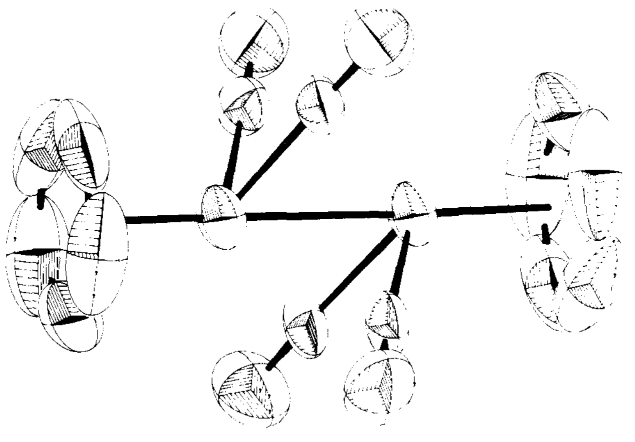

Figure 1. ORTEP II drawing of the molecular structure of $Cp_2Mo_2(CO)_4$. The thermal ellipsoids are drawn at 50% contours.

The molecule lies on a mirror plane which contains the Mo-Mo axis and bisects the Cp rings. Although only C_s symmetry is required, the structure has refined to C_{2h} symmetry within experimental error. The carbonyl groups are disordered, but we have been able to interpret the disorder in terms of a superposition of the structure shown in Figure 1 and a nearly equivalent structure in which the carbonyls "exchange" molybdenums.

The Mo-Mo bond length, 2.448 (1) Å, is ca. 0.8 Å shorter than the Mo-Mo bond in $Cp_2Mo_2(CO)_6$, 3.235 (1) Å,[13] thus confirming the triple bond formulation. The Cr≡Cr distance, 2.280 (2) Å, in $(C_5Me_5)Cr_2(CO)_4$ is 1.00 Å shorter than the Cr-Cr bond in $Cp_2Cr_2(CO)_6$.[14] However, the bond in the latter compound is anomalously long due to steric crowding.

The carbonyl groups lie over the Mo-Mo bond, and probably interact with it. The "short" Mo-C distances average 2.130 ± 0.050 Å and the "long" Mo-C average distance is 2.554 ± 0.050 Å. The carbonyls thus form a "class I" asymmetric bridging system in Cotton and Troup's classification.[15] The average Mo-C-O bond angle is 175.9 ± 1.2°, and the average Mo-Mo-C(carbonyl) angle is 67.4 ± 1.1°.

One of the more striking features of this structure is the near linearity of the Cp-Mo-Mo-Cp axis. The structures of $Cp_2M_2(CO)_6$ (M = Cr, Mo, W)[13,16] show pronounced M-M-Cp angles. This angle is opened to 159° in $(C_5Me_5)_2Cr_2(CO)_4$.[14] The opening of this angle and the position of the carbonyls over the Cr≡Cr bond in the latter compound were ascribed to the nonbonded interactions involving the bulky C_5Me_5 ligand. However, it is clear from the present structure that these bonding features are *not* dictated by nonbonding interactions, and the cause of these unusual structural features must be sought in terms of the electronic influence of the metal-metal triple bond.

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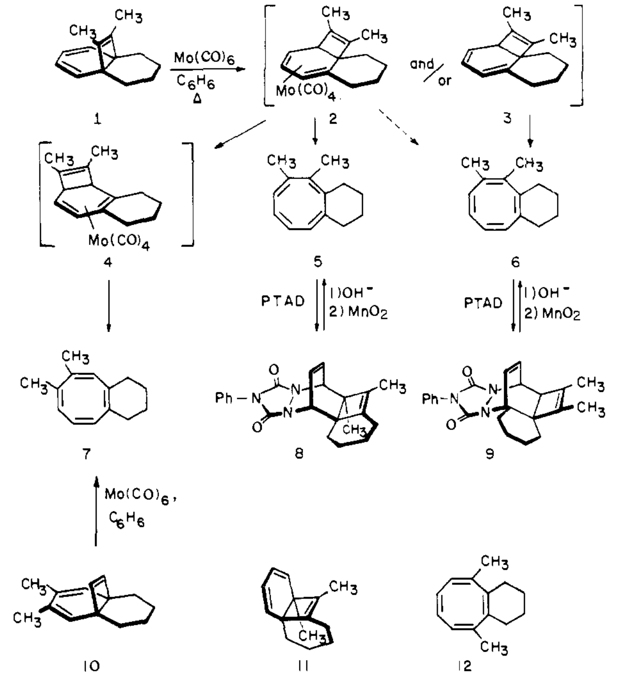
Transition Metal Catalyzed Rearrangement of 11,12-Dimethyl[4.4.2]propella-2,4,11-triene as a Route to Stable Cyclooctatetraene Bond Shift Isomers. Implications for [1,5]-Sigmatropic Migration within the Metal Coordination Sphere

Sir:

Although monosubstitution of the [4.4.2]propella-2,4,11-triene system at C_2 and C_{11} leads to striking regiospecificity[1] during $Mo(CO)_6$-promoted skeletal rearrangement to 1,2-annulated cyclooctatetraenes,[2] further practical exploitation of remaining mechanistic questions is not easily accommodated by these compounds. Qualitative ranking of several possible isomerization schemes has proven possible, but there is yet no insight into the level of metal coordination which becomes available. Working toward this last goal, we here report on the behavior of the title compound (**1**)[3] when subjected to the action of $Mo(CO)_6$ in refluxing benzene (Scheme I). The selection of **1** was predicated upon

Scheme I



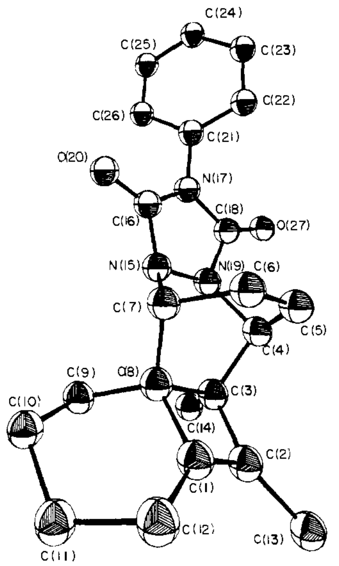


Figure 1. Structure for 8.

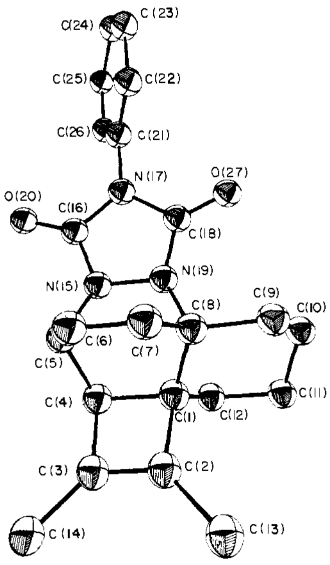


Figure 2. Structure for 9.

our independent discovery[4] that the attachment of four vicinal groups to the cyclooctatetraene ring significantly enhances the barrier to bond shifting such that stable double bond isomers can be readily isolated.

We anticipated that the extent of pπ interaction involving the Mo atom might reflect itself in the subsequent valence isomerization of the hypothetical intermediates **2**[5] and **3** to their cyclooctatetraene counterparts. As concerns free ligand **3**, ring opening should operate under the control of the 1,3-cyclohexadiene moiety and lead by disrotatory central bond cleavage exclusively to **6**.[4] In metal complex **2**, disrotatory opening of the cyclobutene ring is a real possibility as the direct result of different prevailing orbital interactions.[6] With such constraints, the formation of **5** was expected, although it was not known if leakage to **6** would also operate.

At the experimental level, heating of **1** with $Mo(CO)_6$ (0.1 mol equiv) in benzene at 80° for 24-48 hr gave in quantitative yield three products, the mixture consisting of ca. 40% **5**, 36% **6**, and 24% **7**.[7] Direct treatment with excess *N*-phenyltriazolinedione (PTAD) in refluxing ethyl acetate resulted in formation of two adducts, hydrocarbon **7** not being subject to cycloaddition under these conditions.[8] Fractional crystallization from ethyl acetate-hexane resulted in separation of the less soluble **9** mp 195-196°; ^1H NMR ($CDCl_3$) δ 7.2-7.55 (m, 5), 6.04 (d, J = 7 Hz, 2), 4.98 (br q, $J \approx 7$ Hz, 1), 3.10 (v br d, 1), 2.5 (br m, 1), 1.0-2.3 (m, 7), 1.67 and 1.48 (t, J = 1.5 Hz, 3 each)) from **8** (mp 207-207.5°; ^1H NMR ($CDCl_3$) δ 7.25-7.65 (m, 5), 6.25 (m, 2), 4.70 (m, 2), 1.2-2.3 (m, 8), 1.42 and 1.25 (s, 3 each)). The emergent patterns reveal **8** to have two bridgehead protons adjoining nitrogen and a pair of olefinic protons; for **9**, the most revealing features are the signals due to lone bridgehead and allylic hydrogens and the appreciable downfield shifting observed for one methylene proton. To confirm the presence of an unusual laterally fused cyclohexane ring in each of these adducts, their three-dimensional X-ray (Cu K_α) crystal structures were determined (Figures 1 and 2). Crystallographic data for **8** and **9** will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material.

While the crystals of **8** (low quality) belong to the monoclinic system with a = 12.697 (6), b = 6.291 (1), and c = 23.086 (6) Å (β = 88.22 (3)°), those of **9** proved to be orthorhombic with a = 11.304 (1), b = 14.205 (2), and c = 22.899 (2) Å. The systematic extinctions on $0k0$ (absent if $k = 2n + 1$) and $h0l$ ($l = 2n + 1$) for **8** uniquely require space group $P2_1/c$, while the systematic extinctions $0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $hk0$ ($h = 2n + 1$) for **9** require space group P_{bca}. Calculated densities of 1.30 g/cm^3 (Z = 4) and 1.31 g/cm^3 (Z = 8) indicated one molecule per asymmetric unit in each case. After correction of the data for Lorentz, polarization, and background effects, the number of reflections judged observed were 1799 and 2015. Normalized structure factors were computed and phase angles assigned to 500 E's larger than 1.18-1.20 by a multiple solution weighted tangent formula procedure.[9] The phased three-dimensional E synthesis revealed the 27 nonhydrogen atoms.[10] Full-matrix least squares treatment with anisotropic temperature factors assigned to all 27 atoms and subsequent additional refinements converged to the current unweighted residuals R of 11.5 and 4.2%. In general, bond distances and angles agree well with accepted values. No anomalously short intermolecular contracts were observed.

Hydrolysis oxidation[11] of **8** led uniquely to substituted cyclooctatetraene **5** as a result of π-assisted cheletropic ejection of nitrogen to give bicyclo[4.2.0]octatriene **11** and subsequent $_\pi 2_s + {}_\pi 2_s + \sigma 2_s$ (disrotatory) opening of its cyclohexadiene ring. Comparable treatment of **9** led to pure **6**. These two bond shift isomers show olefinic ^1H NMR resonances which, although not sufficient to establish the precise position of π bond fixation, are nevertheless quite mutually distinctive;[12] and these spectra differ from those of **7** and **12**.[3] Resubmission of **5** and **6** to the original reaction conditions did not appear to cause mutual interconversion. Rather, several new, uncharacterized compounds made their appearance (^1H NMR analysis).

Authentic **7** became available through $Mo(CO)_6$-catalyzed isomerization of propellatriene **10**. Identity of structure followed from the superimposable spectra of the two samples.

The data show not only that two stable bond shift isomers are produced in comparable quantities but also that twofold cyclobutene circumambulation can occur along the periphery of the 1,3-cyclohexadiene unit. Hydrocarbons **5** and **6** neither give evidence of $Mo(CO)_6$-promoted interconvertibility nor experience further rearrangement to **7** under the original conditions of its formation. The metal-ligand coordination present in **2** which allows for conversion to **4** is seemingly not attainable when approached from the direction of **5** and **6**. For the present, therefore, the prevailing

[1,5] carbon shifts can be described as processes involving specific coordination of the unsaturated propellane to molybdenum with suprafacial migration operating strictly under the control of the metal. Whether intermediates such as **2** undergo decomplexation to give **3** at rates competitive with ring opening remains an open question.

Lastly, we note that the conversion of **1** to **7** represents to this time a unique example of a metal catalyzed twofold circumambulatory rearrangement.[13]

Supplementary Material Available. The crystallographic data for **8** (fractional coordinates (Table I), bond distances (Table II), and bond angles (Table III)) and **9** (fractional coordinates (Table IV), bond distances (Table V), and bond angles (Table VI)) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3536.

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(5) As before, the η^4 designation is utilized to simplify structural depiction. We do not rule out the possibility of alternative coordination levels involving also, for example, the cyclobutene double bond. This would, however, require the molybdenum carbonyl moiety to reside on the upper face of the tricyclic structure (as presently drawn). Nor do we have information on the question of relative metal–olefin stereochemistry at this stage of our investigation (see ref 2).

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(12) Full spectral details will be given in a subsequent full paper.

(13) We thank the National Cancer Institute (Grant CA-12115), Chevron Research Co., and Atomic Energy Commission for financial support.

(14) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee, 1972–1977; Alfred P. Sloan Foundation Fellow, 1973–1975.

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1,2,3,4-Tetramethylcyclooctatetraene and 1,2,3,8-Tetramethylcyclooctatetraene. Stable [8]Annulene Bond Shift Isomers

Sir:

The cyclooctatetraene (COT) ring system, recognized to possess alternate single and double bonds and a tub (D_{2d}) conformation,[1] can undergo three fundamental structural changes: ring inversion, bond shifting, and valence isomerization. The first of these requires a planar-alternate transition state and is least energy demanding ($\Delta G^\ddagger = 14.7$ kcal/mol for cyclooctatetraenedimethylcarbinol).[2] Bond shifting necessitates attainment of a planar form with equal bond lengths and has a somewhat higher energy barrier ($\Delta G^\ddagger =$ 17.1 kcal/mol for cyclooctatetraenedimethylcarbinol).[2] Isomerization with formation of bicyclo[4.2.0]octa-2,4,7-triene has the most elevated transition state ($\Delta G^\ddagger = 28.1$ kcal/mol).[3] The first two processes are clearly related by virtue of requisite ring flattening.

The recent experimental findings by Ganis, et al.[4] of a significant increase in the free energy of activation for bond shifting in 1,3,5,7-tetramethylcyclooctatetraene ($\Delta G^\ddagger =$ 22.5 kcal/mol at 120°) and supportive theoretical calculations by Allinger and his coworkers[5] leave little doubt that enhanced van der Waals interactions by substituents can seriously impede the attainment of planarity by the [8]annulene ring.[6] On this basis, we have entertained the possibility of preparing shelf stable bond shift isomers of COT, and have directed attention initially to the 1,2,3,4- and 1,2,3,8-tetramethyl derivatives where buttressing effects were expected to contribute additionally to maintenance of the individual tub conformations. Since these isomers should be recalcitrant to interconversion, it appeared equally desirable to develop independent synthetic approaches to the two polyolefins. We here report successful realization of these goals.

The reaction of sulfone **1**[7] with 2 equiv of *n*-butyllithium and excess methyl iodide, followed by lithium aluminum hydride reduction of the dimethylated α-sulfonyl carbanion gave **2** (34%)[8] (Scheme I). Subsequent bromination-dehydrobromination[9] transformed this diene into the corresponding bicyclo[4.2.0]octatriene, the ring opening of which to furnish exclusively **4** (98%) proceeds disrotatorily

Scheme I