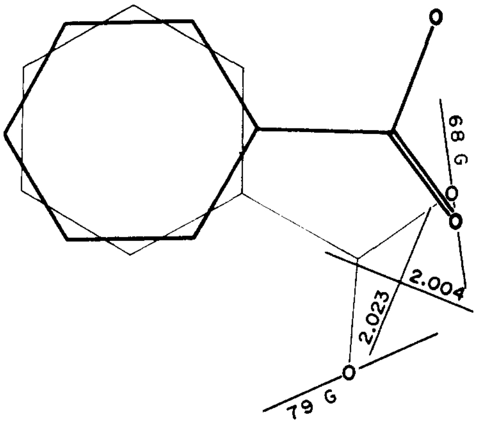

Figure 2. *g* and hfs eigenvectors of benzoyloxy projected on the plane of the original atomic locations in acetyl benzoyl peroxide (heavy lines). Implied radical position indicated by light lines.

isotopic oxygen might influence the spin distribution by perturbation of resonance[14] can be eliminated by the observation that fine-structure splittings in the methyl-benzoyloxy radical pair are identical for labeled and unlabeled material in the same crystal. This measurement would have been sensitive to a shift of 2% spin density between the two oxygens.

Figure 2 projects the unique hfs eigenvectors and the in-plane *g* eigenvectors onto the plane of the benzoyloxy atoms of undamaged acetyl benzoyl peroxide.[15] It is clear that, contrary to previous hypothesis,[10] the radical has undergone substantial in-plane rotation from its original position. The *g* tensor, which was previously used to argue for the $^2A'$ state,[10] is now seen to be in accord with the $^2B_2$ assignment. The vector product of the *g* eigenvectors of Figure 2 diverges from the normal to the original least-squares phenyl plane by 2°; that of the hfs eigenvectors diverges from the normal by 5.6°. Thus the tensors agree that the rotation is in plane and that the conformation of the radical is planar. They differ in assigning the amount of rotation: *g* implies 23° rotation, and hfs implies 30°. We believe this discrepancy is well beyond experimental error.[16]

Using the *g* shifts observed and matrix elements estimated from the INDO LUMOs of Figure 1, one can guess at the energy gaps between the $^2B_2$ ground state and the $^2A_2$ and $^2A_1$ excited states of benzoyloxy. The largest *g* shift predicts that the $^2A_2$ state lies 13 kcal/mol above $^2B_2$. The intermediate *g* shift implies that the $^2A_1$ state lies 55 kcal/mol above $^2B_2$. Even given that the two Σ states should have quite different OCO angles, the latter gap seems too high, especially since the radical is photodecarboxylated by light as red as 25 kcal/einstein.[5f]

The above observations should provide sensitive tests of the quality of wavefunctions for acyloxy radicals, as well as allowing interpretation of the arrangement of numerous radicals and radical pairs in single crystals.

Acknowledgments. We thank Dr. M. D. Newton and Professors N. C. Baird, W. L. Luken, O. Kikuchi, and H. W. Shields for comments and correspondence during this work. The study was supported by the National Science Foundation (DMR 76-01996). The spectrometer was obtained with the aid of an NSF departmental instrument grant.

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(12) Tabulated values of calculated atomic hfs couplings differ by 15% for oxygen.[11] Since the atomic wave functions may change substantially on incorporation into a molecule, an error of 25% or more for molecular applications is not surprising.

(13) The oxygen hfs does not vary significantly from 65 to 4 K.

(14) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071.

(15) These eigenvectors lie within 3° of the phenyl plane before projection.

(16) Angular errors were estimated by a procedure developed by D. W. Walter of these laboratories. It involves rediagonalizing the diagonal tensor after replacing the zero off-diagonal elements by their standard deviations estimated during least-squares refinement of the tensor. The shift in eigenvector direction measures the angular error. The hfs angular errors are given in Table I; those of the *g* eigenvectors are 1.6, 3.9, and 3.8° for the large, intermediate, and small *g* shifts, respectively.

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Received November 2, 1979

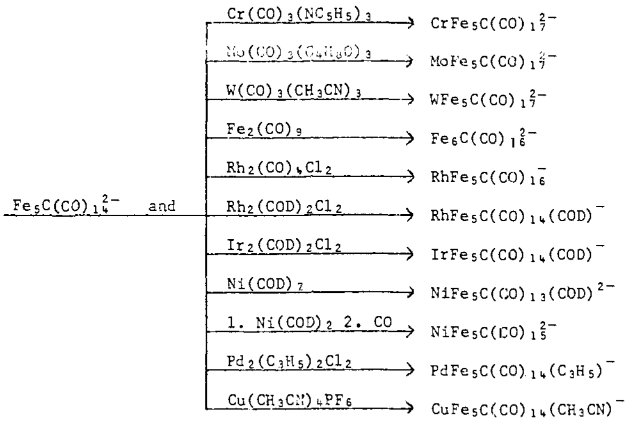
Metal Clusters. 24.[1] Synthesis and Structure of Heteronuclear Metal Carbide Clusters

Sir:

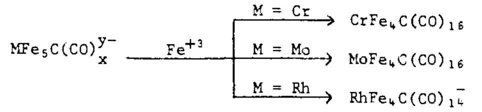
Metal carbide clusters,[2] a well-established and potentially very large group of clusters, are of substantial chemical interest because the carbide carbon atom, if exposed or open to reagent attack, may have an extensive chemistry of some novelty. Also these clusters may provide, by formal analogy, information about carbon as a surface species and as an intermediate in catalytic CO hydrogenation reactions.[3] In the carbide clusters with exposed or peripheral carbide carbon atoms—e.g., $Fe_5C(CO)_{15}$ and its derivatives—we have found a low degree of reactivity[4] and therefore have sought heteronuclear analogues that might prove more reactive.[5] We describe here a general synthesis of heteronuclear metal carbide clusters for the cage[6] octahedral MM'_5C class and for the peripheral[6] square-pyramidal MM'_4C class as well as crystallographic confirmation of the proposed structures.

Octahedral $MFe_5C(CO)_xL_y{}^{z-}$ complexes were prepared by reaction of the anion $Fe_5C(CO)_{14}{}^{2-}$, derived from $Fe_5C(CO)_{15}$ and $Fe(CO)_4{}^{2-}$, with mono- or dinuclear transition-metal complexes that are either coordinately unsaturated or that have readily displaceable ligands (Scheme I).[7a] The heteronuclear $MFe_5C(CO)_xL_y{}^{z-}$ clusters have been isolated as tetraethylammonium salts which were characterized by elemental analysis.[7b] All of these compounds formed black crystals—solution-state colors were purple for the octahedral clusters and ranged from dark green to brown for the square-pyramidal clusters. These include clusters which are the first carbide clusters that contain metal atoms outside of the iron and cobalt groups.[2] Neutral octahedral clusters like $NiFe_5C(CO)_{16}$ showed a parent ion in the mass spectrometric experiment and all mass ions resulting from successive CO loss down to the $NiFe_5C$ ion; this neutral cluster was prepared by oxidation of the anionic $NiFe_5C(CO)_{15}{}^{2-}$ species.

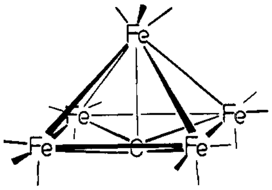
Scheme I



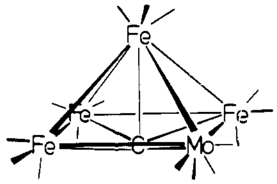
Scheme II



Oxidation of the heteronuclear MM'_5C carbide anions typically[8a] led to removal of one iron atom and the formation of the new class of heteronuclear MM'_4C carbide clusters, Scheme II.[8b,c] ^{13}C NMR data provided critical structural and dynamic ligand exchange information for these clusters. This is neatly illustrated for the parent $Fe_5C(CO)_{15}$ and the derivative $MoFe_4C(CO)_{16}$ clusters. The solid state structure[9] of the former is sketched in **1**. Between 25 and −80 °C, the ^{13}C spectrum of a ^{13}CO-enriched[10] sample of $Fe_5C(CO)_{15}$ was nearly invariant and consisted of two resonances of approximate relative intensities of 3 and 12—a spectral feature consistent with structure **1** only if there is either fast CO exchange (inter- or intrametal site exchange) over inequivalent sites[11] in the basal plane or accidental degeneracy of the inequivalent basal CO ^{13}C resonances. The former (inter- and intrametal) process has been established for other analogous metal clusters[12] and is the probable explanation.[11] For the molybdenum derivative cluster,[13] the ^{13}C spectrum consisted of two CO resonances of approximate relative intensities of 3 and 13 at 20 °C. The more intense resonance broadened with temperature decrease and by −80 °C separated into three separate resonances with relative intensities of ~3:6:4. The latter semilimiting exchange spectrum would be consistent with structure **2**[14] provided that fast ligand exchange *centered* at single metal atoms were operative even at −90 °C. The intermetal ligand exchange process evident in the −90 to 35 °C range is fully localized on the basal set of four metal atoms.[11]



1



2

Consistently, the rhodium analogue of the $MoFe_4C$ cluster, $RhFe_4C(CO)_{14}^-$, also has the unique metal atom in the basal plane. There is one bridging CO ligand between the basal rhodium and one basal iron atom as shown in Figure 1. This stereochemistry was established by a single-crystal X-ray diffraction study[15] of the tetraethylammonium salt of $RhFe_4C(CO)_{14}^-$. Here, notable features of the carbide framework structure are (A) the extension of the carbide carbon atom of ~0.19 Å beyond the basal Fe_3Rh plane and (B) the close similarity[17] between Fe-Fe and Fe-Rh (nonbridged edges) bond distances. Ligand exchange over metal atom sites was fast (^{13}C NMR time scale) at 25 °C in the rhodium cluster.

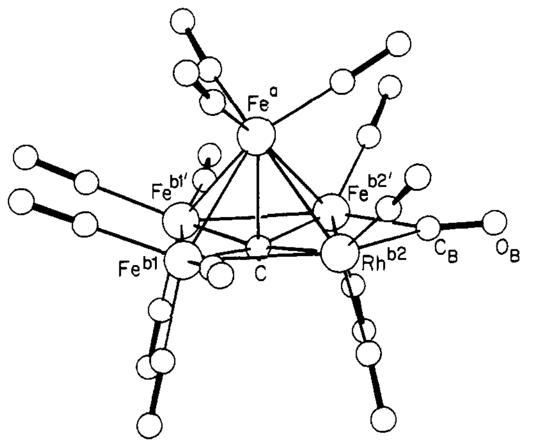


Figure 1. Perspective drawing (adapted from an ORTEP plot) for one isomer of the $RhFe_4C(CO)_{14}^-$ anion as observed in single crystals of its $(C_2H_5)_4N^+$ salt. All metal atoms are represented by large-sized open circles; carbon and oxygen atoms are represented by small open circles. The metal atoms lie at the vertices of a near-square pyramid with three iron atoms and the rhodium atom comprising the square base and the fourth iron atom at the apex. The carbide carbon atom is labeled with a C and is displaced by 0.19 Å from the 4-metal (M^b) basal mean plane on the side opposite Fe^a. Cocrystallization of equal amounts of the two enantiomeric forms of the anion produces a statistically disordered solid-state structure in which the basal M^{b1} sites are always iron atoms and the M^{b2} sites are half iron and half rhodium atoms. The disordered anion utilizes a crystallographic mirror plane which contains Fe^a and one of its carbonyls, the carbide carbon atom, and the single bridging (C_B–O_B) carbonyl ligand. The metal–carbide distances are of three types: Fe^a–C, 1.980 (12); Fe^{b1}–C, 1.868 (8); and M^{b2}–C, 1.941 (8) Å. Average bond lengths of interest follow: Fe–C(terminal CO), 1.763 (12, 17, 25, 5);[16] M^{b2}–C(terminal CO), 1.783 (12, 6, 6, 2); M^{b2}–C_B(bridging CO), 2.131 (13); C–O, 1.148 (13, 8, 19, 8); Fe–Fe, 2.616 (3, 18, 18, 2); Fe–M^{b2}, 2.633 (2, 22, 22, 2); M^{b2}–$M^{b2'}$, 2.779 (2) Å. Average angles: M–C–O(terminal CO), 176 (2, 2, 5, 7);[16] M^{b2}–C_B–O_B, 139.2 (3); M^{b2}–C_B–$M^{b2'}$, 81.4 (6)°.

The octahedral cage carbides from the parent $Fe_6C(CO)_{16}^{2-}$ to the $MFe_5C(CO)_x^{y-}$ derivatives showed a single ^{13}C CO resonance from −80 to +25 °C (a broadening phenomenon was evident for all near −90 °C). For $RhFe_5C(CO)_{16}^-$, the ^{13}C resonance was a doublet with $J_{Rh^{13}C}$(av) $\simeq$ 10 Hz. The related complex, $RhFe_5C(CO)_{14}$(1,5-cyclooctadiene)$^-$ had a ^{13}C CO singlet (apparently all terminal CO ligands are attached only to iron atoms) and two cyclooctadiene carbon resonances, one of which was a doublet with $J_{Rh^{13}C}$ = 9 Hz, a value comparable with typical[18] direct Rh-C spin coupling for olefinic carbon atoms. Thus, it appears that intermetal ligand exchange in most MFe_5C carbide clusters will have very low exchange barriers (<~8 kcal/mol). A crystallographic analysis[15] of the tetraethylammonium salt of the $MoFe_5C(CO)_{17}^{2-}$ cluster anion[17] established an octahedral $MoFe_5C$ framework. The carbon atom is displaced from the plane of the four iron atoms, Fe^1-Fe^4 (Figure 2), toward the molybdenum atom (by 0.1 Å) because the Mo-Fe bond distances are so much larger than the Fe-Fe distances, thus generating a slightly longer Fe^5-C (carbide) distance.

Our synthesis procedure has generality and has the potential

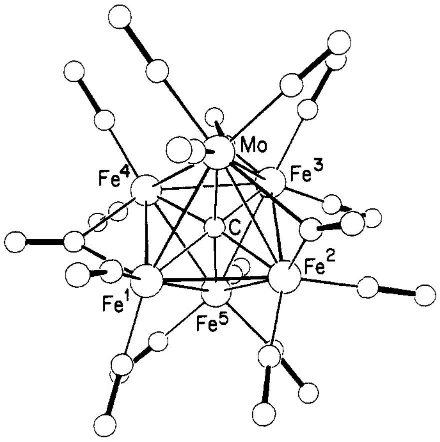


Figure 2. Perspective drawing (adapted from an ORTEP plot) of the $MoFe_5C(CO)_{17}^{2-}$ anion as observed in single crystals of its $(C_2H_5)_4N^+$ salt. Metal atoms are represented by large-sized open circles; carbon and oxygen atoms are represented by small open circles. The anion contains 15 terminally bonded and 2 unsymmetrically bridging carbonyl ligands. The four equatorial iron atoms (1-4) are coplanar to within 0.008 Å and the carbide carbon atom (labeled with a C) is displaced by 0.10 Å from their least-squares mean plane toward the axial molybdenum atoms. Metal-carbide distances are of three types: Mo-C, 2.117 (6); axial Fe^5-C, 1.947 (6); and equatorial Fe-C, 1.894 (7, 9, 17, 4) Å.[16] Average bond lengths of interest follow: Fe-C(terminal carbonyl), 1.757 (8, 12, 35, 12);[16] Mo-C(terminal CO), 1.932 (8, 6, 9, 3); Fe^1-C(bridging CO), 1.882 (8); Fe^4-C(bridging CO), 2.050 (7); Fe^2-C(bridging CO), 1.841 (8); Mo-C(bridging CO), 2.413 (8); C-O, 1.155 (9, 5, 15, 17); Mo-Fe, 2.915 (2, 54, 107, 4); Fe^5-Fe, 2.643 (2, 11, 21, 4); equatorial Fe-Fe, 2.673 (2, 61, 92, 4) Å; Average angles: M-C-O(terminal), 174 (1, 4, 13, 15); M-C-O(bridging), 139 (1, 8, 10, 4)°.

for preparing carbide clusters with many different metal atoms. The chemical and structural features of these new clusters are under investigation.

Acknowledgment. This research was generously supported by a grant from the National Science Foundation and aided by a loan of rhodium metal from Matthey Bishop Co. and by support of the computational research by the University of Nebraska Computer Center. We also acknowledge the elemental analyses by Mr. Vazken Tashinian of the U.C.B. Microanalytical Laboratory and mass spectrometric data from Professor John Shapley.

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(1) Preceding paper in this series: Muetterties, E. L.; Band, E.; Kokorin, A.; Pretzer, W. R.; Thomas, M. G. *Inorg. Chem.*, in press.

(2) Tachikawa, M.; Muetterties, E. L., *Prog. Inorg. Chem.*, in press.

(3) For a review of this literature see Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979,** *79,* 479.

(4) Tachikawa, M.; Muetterties, E. L., unpublished results for $Fe_5C(CO)_{15}$.

(5) It is notable that simple ligand substitution can effect a substantial stereochemical change upon the carbide carbon atom in a cluster. For example, the carbide carbon atom is centered in the Ru_6 octahedron of $Ru_6C(CO)_{17}$ but is significantly displaced away from the substituted ruthenium atom in η^6-$C_6H_3(CH_3)_3Ru_6C(CO)_{14}$. Cf. Mason, R.; Robinson, W. R. *Chem. Commun.* **1968**, 468.

(6) We[2] define (1) the cage carbide cluster class structurally as carbide clusters in which the carbide carbon atom is enclosed by the polyhedron described by the cluster metal atoms and (2) the peripheral carbide clusters as those that have a carbide carbon atom partially or wholly extending beyond a face of the polyhedron described by the cluster metal atoms.

(7) (a) A typical synthetic procedure for the preparation of a six-atom carbide cluster is that for $[(C_2H_5)_4N]_2MoFe_5C(CO)_{17}$. To a tetrahydrofuran solution of $[(C_2H_5)_4N]_2Fe_5C(CO)_{14}$ (100 mg/20 mL, 0.11 mmol) was added 45 mg of $Mo(CO)_3(C_4H_8O)_3$ (0.11 mmol). After 30 min of stirring, the solvent was removed under reduced pressure affording a deep purple solid. Crystallization of the solid from methanol gave black crystalline $[(C_2H_5)_4N]_2MoFe_5C(CO)_{17}$ (63 mg, 0.056 mmol) (51% yield). More product of lower purity was obtained from the supernatent. (b) Sample analytical data for $[(C_2H_5)_4N]_2NiFe_5C(CO)_{15}\cdot$(tetrahydrofuran). Calcd: C, 39.11; H, 4.50; N, 2.61; Fe, 26.0; Ni, 5.46. Found: C, 38.92; H, 4.34; N, 2.57; Fe, 26.1; Ni, 5.31.

(8) (a) An established exception is the conversion of $NiFe_5C(CO)_{15}^{2-}$ into $NiFe_5C(CO)_{16}$ on oxidation. (b) The synthesis of $MoFe_4C(CO)_{16}$ is typical for the preparation of the five-atom carbide clusters. To a suspension of $[(C_2H_5)_4N]_2MoFe_5C(CO)_{17}$ (200 mg) in toluene (50 mL) was added a 10% aqueous ferric chloride solution. The two-layer system was stirred vigorously until all of the solid $[(C_2H_5)_4N]_2MoFe_5C(CO)_{17}$ dissolved. The green-brown toluene layer was collected, and the solvent was removed under reduced pressure. Crystallization of the solid from dichloromethane at −78 °C afforded black crystals of $MoFe_4C(CO)_{16}$ (50% yield). (c) Sample analytical data for $[(C_2H_5)_4N]RhFe_4C(CO)_{14}$. Calcd: C, 32.09; H, 2.34; N, 1.63; Rh, 11.96; Fe, 25.96. Found: C, 31.33; H, 2.35; N, 1.58; Rh, 12.0; Fe, 25.7. The neutral $MoFe_4C(CO)_{16}$ and $CrFe_4C(CO)_{16}$ complexes yielded mass spectra that included the parent ion and all mass ions resulting from CO loss down to the $MoFe_4C$ and $CrFe_4C$ ions, respectively.

(9) Braye, E. H.; Dahl, L. F.; Hubel, W.; Wampler, D. L. *J. Am. Chem. Soc.* **1962,** *84*, 4633.

(10) The ^{13}CO-enriched sample was prepared by ^{13}CO interchange with $Fe_5C(CO)_{15}$ in toluene solution at ~250 mm of 90% ^{13}CO at 80 °C.

(11) Two types of ligand exchange processes appear operative if all data for these two M_5C clusters as well as for $Fe_5C(CO)_{14}^{2-}$ and $Fe_5C(CO)_{14}[P(CH_3)_2C_6H_5]$[4] are considered. The faster of the two processes would be ligand exchange centered at a single metal site and the slower the intermetal exchange of the eight CO ligands (basal sites and equatorial positions) that are nearly coplanar with the four basal metal atoms. Facile ligand exchange in clusters commonly involves ligands that are coplanar with the metal atoms in a cluster polyhedral face.[12]

(12) For a review of cluster rearrangements see Band, E.; Muetterties, E. L. *Chem. Rev.* **1978,** *78*, 639.

(13) This cluster has also been prepared by ferric iron reaction with $MoFe_5C(H)(CO)_{16}^{3-}$ which had been prepared earlier from the reaction of $Mo_2(OCOCH_3)_4$ and $Fe(CO)_4^{2-}$: Sievert A. C.; Smart, J. C., unpublished work. Sievert, A. C. Ph.D. Thesis, University of California (Berkeley), 1979.

(14) A crystallographic analysis of $MoFe_4C(CO)_{16}$ is still in progress.

(15) Large well-shaped single crystals of $[(C_2H_5)_4N]RhFe_4C(CO)_{14}$ (**3**) and $[(C_2H_5)_4N]_2MoFe_5C(CO)_{17}$ (**4**) were obtained by cooling their methylene chloride (**3**) or methanol (**4**) solutions. Single crystals of **3** are orthorhombic, space group $Pnnm$-D_{2h}^{12} (No. 58) with a = 17.267 (8), b = 12.210 (5), c = 14.406 (6) Å; Z = 4 Those of **4** are triclinic, space group $P\bar{1}$-C_i^1 (No. 2) with a = 12.662 (6), b = 16.607 (6), c = 11.609 (5) A; α = 91.86 (3), β = 117.94 (3), γ = 89.74 (3)°; Z = 2. Three-dimensional X-ray diffraction data were collected for those independent reflections of both compounds having $2\theta_{Mo\ K\bar{\alpha}} < 60.4°$ on a computer-controlled four-circle Syntex $P\bar{1}$ autodiffractometer using graphite-monochromated Mo $K\bar{\alpha}$ radiation and full (1° wide) ω scans. The metal atoms for both compounds were located using direct methods (MULTAN); the remaining anionic and cationic nonhydrogen atoms were located by standard difference Fourier techniques. The resulting structural parameters have been refined to convergence [R(unweighted, based on F) = 0.040 for 1562 independent reflections of **3** and R = 0.043 for 4187 independent reflections of **4** having $2\theta_{Mo\ K\bar{\alpha}} <$ 43° and $I > 3\sigma(I)$] using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all anionic nonhydrogen atoms and isotropic thermal parameters for all cationic nonhydrogen atoms of both compounds. Refinement is continuing for both compounds with those reflections having $2\theta_{Mo\ K\bar{\alpha}} < 60.4°$ and models which include anisotropic thermal parameters for all nonhydrogen atoms.

(16) The first number in parentheses following an averaged value of a bond length or angle is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

(17) Because of the disorder, these distances cannot be compared in a precise fashion.

(18) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976,** *20,* 299.

(19) Also formed in the $Mo_2(OCOCH_3)_4$ reaction[13] with $Fe(CO)_4^{2-}$.

(20) Camille and Henry Dreyfus Teacher-Scholar.

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Photogeneration of Intermediates Involved in Catalytic Cycles. β-Hydride Elimination from the 16-Electron Alkyl Species Generated by Irradiation of Tricarbonyl(η^5-cyclopentadienyl)(n-pentyl)tungsten(II)

Sir:

Study of many of the intermediates in catalytic cycles is often difficult owing to the fact that the rate-limiting step precedes the chemistry of the intermediate under consideration. Optical irradiation of thermally inert precursors to certain intermediates may allow study of reactive species, if

0002-7863/80/1502-1727$01.00/0