] suggested that $CpXMC_4R_4$ metallacycles should exhibit the *folded* metallacyclopentatriene structure I for metals with a d^2 electron configuration, whereas a planar metallacyclopentatriene structure II would be the ground-state structure for metals with a d^4 or higher electron configuration and that $CpX_2M(C_4R_4)$ metallacycles would adopt a "normal" metallacyclopentadiene structure III regardless of electron count. (Note, the electron counts are obtained by assigning a −2 charge to the C_4R_4 ligand.)



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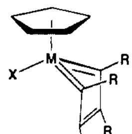

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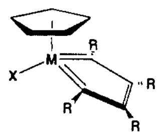

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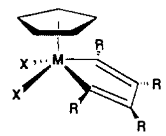


III

Support for these conclusions is afforded by the recent characterizations by Singleton et al.[3] of **2** and **3** which are examples of structure types II and III, respectively. Here, we report the synthesis of the first example of structure I and a novel M_2C_4 cluster.

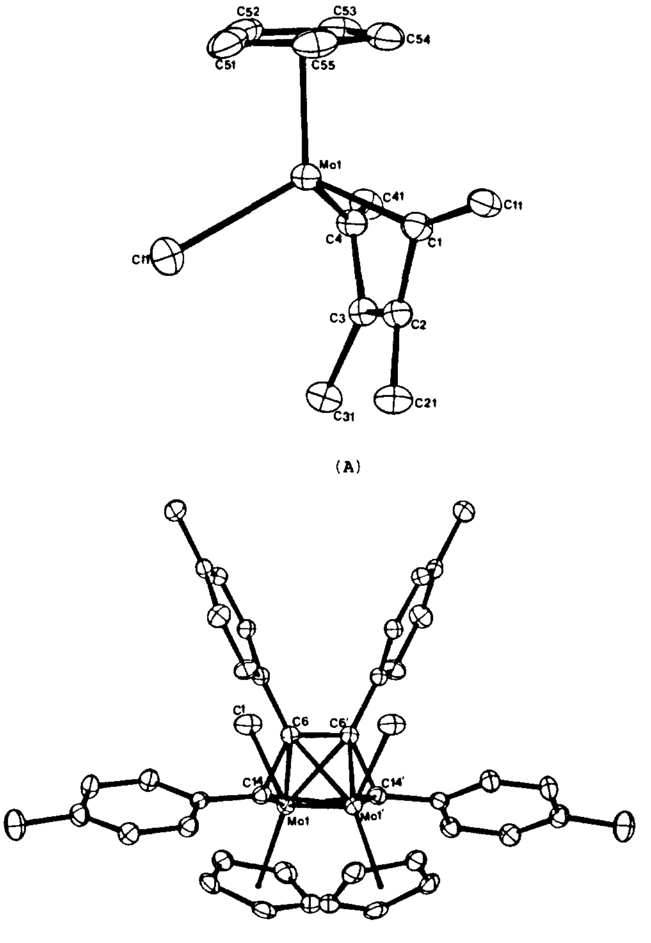
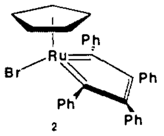


Figure 1. (a) ORTEP plot (50% thermal ellipsoids) for $CpMoCl(C_4Ph_4)$ (only ipso carbons of phenyl rings shown). (b) ORTEP plot (50% thermal ellipsoids) of $(CpMoCl)_2(\mu,\eta^4\text{-}C_4Ar_4)$ (Ar = *p*-tolyl).



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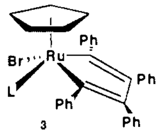
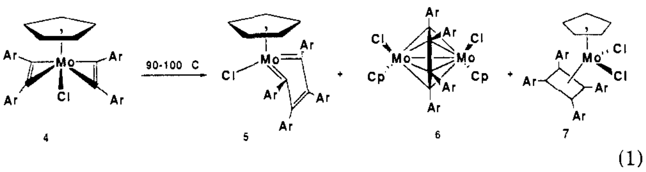


3

Heating a toluene solution of **4** (Ar = phenyl or *p*-tolyl) to 90–100 °C for 18 h produces a mixture of compounds **5**, **6**, and **7** (eq 1). Compound **5** may be isolated by fractional crystallization of the solids obtained by removal of the toluene solvent, while **6** and **7** are readily purified by chromatography over SiO_2 with CH_2Cl_2 eluant.[5] Compound **5** is produced preferentially



(1)

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[5] $CpMoCl(C_4Ph_4)$ (**5**): ^1H NMR (300 MHz, $CDCl_3$) δ 7.3–7.0 (m, 20 H), 5.71 (s, 5 H); $m/z = 554$. $Cp_2Mo_2Cl_2(C_4Ph_4)$ (**6**): ^1H NMR (300 MHz, acetone-d_6) δ 7.5–6.6 (m, 20 H), 5.49 (s, 10 H); $Cp(\eta^4C_4Ph_4)MoCl_2$ paramagnetic, $g = 2.005$, $A_{Mo} = 36$ G. All new compounds give satisfactory elemental analyses.

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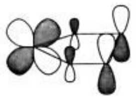
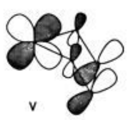
at lower temperatures and by the addition of excess alkyne to the solution, while formation of **6** is favored by longer reaction times, higher temperature, and no added alkyne. The paramagnetic cyclobutadienyl complex **7** is obtained only in very small amounts under any of these conditions. The structures of all three complexes have been confirmed by single-crystal X-ray analysis.[6]

Figure 1A is an ORTEP drawing of the structure of **5** (Ar = phenyl). The Mo–C1 and Mo–C4 distances are 1.946 (4) and 1.941 (4) Å, respectively, and are consistent with Mo=C bond orders of **2**.[7] The π-bonding in the metallacycle is not as localized in **5** as it is in **1** where there is a definite alternation in C–C bond lengths (C–C = 1.48, C=C = 1.39). In **5**, the C1–C2 and C3–C4 distances are 1.42 Å, and the C2–C3 bond is slightly longer, 1.44 Å. The structure of **5** is thus an example of the theoretically anticipated continuum between a metallacyclopenta*di*ene and a metallacyclopenta*tri*ene (see ref 1).

The MoC_4 ring is folded along the C1⋯C4 vector (dihedral angle = 117° versus 120° for **1**). According to our EHMO analysis, this folding results in a relief of anti-bonding interactions between Mo and C2, C3 despite the closer approach of C2, C3 (2.364 (4) and 2.350 (4) Å, respectively). In the planar structure, π-back bonding between Mo and the π_3* LUMO of the C_4R_4 ligand results in anti-bonding interactions between Mo and C2, C3 as a result of the nodal properties of the LUMO (see IV). When the ring is folded, one lobe of the d-orbital lies in the nodal plane of the C2, C3 p-orbitals, and the d–p overlap approaches zero (see V).

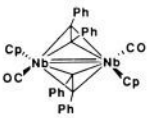

IV


V

The structure of **6** (Ar = *p*-tolyl) is shown in Figure 1B. Assuming that the $R_4C_4^{2-}$ ligand donates a total of eight electrons to the dimolybdenum frame, each Mo has a 16-electron count. However, if the cluster-counting rules[8] are invoked, each R–C unit is counted as a three-electron vertex, and each CpClMo group is considered to donate 6 + 6 – 12 = 0 electrons to cluster bonding, then the Mo_2C_4 cluster core has six bonding electron pairs (S). Hence, S = N (number of vertices) and a bicapped tetrahedral geometry is predicted.[8b] The structure of **6** may indeed be considered to be a bicapped tetrahedron (the two terminal R–C groups each span a triangular M_2C face).

Compound **6** differs from previously reported "fly-over" complexes[9] in that the two terminal carbons of the R_4C_4 bridging ligand and the two Mo atoms are nearly coplanar and the R_4C_4 plane is nearly perpendicular to the Mo–Mo vector. Some relevant distances are as follows: Mo–Mo′ = 2.933 (1), Mo1–C14 = 2.065 (3), Mo1–C14′ = 2.082 (3), Mo1–C6 = 2.240 (3), Mo1–C6′ = 2.271 (3), C6–C14 = 1.478 (5), and C6–C6′ = 1.504 (6) Å. The Mo–C14 bond lengths are just outside the range normally associated with Mo=C alkylidenes,[7] and the Mo–C6 distances are about 0.05 Å shorter than usual Mo–C single bonds.

The structure of **6** is even more astonishing when compared to that of the isoelectric complex $[CpNb(CO)]_2(Ph_2C_2)_2$ (**8**). In compound **8**, the alkynes remain uncoupled, and the Nb atoms achieve an 18-electron count by forming a Nb=Nb double bond.[10]



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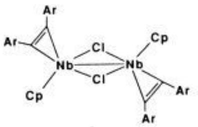

9

In a similar vein $(CpNbCl)_2(R_2C_2)_2$ (**9**), which has two electrons less than **6**, adopts an 18-electron count, chloro-bridged structure.[11] Further investigations of the factors which control the structures of $M_2(CR)_4$ complexes are in progress.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8619864) for support of this research. We also thank W. M. Butler and M.-S. Lah for the X-ray structure determinations.

Supplementary Material Available: Tables of crystallographic statistics, atomic coordinates, selected bond distances and angles and ORTEPS with complete numbering schemes for compounds **5**·CH_2Cl_2, **6**, and **7**-CH_2Cl_2 (11 pages). Ordering information is given on any current masthead page.

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[6] Summary of crystallographic data (complete table in Supplementary Material). For **5**·CH_2Cl_2 (Ar = phenyl) a = 10.039 (4) Å, b = 11.7609 (3) Å, c = 12.674 (8) Å, α = 92.21 (4)°; β = 87.35 (4)°, γ = 104.05 (3)°, space group = $P\bar{1}$, Z = 2, R = 0.038. For **6** (Ar = *p*-tolyl): a = 16.354 (2) Å, b = 10.436 (2) Å, c = 20.955 (7) Å, β = 103.19 (2)°, space group = $C_{2/c}$, Z = 4, R = 0.025. For **7**·CH_2Cl_2 (Ar = phenyl): a = 27.12 (4) Å, b = 11.42 (1), c = 19.32 (2) Å, orthorhombic, space group = *Pbca*, Z = 8, R = 0.062.

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Synthesis and Characterization of 12-Vertex Dinuclear Cobaltaborane Complexes Containing the $Co_2(CO)_5$ Moiety and SEt_2 Cage Substituents

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Although many parallels exist between metal carbonyl and boron hydride clusters, examples of larger boron hydride polyhedra that incorporate metal carbonyl cluster fragments are lacking. Furthermore, while a few dinuclear icosahedral metallaborane and metallacarborane clusters bearing cyclopentadiene ligands have been reported,[2] the synthesis of similar clusters possessing carbonyl groups have not been described. We report herein the synthesis of icosahedral dicobaltaborane carbonyl complexes of the type *closo*-$B_{10}H_8(SEt_2)_2Co_2(CO)_5$.

Reactions of the decaborane–Lewis base complex *arachno*-$B_{10}H_{12}(SEt_2)_2$ with alkynes to give *closo*-1,2-$C_2B_{10}H_{12}$ or its C-substituted derivatives are well known.[3] Analogous insertions of transition-metal carbonyl cluster fragments into the decaborane cage to produce dinuclear icosahedral metallaboranes have not been previously exploited. We have recently found that reactions of *arachno*-$B_{10}H_{12}(SEt_2)_2$ with $Co_2(CO)_8$ or $Co_4(CO)_{12}$ result in

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