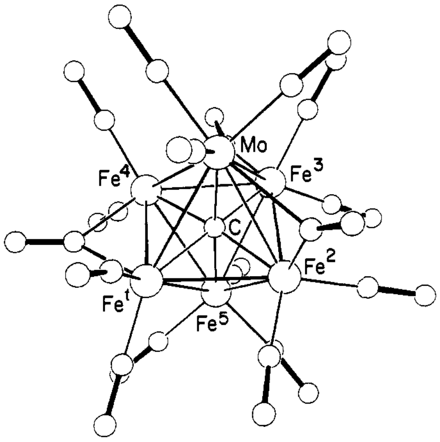

Figure 2. Perspective drawing (adapted from an ORTEP plot) of the Mo$Fe_5C(CO)_{17}^{2-}$ anion as observed in single crystals of its $(C_2H_5)_4N^+$ salt. Metal atoms are represented by large-sized open circles; carbon and oxygen atoms are represented by small open circles. The anion contains 15 terminally 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.

References and Notes

(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(4) Tachikawa, M.; Muetterties, E. L., unpublished results for $Fe_5C(CO)_{15}$.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 $[(C_2H_5)_4N]_2NiFe_5C(CO)_{15}$·(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 P1 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

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Table I. Infrared Band Maxima for Relevant Complexes[a]

complex	solvent; T, °C	ν_{CO}, cm^{-1} (ϵ, M^{-1} cm^{-1} or rel abs)	
$(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$	isooctane; 25	2016 (6800)	1926 (11 000)
$(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})H$[b]	isooctane; 25	1973 (1.0)	1900 (1.9)
$(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})H$[c]	1-pentene; 25	1972 (1.0)	1898 (1.9)
$(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-pentyl})$	isooctane; 25	1932 (1.0)	1858 (2.1)
$(\eta^5\text{-}C_5H_5)W(CO)_3H$[d]	isooctane; 25	2026 (1.0)	1936 (2.2)
$(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$[d]	isooctane; 25	2021 (6200)	1932 (13 600)
$(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_3$	isooctane; 25	1936 (1.0)	1861 (1.2)
$(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl})$	paraffin matrix; −189	1948 (1.0)	1862 (1.0)
$(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$	paraffin matrix; −233	1955 (1.0)	1865 (1.0)
$[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$	isooctane; 25	1960 (9800)	1912 (7700)

[a] Data were recorded using a Perkin-Elmer Model 180 infrared spectrometer. [b] From irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ at 25 °C. [c] From irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ in the presence of 1-pentene at 25 °C. [d] These compounds were prepared by the method outlined in Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

the photoreaction can be carried out at temperatures low enough that the intermediate is thermally inert. We report our preliminary findings concerning such a system in connection with β-hydride elimination from coordinatively unsaturated metal alkyls. The possibility of β-hydride elimination is an important consideration in whether metal alkyls can be isolated in the first place.[1] β-Hydride elimination is also of possible consequence in catalytic hydrogenation, hydrosilation, isomerization, metathesis, hydroformylation, and oligomerization of olefins as well as in the hydrogenolysis and other heterogeneous catalytic reactions of hydrocarbons.

Irradiation (355 nm ± 20 nm; 1.6×10^{-6} einstein/min) of the thermally inert $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$[2] in degassed isooctane solution at 25 °C results in disappearance of the starting material with a 366-nm quantum yield of 0.58 ± 0.05. Following the photoreaction by IR spectroscopy in the CO stretching region reveals the initial growth of absorptions at 1973 and 1900 cm^{-1} (Figure 1) as absorptions for the starting material decline. Secondary photoproducts are observed that are assigned as $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$ by IR, ^{1}H NMR, and UV-visible spectroscopy; see Table I. To minimize the importance of the secondary photoproducts, we have flash photolyzed ~10^{-3} M, degassed 3.0-mL isooctane solutions of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$. We have used a 2000-J, ~50-μs xenon flash through Pyrex glass to yield up to 90% disappearance in a single flash with nearly exclusive formation of the product characterized by the 1973- and 1900-cm^{-1} absorptions. The photoproduct is somewhat air sensitive but is relatively coordinatively inert at 25 °C, and isooctane solutions can be evaporated at 25 °C to dryness without decomposition. The solid can then be dissolved in C_6D_6 or $C_6D_5CD_3$ for ^{1}H NMR spectra. The ^{1}H NMR spectra show a resonance at δ −5.9 consistent with a metal hydride and a complex signal at δ 4.5–5.0 consistent with the vinyl protons of a coordinated alkene. The species reacts with CCl_4 at 25 °C to form $HCCl_3$ as does $(\eta^5\text{-}C_5H_5)W(CO)_3H$. Thus, we identify the photoproduct as $(\eta^5\text{-}C_5H_5)W(CO)_2(\text{pentene})(H)$. The same product results from irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ in the presence of 1-pentene (Table I), consistent with the fact that the principal result of irradiating $(\eta^5\text{-}C_5H_5)W(CO)_3H$ is CO substitution.[3a] Prolonged irradiation of $(\eta^5\text{-}C_5H_5W(CO)_3(n\text{-pentyl})$ results in the formation of 1-pentene (and small amounts of the 2-pentenes) and n-pentane, consistent with the secondary photoproducts $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$. The lack of significant quantity of the 2-pentenes and the formation of the same product from photosubstitution of CO by 1-pentene in $(\eta^5\text{-}C_5H_5)W(CO)_3H$ lead us to conclude that the IR absorptions at 1973 and 1900 cm^{-1} are associated with $(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H)$ from irradiating $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$.

For species similar to $(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H)$, the relative intensity of the two infrared bands has been used to determine the OC–W–CO angle.[1] Using the relative intensities we determine the OC–W–CO angle to be ~108°. This angle suggests that the alkene–hydride product is principally the trans isomer, though the cis isomer is possibly formed first. Further structural proof is currently being pursued.

Irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ in degassed toluene solution of 0.5 M PPh_3 results in the growth of IR absorption at 1936 and 1845 cm^{-1} (Figure 1); these bands are similar in position and relative intensity to those resulting from irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ under the same conditions.[4] The product is *not* $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(H)$, since the IR spectrum is not that found for this hydride.[3b] We conclude that the product is that resulting from CO photosubstitution by PPh_3, $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-pentyl})$. Reaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H)$ with PPh_3 at 25 °C does occur[5] to yield the same species, but the rate is too slow to be the mechanism for the photosubstitution of CO by PPh_3 at 0.5 M PPh_3. These results suggest that CO ejection in the primary chemical result of exciting $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ just as has been suggested for other $(\eta^5\text{-}C_5H_5)M(CO)_3R$ compounds (M = Mo, W; R = Cl, Br, I, $-CH_3$, $-H$, $-CH_2C_6H_5$).[3,4,6]

Low-temperature irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ in hydrocarbon matrices provides direct evidence for the steps[7]

$$(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl}) \xrightarrow{h\nu} (\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) + CO \tag{1}$$

$$(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) + CO \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl}) \tag{2}$$

$$(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) + PPh_3 \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-pentyl}) \tag{3}$$

$$(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl}) \xrightarrow{\Delta} (\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H) \tag{4}$$

The irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3R$ (R = $-CH_3$, $-n$-pentyl) at 77 K in a hydrocarbon matrix (toluene or hexane) containing PPh_3 followed by warmup to 298 K results in formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(R)$. Monitoring the IR spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3R$ at 77 K in a paraffin matrix reveals the growth of two absorptions at nearly the same position and relative intensity for R = CH_3 and n-pentyl (Figures 1 and 2). Accompanying the IR spectral changes are large visible spectral changes; the matrix turns from nearly colorless or pale yellow to blue. The two IR absorptions and the blue color are attrib-

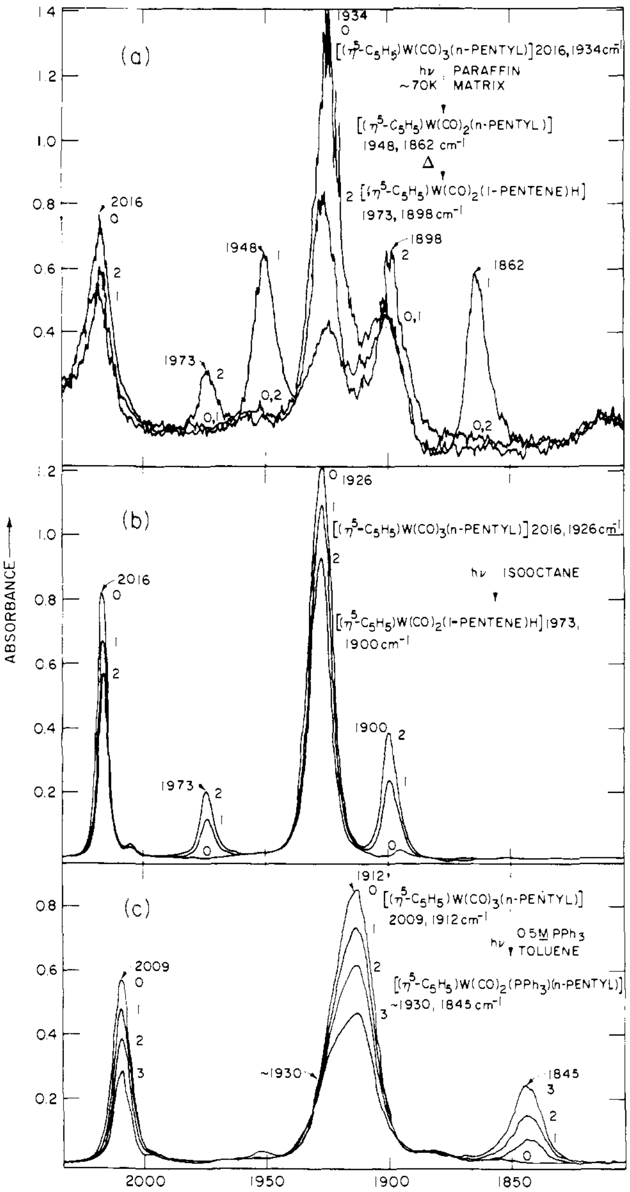

Figure 1. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$. (a) Trace 0 shows $\sim 2 \times 10^{-3}$ M $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ in a paraffin matrix at -189 °C before irradiation. Trace 1 is obtained after 5-min irradiation and shows formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(n\text{-pentyl})$. Trace 2 is obtained after warming to 25 °C showing formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})H$. (b) Trace 0 shows 1.5×10^{-3} M $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ in degassed isooctane. Traces 1 and 2 are after one and two flashes at 25 °C from a xenon flash lamp, respectively. Formation of $(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})H$ is observed. (c) Trace 0 shows 1.5×10^{-2} M $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ in degassed toluene containing 0.5 M PPh_3. Traces 1, 2, and 3 are after 15-, 35-, and 65-s irradiation, respectively. The observed product is $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)(n\text{-pentyl})$.

uted to the 16 e^- $(\eta^5\text{-}C_5H_5)W(CO)_2R$. Warmup in the paraffin matrix leads to nearly complete regeneration of $(\eta^5\text{-}C_5H_5)W(CO)_3R$ for R = $\text{-}CH_3$ presumably via a recombination process as shown in eq 2, but for R = -n-pentyl regeneration of $(\eta^5\text{-}C_5H_5)W(CO)_3R$ is only partial; there is significant conversion into the species $(\eta^5\text{-}C_5H_5)W(CO)_2(1\text{-pentene})(H)$ on the basis of the IR peaks that grow in upon warmup (Figure 1). Thus, we can spectroscopically monitor the β-hydride transfer from the 16 e^- alkyl species (eq 4). This process appears to occur at temperatures as low at -100 °C; the rate constant at this temperature is $\sim 5 \times 10^{-4}$ s^{-1}.

In summary, irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ results in loss of CO as a primary photoprocess followed by β-hydride transfer to yield an alkene-hydride complex. The photogenerated, coordinatively unsaturated metal alkyl intermediate has been observed at low temperatures. These results show that it will be possible to evaluate factors controlling the rate of β-hydride transfer.

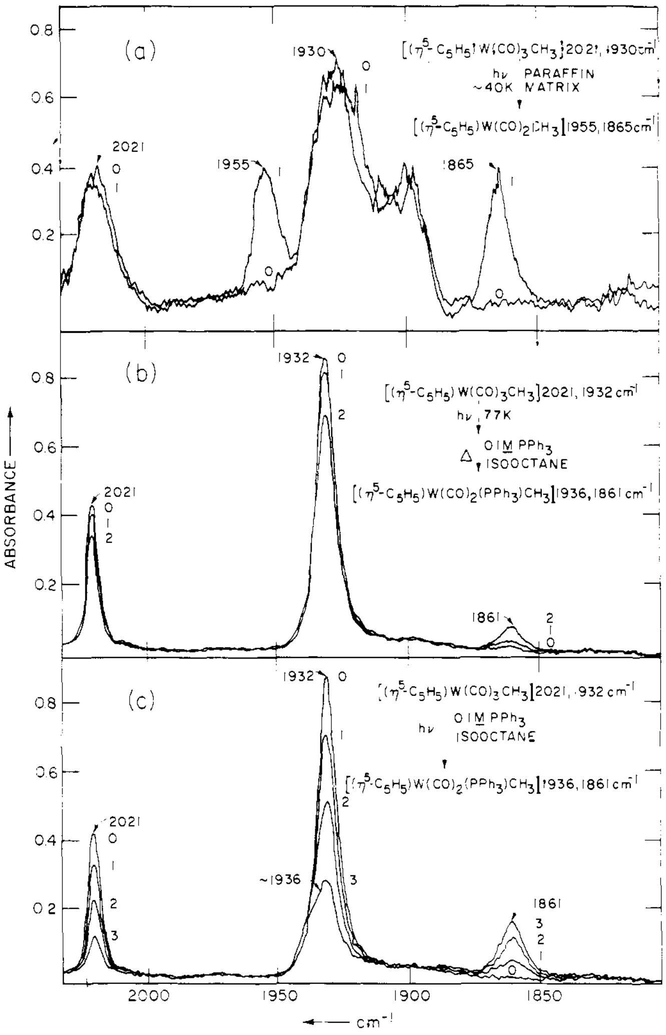

Figure 2. Infrared spectral changes accompanying irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$. (a) Trace 0 shows $\sim 8 \times 10^{-3}$ M $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ in a paraffin matrix at -233 °C before irradiation. Trace 1 is obtained after 28-min irradiation and shows formation of $(\eta^5\text{-}C_5H_5)W(CO)_2CH_3$. (b) Trace 0 shows 8.0×10^{-4} M $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ in degassed isooctane containing 0.1 M PPh_3 before irradiation. Traces 1 and 2 are after 15- and 60-min irradiation, respectively, at -196 °C followed by warming to 25 °C. The observed product is $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_3$. (c) Trace 0 shows 8.0×10^{-4} M $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ in degassed isooctane containing 0.1 M PPh_3 before irradiation. Traces 1, 2, and 3 are after 1-, 3-, and 7-min irradiation, respectively, at 25 °C. The observed product is $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)CH_3$.

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(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley: New York, 1972; p 757.

(2) $(\eta^5\text{-}C_5H_5)W(CO)_3(n\text{-pentyl})$ was prepared by reaction of $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$ with n-pentyl iodide in THF solutions. The product is a solid (mp 65 °C). The elemental analysis is satisfactory (Alfred Bernhardt, West Germany). Calcd: C, 38.64; H, 3.99. Found: C, 38.50; H, 3.91. The mass spectrum shows a parent peak region consistent with this species. The ^1H NMR spectrum in $CDCl_3$ shows a singlet at δ 5.32 for the C_5H_5 moiety and a complex signal

in the δ 1.0–1.5 range for *n*-pentyl. The integration of the singlet to multiplet is the expected 5:11. The UV-visible absorption exhibits a shoulder at 250, a maximum at 310 (ϵ 2700 M^{-1} cm^{-1} in isooctane), and a shoulder at 350 nm.

(3) (a) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613. These authors suggest W–H cleavage by light, initiating radical substitution processes. Preliminary results in our laboratory show evidence that dissociative loss of CO is a significant result of optical excitation of (η^5-C_5H_5)W(CO)$_3$H. (b) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715.

(4) Severson, R. G.; Wojcicki, A. *J. Organomet. Chem.* **1978**, *157*, 173.

(5) We find that PPh_3 reacts with (η^5-C_5H_5)W(CO)$_2$(1-pentene)H to yield (η^5-C_5H_5)W(CO)$_2$(PPh$_3$)(*n*-pentyl). Presumably, the reaction occurs as a result of the reversion of the alkene–hydride to the alkyl followed by scavenging by PPh_3. Rate of reaction as a function of PPh_3 concentration supports this mechanism. The approximate rate of conversion of (η^5-C_5H_5)W(CO)$_2$(1-pentene)H into (η^5-C_5H_5)W(CO)$_2$(*n*-pentyl) is $\sim 2 \times 10^{-3}$ s^{-1} at 25 °C. The slow rate may be due to the fact that the alkene–hydride is the trans isomer.

(6) (a) Alway, D. G.; Barnett, K. W. *Adv. Chem. Ser.* **1978**, No. 168, 115. (b) Mills, W. C., III; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 5830. (c) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(7) Low-temperature infrared data were obtained using a Cryogenics Technology Incorporated Spectrim II cryocooler using a sample compartment equipped with NaCl windows. Paraffin solutions of (η^5-C_5H_5)W(CO)$_3$R were prepared by heating the paraffin to the melting point ($\sim$70 °C) and dissolving the complex. The solution was then coated onto sapphire flats and mounted in the cryocooler for irradiation and spectroscopic measurements.

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Heterodinuclear Di-μ-sulfido Bridged Dimers Containing Iron and Molybdenum or Tungsten. Structures of $(Ph_4P)_2(FeMS_9)$ Complexes (M = Mo, W)

Sir:

Molybdenum K-edge X-ray absorption fine structure (EXAFS) analyses have been reported for the MoFe protein components of the *Clostridium pasteurianum*[1] and *Azotobacter vinelandii*[2] (Az. v.) nitrogenases, and for the FeMo cofactor[2] (FeMo-co) from Az. v.[3] These studies have lead to the conclusion that the Mo coordination environments are very similar, and in all cases the Mo is coordinated by three or four S atoms at 2.3 Å and is at close proximity (<3 Å) to two or three Fe atoms.

A partial adherence to the above coordination requirements for the Mo atom is found in the structures of the "double cubane" cluster complexes $[Mo_2Fe_6S_9(SEt)_8]^{3-}$ [4] and $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (R = Et;[4] R = Ph;[5] R = SCH_2CH_2OH[6]). The EXAFS spectra of the Mo centers in the ethyl derivatives of these clusters are very similar to those obtained for the nitrogenase systems.[4] Because of basic differences in the Mo:Fe:S atom ratios between the FeMo proteins, the FeMo-co, and the "double cubanes", the latter cannot be considered complete analogues. However, it seems likely that Mo-containing fragments in the "double cubanes" may be identical with fragments in FeMo-co and the nitrogenases.[4]

In our approach to the construction of Mo-Fe-S clusters in appropriate Mo:Fe ratios we have initiated synthetic efforts toward the isolation of molecular "building blocks" that contain Fe, S, and Mo, which eventually may be used in the synthesis of clusters of higher complexity. In a recent publication we reported[7] on the synthesis and structural characterization of one such molecule, $(Et_4N)_2[(PhS)_2FeS_2MoS_2]^{2-}$ (I) (Figure 1). In this communication we report on the tungsten analogue of this complex, $[(PhS)_2FeS_2WS_2]^{2-}$ (II), and the reactions of I and II with trisulfides. The complex II was obtained by the reaction of $[WS_4]^{2-}$ with an equimolar amount of $[Fe(SPh)_4]^{2-}$ [8] in dimethylformamide (DMF) and isolated, in near-quantitative yields, as red crystals of the Ph_4P^+ or Et_4N^+ salts, upon addition of diethyl ether to the DMF solutions, Anal. Calcd for $WFeS_6C_{60}H_{50}P_2$: C, 56.96; H, 3.98; S, 15.2; Fe, 4.41. Found: C, 56.92; H, 4.01; S, 15.09; Fe, 4.40. The visible spectrum (DMF) of this paramagnetic compound (μ_{eff}^{corr} = 4.73 μ_B at 298 K) is characterized by absorptions at 540 nm (sh), 466 (sh), 432 (ϵ 6890), 409 (11 300), and 375 (8310). Single-crystal diffraction patterns of the Et_4N^+ salt of II are very similar to those of I and show that the two complexes are isomorphous and very likely isostructural. An $S = 2$ ground state is suggested by the magnetic moment of II, and the simple Curie-Weiss magnetic behavior, evident in the temperature dependence of the isotropically shifted proton resonances,[9] rules out the population of higher spin states at a temperature as high as 352 K. The ^{57}Fe Mössbauer spectrum of II at 4.2 K shows a single doublet with a quadrupole splitting (QS) of 2.24 (1) mm/s and an isomer shift (IS) of 0.48 (1) mm/s (relative to Fe metal at 298 K). These values are similar to those obtained for I at 4.2 K (QS, 1.96 (1); IS, 0.45 mm/s) and suggest that the electronic environment of the Fe atom is rather insensitive to a change from Mo to W in the heterodinuclear dimers. By Mössbauer, isomer shift criteria established for the iron-sulfur proteins and their synthetic analogues, a value of +0.45 mm/s is intermediate between those observed for high-spin Fe(II) and Fe(III) in tetrahedral sulfur environments.[10]

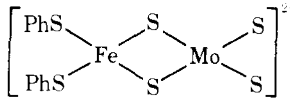
(I)

Figure 1.

The reactions of the Ph_4P^+ salts of either I or II with 10 equiv of RSSSR (R = C_7H_7) in warm DMF proceed readily. Upon cooling and dilution with absolute ether, these DMF solutions deposit X-ray isomorphous crystals of the $(Ph_4P)_2[(S_5)FeS_2MS_2]$ salts as the hemi-DMF solvates (M = Mo, dark brown crystals, 86% yield; M = W, dark red crystals, 79% yield). Anal. Calcd for $FeMoS_9C_{48}H_{40}P_2 \cdot {}^1/_2(C_3H_7ON)$ (III): C, 51.44; H, 3.80; N, 0.61; P, 5.36; S, 24.97; Mo, 8.30. Found: C, 50.62; H, 3.84; N, 0.64; P, 5.22; S, 24.23; Mo, 8.43. Anal. Calcd for $FeWS_9C_{48}H_{40}P_2 \cdot {}^1/_2(C_3H_7ON)$ (IV): C, 47.56; H, 3.54; N, 0.56; S, 23.32; Fe, 4.51. Found: C, 46.75; H, 3.25; N, 0.41; S, 21.9. Electronic spectra for IV: 550 nm (ϵ 1250), 464 (sh), 425 (7480), 398 (7830), 366 (9390). The magnetic moments (μ_{eff}^{corr}) of III and IV, 4.90 and 4.90 μ_B at 298 K, respectively, again indicate $S = 2$ ground states for these complexes. The Mössbauer spectrum of IV (in liquid N_2) consists of a single doublet and shows a quadrupole splitting of 1.66 (1) mm/s and an isomer shift of 0.51 (1) mm/s.

Single crystal, X-ray diffraction, intensity data on III and IV were collected on a Picker-Nuclear FACS-I automatic diffractometer using a θ–2θ scan technique.[11] The data corrected for Lorentz, polarization, and absorption effects were used for the solution of the structures by conventional Patterson and Fourier techniques. Refinement by full-matrix least-squares methods has progressed to conventional R = 9.5% for III and 8.5% for IV using isotropic thermal parameters for the carbon atoms and the DMF-solvate molecule and anisotropic thermal parameters for all other atoms. The hydrogen atoms have not been included in the refinement process as yet. The structures of the anions (Figure 2) show the tetrahedrally coordinated Fe atoms bound by S_5^{2-} bidentate chelates and by the MS_4^{2-} (M = Mo, W) units which also serve as bidentate chelates. The S_5^{2-} anion, although not a common ligand, occurs as a bidentate chelate in $[Fe_2S_{12}]^{2-}$,[12] $(PtS_{15})^{2-}$,[13] and $Ti(Cp)_2S_5$.[14] In the structures of $[Fe_2S_{12}]^{2-}$ and $(PtS_{15})^{2-}$, the MS_5 "ring" units are found in the chair conformation

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