

conclusion that the decomposition mechanism (Scheme III) is initiated by an intramolecular hydrogen (deuterium) transfer from the methoxyl group to the olefinic terminus to afford the 1,4-diradical **16** which closes to silaoxetane **9D** which in turn proceeds directly to products.¹⁴

If indeed this mechanism, which fits all the known facts of this decomposition, is correct, one would expect an isotope effect between **3** and **3D**, albeit small at such extreme temperatures. Compounds **3** and **3D** were pyrolyzed in a stirred-flow reactor¹⁵ at 695.4 °C (60 mL/min of He), and from the apparent rate constants for formation of **5** and **5D** k_H/k_D was determined to be 1.34 ± 0.08 , consistent with C-H(D) cleavage in the transition state.

Current efforts, which will be reported in a full paper along with complete details of this work, include synthetic modification of **3** so as to promote silaallene formation and/or reduced decomposition temperatures to allow obtainment of reliable Arrhenius parameters for this process. The generality of intramolecular H-atom transfer to produce diradicals is also being probed in carbon systems devoid of silicon.

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(14) It is, of course, possible to write the mechanism of Scheme III as an ionic process initiated by hydride transfer. However, in the absence of solvent stabilization, the energetics of charge separation are normally considered to be prohibitive.

(15) Our stirred-flow reactor is modeled after the design of Davidson.¹⁶

(16) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* 1975, 71, 972.

Formation of a Trishomocubane Structure Containing Three Rhenium and Eight Arsenic Atom Vertices. The Crystal Structure of $\{cyclo-[(AsMe)_7(As)Re(CO)_4]Re_2(CO)_6\}$

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Summary: Pentamethylcyclopentaarsine, $cyclo-(AsMe)_5$, reacts with $Re_2(CO)_{10}$ to form $\{cyclo-[(AsMe)_7(As)Re(CO)_4]Re_2(CO)_6\}$ in 26% yield. The product has been structurally characterized by X-ray methods. The 11 heavy atoms form a trishomocubane structure analogous to that found in $[(AsMe)_5Mo_2(CO)_6]$; as compensation for the additional electron of each $Re(CO)_3$ group (compared to $Mo(CO)_3$), one of the As units has, through demethylation, converted from a two-electron to a one-electron donor. Another of the positions is occupied by a $Re(CO)_4$ group which functions as the isolobal equivalent of a second naked As atom.

We have proposed¹ that transition-metal, main-group hybrid clusters containing a majority of main-group atoms generally form structures explicable (but not always pre-

(1) Rheingold, A. L.; Fountain, M. E.; DiMaio, A.-J. *J. Am. Chem. Soc.* 1987, 109, 141.

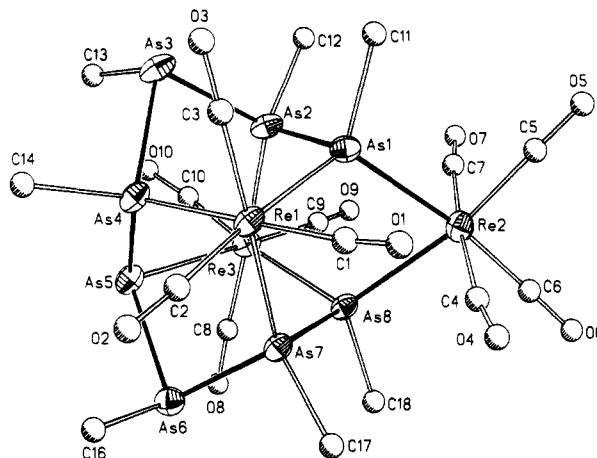


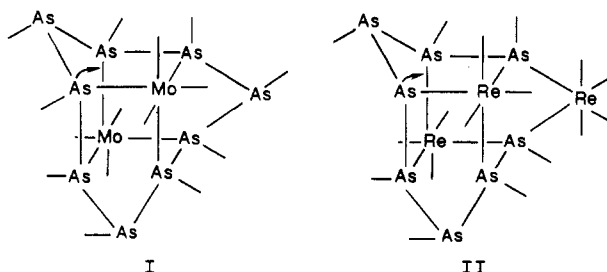
Figure 1. Molecular structure and labeling scheme for II as viewed approximately along the Re(1)---Re(3) vector with 40% probability thermal ellipsoids.

Table I. Selected Bond Distances and Angles for II

(a) Bond Distances (Å)			
Re(1)-As(1)	2.605 (3)	As(1)-As(2)	2.443 (5)
Re(1)-As(4)	2.543 (4)	As(2)-As(3)	2.419 (5)
Re(1)-As(7)	2.567 (4)	As(3)-As(4)	2.414 (5)
Re(2)-As(1)	2.602 (4)	As(4)-As(5)	2.437 (6)
Re(2)-As(8)	2.601 (3)	As(5)-As(6)	2.406 (5)
Re(3)-As(5)	2.646 (3)	As(7)-As(8)	2.432 (5)
Re(3)-As(8)	2.612 (4)		

(b) Bond Angles (deg)			
As(1)-Re(1)-As(4)	90.5 (1)	As(3)-As(4)-As(5)	104.5 (2)
As(1)-Re(1)-As(7)	84.8 (1)	As(4)-As(5)-As(6)	97.9 (2)
As(4)-Re(1)-As(7)	85.7 (1)	As(5)-As(6)-As(7)	95.4 (2)
As(1)-Re(2)-As(8)	77.7 (1)	As(6)-As(7)-As(8)	95.2 (2)
As(2)-Re(3)-As(5)	90.2 (1)	Re(1)-As(1)-Re(2)	118.7 (1)
As(2)-Re(3)-As(8)	95.3 (1)	Re(3)-As(8)-Re(2)	119.9 (1)
As(5)-Re(3)-As(8)	95.9 (1)	Re(2)-As(1)-As(2)	104.0 (2)
As(1)-As(2)-As(3)	96.3 (2)	Re(2)-As(8)-As(7)	102.7 (2)
As(2)-As(3)-As(4)	86.5 (2)		

dictable) by application of two concepts: (1) the overall cluster structure will have isolobal relationships to known (or expected) *main-group* structures and (2) the *main-group* component will undergo structural modifications as needed to fulfill the steric and electronic demands of the transition-metal components. We illustrated these concepts with the structure of $[cyclo-(AsPh)_9Mo_2(CO)_6]$ (I) which formed an isolobal trishomocubane structure in good yield from $Mo(CO)_6$ and $cyclo-(AsPh)_6$. As a test of these concepts, we were curious to learn the results of substituting a metal center of higher electron count, e.g., $Re(CO)_3$ for $Mo(CO)_3$. If a trishomocubane structure persisted, what structural accommodations would be necessary in the *main-group* and *transition-metal* portions of the structure? To this end we now report the product of the reaction of $Re_2(CO)_{10}$ with $cyclo-(AsMe)_5$ which does lead to a trishomocubane structure, $\{cyclo-[(AsMe)_7(As)Re(CO)_4]Re_2(CO)_6\}$ (II), but with some unusual structural accommodations needed to achieve this result.



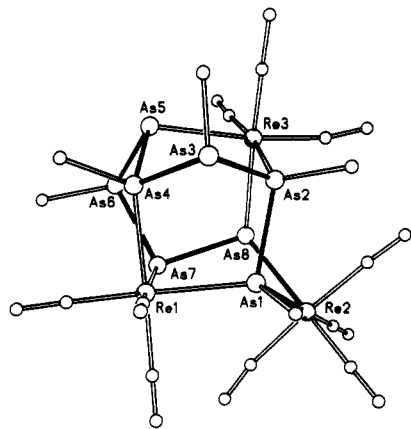
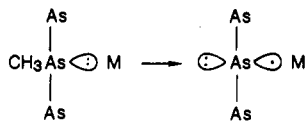


Figure 2. The structure of II emphasizing the trishomocubane-like cluster framework.

Arsenomethane, *cyclo*-(AsMe)₅, reacts with Re₂(CO)₁₀ in toluene (120 °C, 30 atm) to produce a 26% yield of II.² The structure of II³ (Figures 1 and 2, Table I) contains a nine-membered As₈Re ring coordinated to two Re(CO)₃ groups in the 1,4,7 and 2,5,8 As-atom ring positions. Overall, the 11 heavy atoms form a trishomocubane structure very similar to that found in [(AsPh)₅Mo₂(CO)₆] (I), P₁₁^{3-,4} and (CH)₈(CH₂)₃.⁵ In comparison to Mo(CO)₃ in I, each 13-electron Re(CO)₃ group requires one fewer electron for completion of an octadecet electron configuration. For Re(3), this is achieved by the demethylation of As(5) which converts arsenic from a two-electron donor to a one-electron donor:



(2) A heavy-wall Carius tube (1.9 × 30 cm) was charged with equimolar quantities of *cyclo*-(AsCH₃)₅ (1.21 g) and Re₂(CO)₁₀ (0.82 g) in 10.0 mL of toluene, degassed, and sealed. After being heated to 130 °C for 48 h, the resulting bright yellow solution was filtered to remove unreacted Re₂(CO)₁₀, concentrated, and eluted with mixed hexanes on an alumina column to remove remaining starting material. Further elution with 1:9 toluene/hexanes afforded a single yellow band of II from which a 26% yield (0.46 g) of yellow, air-stable crystals was obtained following recrystallization from CH₂Cl₂: mp 307–310 °C dec; IR (KBr, cm⁻¹) 2084 (s), 2002 (s), 1920 (s); ¹H NMR (CDCl₃, ppm) 2.48, 2.44, 2.27, 2.12, 1.96, 1.59, 1.20 (all methyl singlets). Anal. Calcd for C₁₇H₂₁As₈O₁₀Re₃: C, 13.22; H, 1.36; As, 38.88. Found: C, 13.56; H, 1.35; As, 39.14.

(3) Crystal data for C₁₇H₂₁As₈O₁₀Re₃ (293 K): triclinic, P1̄, *a* = 9.917 (2) Å, *b* = 10.401 (3) Å, *c* = 19.560 (6) Å, *α* = 102.26°, *β* = 97.39°, *γ* = 107.97 (2)°, *V* = 1834 (1) Å³, *Z* = 2, *μ*(Mo K α) = 177.8 cm⁻¹, *D*(calcd) = 2.794 g cm⁻³. Only crystals of moderate quality could be obtained, the best by recrystallization from CH₂Cl₂/pentane. A yellow specimen (0.13 × 0.13 × 0.32 mm) was used for data collection (Nicolet R3m diffractometer) to a maximum observed 2 θ of 45°. Of 4795 independent (*R*_{int} = 3.1%) absorption-corrected reflections, 2593 with *F*_o ≥ 4 σ (*F*_o) were considered observed. Direct methods provided the 11 heavy-atom positions. A molecule of CH₂Cl₂ occurs in the lattice for each cluster molecule. Anisotropic refinement was confined to Re, As, and Cl atoms. Hydrogen atoms were incorporated as idealized contributions. At convergence *R*(*F*) = 5.52%, *R*(*wF*) = 6.66%, GOF = 1.07, $\Delta\rho$ = 0.006, ρ_{max} = 2.1 e Å⁻³ (1.0 Å from Re(3)), and *N*_o/*N*_t = 11.3. SHELXTL software (Nicolet Corp., Madison, WI) was used for all computations.

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(5) Underwood, G. R.; Ramamoorthy, B. *Tetrahedron Lett.* 1970, 4125. Smith, E. C.; Barborak, J. C. *J. Org. Chem.* 1976, 41, 1433.

In support of this conclusion is the Re(3)–As(5) bond distance, 2.646 (3) Å, which is significantly longer than the other two Re(3)–As bonds, 2.553 (4) and 2.612 (4) Å. For Re(1), a different solution is found; the ninth ring As atom in I is replaced by a 15-electron Re(CO)₄ group (an As-atom isolobal analogue). Thus As atoms 1 and 8, which complete the octahedral coordination of Re(2), must together contribute three electrons. If As(8) donates one electron and As(1) donates two to Re(2), then As(1) donates only one electron to Re(1), completing its octadecet. Affirmation is found in the Re(1)–As(1) distance, 2.605 (3) Å, which is longer than the other Re(1)–As bonds, 2.543 (4) and 2.567 (4) Å.

Figure 2, which emphasizes the trishomocubane structure, shows that the two Re(CO)₃ units occupy positions equivalent to those of the Mo(CO)₃ units in I and that the three edge “flap” positions are occupied by two MeAs groups (As atoms 3 and 6) and by the Re(CO)₄ unit. The naked As atom, As(5), is necessarily in a corner position as it is bound to a Re atom.

The coordination environment about the three Re atoms is essentially octahedral; the largest deviation is the As(1)–Re(2)–As(8) angle of 77.7 (1)°, the apparent result of the preservation of the trishomocubane framework despite As–Re distances 0.15 Å longer than the As–As distances at this position in I.

II is thermally much more stable than I; between 120 and 170 °C I forms a succession of products as the temperature is raised.¹ In contrast, II is unchanged after 72 h at 200 °C.

West investigated photochemical and thermal reactions of *cyclo*-(AsCH₃)₅ and Mn₂(CO)₁₀.⁶ Photolysis at room temperature (sunlight through Pyrex) produced [*catena*-(AsCH₃)₅Mn₂(CO)₈] with a proposed structure likely similar to that of the isoelectronic complex [*catena*-(AsCH₃)₅Mo₂Cp₂(CO)₄];⁹ thermolysis at 150° C in benzene produced [(AsCH₃)₅Mn₂(CO)₆] of unknown structure.⁷ We are currently reinvestigating the Mn₂(CO)₁₀-cyclopolyarsine reactions and exploring reactions of Mn₂(CO)₁₀, Re₂(CO)₁₀, and MnRe(CO)₁₀ with cyclopolyarylsines.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (5 pages); a listing of structure factors (29 pages). Ordering information is given on any current masthead page.

(6) Elmes, P. S.; West, B. O. *J. Organomet. Chem.* 1971, 32, 365.

(7) West proposed⁸ that [(AsCH₃)₅Mn₂(CO)₈] was structurally related to [(AsPr)₅Mo₂(CO)₈] which contains an eight-membered chain terminally bonded to two Mo(CO)₃ groups joined by a metal–metal bond, the same structure we obtain from the thermolysis of I.⁹

(8) West, B. O. In *Homoatomic Rings, Chains and Macromolecules of the Main-Group Elements*; Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; p 409.

(9) Rheingold, A. L.; Churchill, M. R. *J. Organomet. Chem.* 1983, 243, 165.