nistic insights. The above results provide substantial evidence for the viability of a mechanism for carbon-carbon bond cleavage of alkanes which involves direct insertion of a metal into the carbon-carbon bond as a first step. Thermochemical data indicating strong metal-carbon bonds corroborate this hypothesis. Further studies are underway in our laboratories to extend this technique to other systems.

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(4) This method of ionization minimizes the production of excited states. Attenuation experiments[5] showed no evidence of appreciable amounts of such states.
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(6) Similar schemes have been proposed: Remick, R. J.; Asunta, T. A.; Skell, P. S. *J. Am. Chem. Soc.* **1979**, *101*, 1320. Allison, J.; Freas, R. B.; Ridge, D. P. *Ibid.* **1979**, *101*, 1332.
(7) Sometimes referred to as Stevenson's rule,[8] this observation is a straightforward conclusion of RRKM theory.[1]
(8) Stevenson, D. P. *Discuss. Faraday Soc.* **1951**, *10*, 35.
(9) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.
(10) This value agrees with the range of 56 kcal/mol < D°(Co$^+$-CH$_3$) < 69 kcal/mol reported by Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

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Preference for the Syn Ene Additions of ${}^1O_2$ to 1-Methylcycloalkenes. Correlation with Ground-State Geometry

Sir:

We[1,2] and others[3] have recently demonstrated a strong, unexpected preference for the ene-type additions of ${}^1O_2$ at the disubstituted side of simple, acyclic, trisubstituted [(-CH$_2$R)$_3$] olefins: preference for the syn ene additions (PSEA). We now point out that the 4-, 5-, 7-, 8- (with *Z* geometry), and 12-membered (*Z* and *E* geometry) 1-methylcycloalkenes also show a PSEA (Scheme I) and that only 1-methylcyclohexene and its derivatives do not. Preoccupation with the latter, mainly terpenes, has obscured the fact that *PSEA is the rule in acyclic and cyclic systems, cyclohexenes excepted.* (*E*)-1-Methylcyclooctene, the 9 to 11 rings, and ≥12 rings have not yet been investigated.[4,5] We rely largely on published photooxygenation studies;[6] that these were carried out in different solvents and at different temperatures does not matter because product distributions are known to be insensitive to changes of either, and even of phase.[6,7] The available data are collected in Chart I. In the *Z* series, the 4, 5, and 7 rings (**1, 2, 4**) show a very strong PSEA, the 8 and 12 rings [(*Z*)-**5**, (*Z*)-**6**] a less pronounced PSEA, and the 6 ring (**3**) none. (*E*)-1-Methylcyclododecene [(*E*)-**6**] also shows a very strong PSEA. 1-Ethyl- or 1-propylcycloalkenes would be more suitable substrates for demonstrating the PSEA[5] and Chart I includes data on (*Z*)- and (*E*)-1-ethylcyclododecene [(*Z*)-, (*E*)-**7**], which parallel those for the 1-methylcyclododecenes [(*Z*)-, (*E*)-**6**].

Scheme I

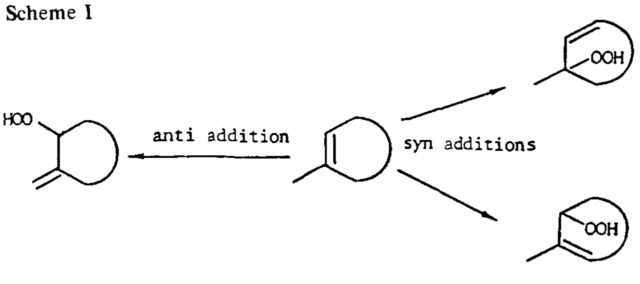
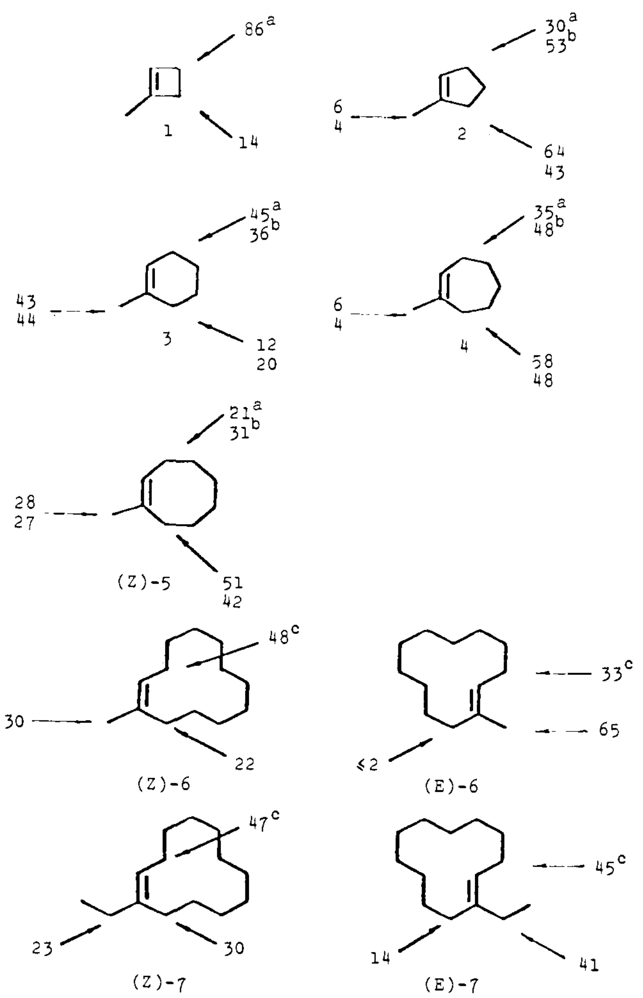


Chart I. Ene Additions of ${}^1O_2$ to 1-Methyl- and 1-Ethylcycloalkenes. Product Distributions[a]



[a] In percent; the arrows indicate the sites of the H-atom abstractions throughout; (a) ref 8; (b) ref 9; (c) note 10.

Chart II summarizes the available data on terpenes and data on a related substrate, **11**. The simple 4- and 5-substituted 1-methylcyclohexenes (**9–12**) all show no PSEA,[11] like the parent, **3**. The derived bicyclo[4.1.0]heptenes, 3-carene (**13**) and 2-carene (**14**),[18] do show a PSEA, as does the cyclopentene-derived bicyclo[3.1.0]hexene, 3-thujene (**8**).

It appears that ground-state geometry and reactivity, PSEA, can be correlated; we note that the ground-state geometries of the $H{-}C_n{-}C_1{=}C_2{-}C_3{-}H$ sites of the (*Z*)-cycloalkenes in Charts I and II are essentially of only two types (A, B), and that all rings with one type of geometry (A) show a PSEA and all rings with the other (B) do not. In the former, the 4-, 5-, 7-,

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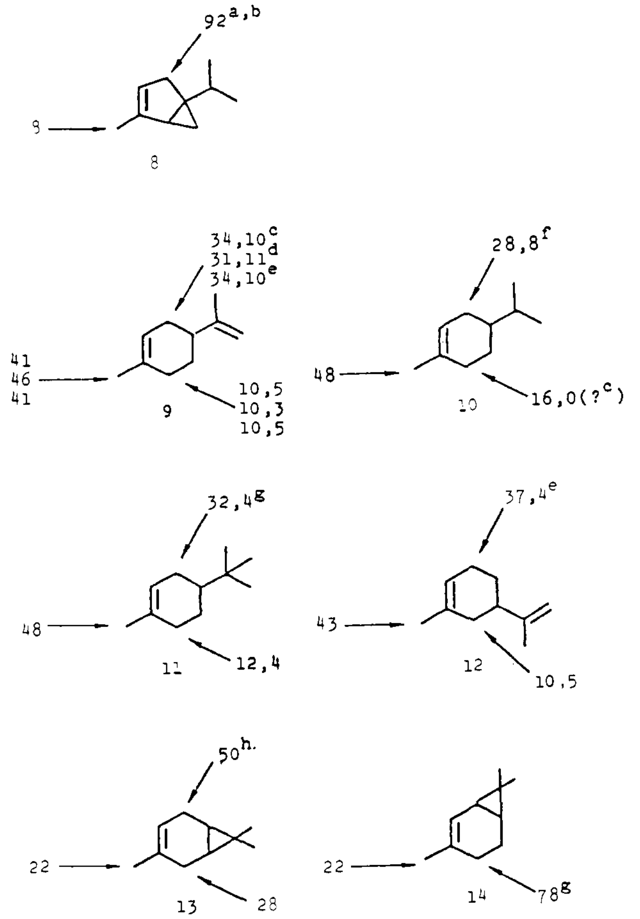
Chart II. Ene Additions of $^1O_2$ to Substituted 1-Methylcycloalkenes. Product Distributions



[a] The two ene additions involving H-atom abstraction at the methyl group are added. In the case of **9–12**, the two ene additions involving H-atom abstraction at the methylene groups are listed separately; the first number indicates abstraction of the pseudo-axial, the second abstraction of the pseudoequatorial H-atom if the assumption is made that only half-chair conformers with equatorial substituents react: (a) ref 12; (b) only the H atom which is on the same side as the isopropyl group is abstracted; (c) ref 13; (d) ref 14; (e) ref 15; (f) ref 16; (g) note 10; (h) ref 17.

8-, and 12-membered (Z)-1-methylcycloalkenes, one of the carenes, and the thujene, the allylic C—H bonds which emanate from *both* cis-oriented C atoms (C_3 and C_n) and lie above the plane of the double bond are roughly perpendicular to that plane, as in A; in the latter, the various 1-methylcyclohexenes, only one of these C—H bonds is roughly perpendicular, as in B.[19]

We hypothesize that the geometrical element A, a ground-state property, may be reflected in the transition state(s) involved in the syn ene additions: ene additions of $^1O_2$ occurring at *this site* (A) may be favorable.[29,31] Much current work still centers on defining the mechanism of the ene-type addition per se.[6,30] Our hypothesis seems to be most compatible with the perepoxide model, but a discussion of this point would be fruitless.

The bicyclic compounds (**8**, **13**, **14**) probably have fixed ground-state geometries. In these systems, it is possible to verify whether $^1O_2$ indeed attacks at site A. Unfortunately, only the geometry of 3-thujene (**8**) is accurately known;[19] $^1O_2$ does attack only at site A (Chart II).

The other rings undergo rapid conformational changes. In the case of the (Z)-cyclododecenes, there are probably two dominant conformers of comparable stability; in all other cases, a single conformer dominates. In every case, other conformers have small populations and our correlation is of course based on the geometries of the dominant conformers. The bimolecular ene additions are much slower than the various conformational changes and nondominant conformers *could* be involved in the reactions with $^1O_2$.[5,32]

The correlation cannot be extended to open-chain, trisubstituted olefins, because the preferred geometries of their H—C_a—C=C—C_b—H (C_a, C_b cis) sites are not known. The effects which are responsible for the PSEA in the case of trisubstituted olefins may also manifest themselves in the case of tetra- and 1,2-disubstituted olefins; experiments to verify this are underway.

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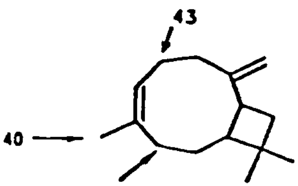
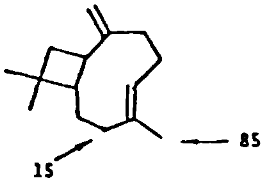
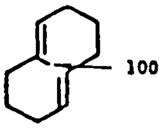


(Z)-15



(E)-15



(E,E)-16

(5) We plan to study the reactions of $^1O_2$ with the missing 1-methylcycloalkenes, with the complete set of 1-ethyl- or 1-propylcycloalkenes, and with conformationally fixed substrates. In the case of the 1-methylcycloalkenes, ene additions involving abstractions of CH_3-bound and CH_2-bound H atoms compete. The intrinsic reactivities of these C—H bonds may differ somewhat and a statistical factor may favor the reactions at the methyl groups (compare the ene additions to (Z)-**6** and (Z)-**7**). In the case of 1-ethyl- or 1-propylcycloalkenes, all three ene additions involve abstractions of CH_2-bound H atoms. On the basis of the results with (Z)- and (E)-**7** and of those with acyclic substrates,[1,2] we conclude that extrapolation from the 1-methyl- to other simple 1-alkylcycloalkenes with longer side chains is already justified.

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(11) It has been stressed that cyclohexenes are abnormally unreactive.[6b,c] For similar data on steroidal, cyclohexene-derived substrates, see ref 6d.

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(18) The reported product ratio (Gollnick, K.; Schade, G. *Tetrahedron Lett.* **1966**, 2335) contradicted our rule. Reinvestigation[10] showed that this ratio must be inverted.

(19) Direct structural information is only available in the case of 1-methylcyclobutene (**1**), 3-thujene (**8**), and 3-carene (**13**). In the other cases, we extrapolate from the geometries of the stable conformers of the parent (*Z*)-cycloalkenes which are all known. The stable conformers of cyclobutene[20] and 1-methylcyclobutene[21] are planar. The pairs of allylic C—H bonds on each side of the ring have identical, mirror-symmetric orientations as in A. The stable conformers of cyclopentene, the envelope conformation,[22] and of cycloheptene, the mirror-symmetric chair,[22,23] both have pairs of allylic C—H bonds in identical, mirror-symmetric orientations on either side of the ring; one pair has quasi-axial orientations as in A and the other has quasi-equatorial orientations. The stable conformer of (*Z*)-cyclooctene[22,23] and both stable conformers of (*Z*)-cyclododecene[24] have no symmetry, but have a pair of allylic C—H bonds in nonidentical, quasi-axial orientations on one side of the ring, approximately as in A, and a pair in quasi-equatorial orientations on the other side. In contrast, the stable conformer of cyclohexene, the half-chair,[25] has pairs of allylic C—H bonds with *different* orientations, quasi-axial and quasi-equatorial, on each side of the ring, as in B. 3-Thujene (**8**) is essentially planar[26] and has a pair of allylic C—H bonds in different orientations but approximately as in A on one side of the ring. The geometry of 3-carene (**13**) is not known with certainty; it is either one of the boats[22c,27] or a planar form.[22c,28] The former has a local geometry similar to that of cyclopentene and -heptene, the latter one similar to that of cyclobutene. The geometry of 2-carene (**14**) is unknown.

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(29) This hypothesis is reminiscent of, but different from, the previously established rule that an individual ene addition is favorable when the ground-state geometry of the substrate is such that the (single) C—H bond being broken is roughly perpendicular to the plane of the double bond.[6] This rule is almost solely based on data on half-chair cyclohexenes, which have only one such C—H bond, and are exceptions to our rule.

(30) For recent work, see: (a) Jefford, C. W. *Tetrahedron Lett.* **1979**, 985, and references cited therein. (b) Grdina, B.; Orfanopoulos, M.; Stephenson, L. M. *Ibid.* **1979**, 4351, and references cited therein.

(31) One of us has previously advanced this hypothesis,[2a] on the basis that the constitutional requirement for the PSEA to acyclic substrates appears to be the presence of the element HC$_a$—C═C—C$_b$H (C$_a$, C$_b$ cis).

(32) I.e., the Curtin–Hammett principle is applicable: the product composition depends on the relative energies of the transition states and *not* on the populations of the ground-state conformations. The Hammond postulate, however, may also be applicable: the transition states should resemble the reactants (provided that the rate-determining step is strongly exothermic; this may *not* be the case if a perepoxide or some related species is involved).

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Isolation and Characterization of $[Rh_5(CO)_{10}(\mu_2\text{-}CO)_5]^-$: A Key Product in Rhodium Carbonyl Chemistry

Sir:

The dianion[1] $[Rh_{12}(CO)_{30}]^{2-}$ is known to react reversibly at room temperature with carbon monoxide. This reaction produces a labile species which previously was tentatively formulated as $[Rh_{12}(CO)_{\sim 34}]^{2-}$ on the basis of volumetric measurements of absorbed CO in THF,[2] and which has characteristic IR[2] and ^{13}C NMR[3] spectra. For several years we have tried to clarify the nature of this species because of its relevance both in rhodium carbonyl chemistry[3] and in the catalytic synthesis of ethylene glycol.[4] We now report that we have been able to reformulate the "$[Rh_{12}(CO)_{\sim 34}]^{2-}$" species as $[Rh_5(CO)_{15}]^-$ and to obtain this pentanuclear cluster starting from $Rh_4(CO)_{12}$ and the $[Rh(CO)_4]^-$ anion.

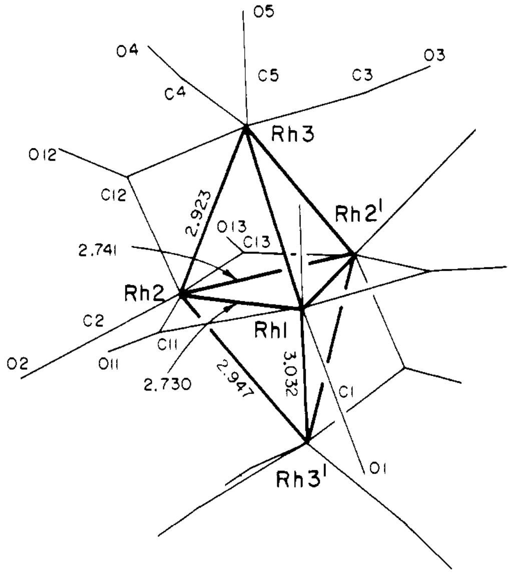

Figure 1. Atomic numbering scheme and Rh–Rh distances. Estimated standard deviations in distances are <0.001 Å.

At low temperature (−78 °C), reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with carbon monoxide (1 atm P) in THF led to slow precipitation of $Rh_6(CO)_{16}$ in such a way that the resultant equilibrium shifted toward formation of the labile species. From the filtered solution maintained under CO at −10 °C, it was possible in fact to obtain red-brown crystals of an extremely reactive anionic species as the bis(triphenylphosphino)iminium (PPN) salt. The precipitation was carried out by means of slow diffusion of 2-propanol saturated with CO. The X-ray structural analysis presented here shows the anionic species to be $[Rh_5(CO)_{15}]^-$. The IR spectrum of this product in THF is identical with that previously reported[2] [2045 (s), 2010 (vs), 1868 (m), 1838 (ms), and 1785 (m) ± 10 cm^{-1}] but this solution is unstable at room temperature under N$_2$. The same species subsequently was obtained in ~80% yield using the following redox condensation reaction:

$$Rh_4(CO)_{12} + [Rh(CO)_4]^- \xrightarrow[\text{THF}]{\text{CO}} [Rh_5(CO)_{15}]^- + CO \quad (1)$$

The $[PPN]^+[Rh_5(CO)_{15}]^-$ salt has been characterized by single-crystal X-ray diffraction techniques. The compound crystallizes in space group $P2/a$, with cell dimensions a = 19.313 (3), b = 9.375 (2), c = 14.804 (2) Å; β = 93.20 (1)°; and Z = 2. Observed and calculated densities are in satisfactory agreement: ρ_{obsd} = 1.81 and ρ_{calcd} = 1.83 g cm^{-3}, assuming a formula weight of 1473. Diffraction data were obtained with an Enraf-Nonius CAD4 diffractometer, using Nb-filtered Mo K$\bar{\alpha}$ (λ = 0.71069 Å) radiation. The structure was solved by standard heavy-atom methods and refined by a full-matrix least-squares procedure to yield an unweighted agreement factor on F^2 of R = 0.050 for 5837 reflections with $(\sin\theta/\lambda) < 0.65$ Å^{-1}.[5]

The structure of the $[Rh_5(CO)_{15}]^-$ anion in the crystalline state is illustrated in Figures 1 and 2. The metal atoms form a trigonal bipyramid, and the anion as a whole possesses crystallographic C_2 symmetry. A twofold axis passes through one of the Rh atoms in the equatorial plane [Rh(1)] and a bridging carbonyl ligand [CO(13)].[6] Altogether, there are ten terminal carbonyls [three each on the axial Rh(3) and Rh(3′),

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