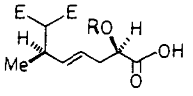
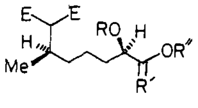
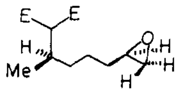
two steps) gave lactone **9**[9] ($[\alpha]^{25}_{D}$ −46.8°, c 1.0, $CHCl_3$) which was benzoylated (PhCOCl, pyridine, CH_2Cl_2, 95%) to produce **10** ($[\alpha]^{25}$D −19.7°, *c* 1.0, $CHCl_3$, mp 88–90 °C), the purity of both compounds confirmed by chromatographic and ^1H and ^{13}C NMR criteria. The critical alkylation of **10** (1.3 equiv of sodiomalonate, 5% $Pd(PPh_3)_4$, THF, 95%) proceeded smoothly to yield **11**[9] ($[\alpha]^{25}_{D}$ −9.95°, *c* 1.11, $CHCl_3$) whose diastereomeric purity was established by 50.10-MHz ^{13}C NMR spectroscopy.

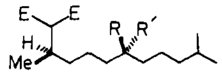

11 E = CO_2Me
R = COPh

Reduction of **11** (1 atm of H_2, PtO_2, EtOAc, 91%) produced **12**[9] ($[\alpha]^{25}_{D}$ +1.26°, *c* 2.2, $CHCl_3$), also diastereomerically pure by 50.10-MHz ^{13}C NMR spectroscopy. The epoxide **15**[9] was pro-


12 R = COPh; R′ = O; R″ = H
13 R = COPh; R′ = H,H; R″ = H
14 R = COPh; R′ = H,H; R″ = Ts


15

duced by the straightforward series of steps of reduction to alcohol **13** [5 equiv of $BH_3 \cdot S(CH_3)_3$, Et_2O, 93%], tosylation to **14** (2.2 equiv of TsCl, pyridine, 90%), and base catalyzed cyclization to **15** (1.3 equiv of NaOMe, MeOH, 60%) which was purified by preparative high-performance LC (25% EtOAc in hexane).[12] Organocuprate epoxide opening[13] (isopentylcopper cyanide, Et_2O, −10 °C, 64%) gave the enantiomerically pure alcohol **16**[9] ($[\alpha]^{25}_{D}$ +4.42°, *c* 2.78, $CHCl_3$), whose stereochemical purity was established chromatographically and spectrally by 270-MHz ^1H and 50.10-MHz ^{13}C NMR spectroscopy.


16 R = OH; R′ = H
17 R = OTs; R′ = H
18 R = H; R′ = Me

Creation of the last chiral center required tosylation to **17** (2.2 equiv of TsCl, pyridine, 75%) and organocuprate coupling [5 equiv of $Li(CH_3)_2Cu$, ether, −15 °C]—a sequence that produced the desired **18** contaminated by elimination products. Separation of the olefin was facilitated by selective epoxidation (0.5 equiv of *m*-chloroperbenzoic acid, CH_2Cl_2). Decarbomethoxylation (KOAc, Me_2SO, 140 °C) of the mixture of **18** and epoxidized olefins produced a readily resolved (high-performance LC, 2% EtOAc in hexane) mixture from which pure **1**[9] was isolated in 26% overall yield from the starting tosylate. Optically active **1** ($[\alpha]^{25}_{D}$ +4.44°, *c* 1.12, $CHCl_3$) was diastereomerically pure as established by 67.9-MHz ^{13}C NMR spectroscopy.[1] Its enantiomeric purity was established by saponification (2.5 equiv of KOH, 4:1 $CH_3OH:H_2O$, 69%) to give the corresponding acid ($[\alpha]^{25}_{D}$ +5.39°, *c* 1.82, $CHCl_3$) which agrees with the reported rotation for this acid ($[\alpha]^{25}$D +5.43°, *c* 5.0, $CHCl_3$) derived from phytol.[14]

We have previously shown that both γ-butyrolactones and δ-valerolactones serve as substrates in this stereorelay process.[1,2] The availability of both structural types from carbohydrates provides an approach for the chiral synthesis of natural products with a great ability to vary the separation between the chiral centers. The demonstrated facile synthesis of **1**, where the chiral centers are in a 1,5 relationship, from such a common sugar as D-glucose, attests to this fact. Acyclic units bearing a large number of chiral centers, such as the macrocyclic rings of the ansa ring antibiotics,[15,16] represent another challenge for this methodology.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs. Dr. Noal Cohen, Hoffman-LaRoche Co., generously provided us with authentic comparison samples.

Supplementary Material Available: A detailed description of spectral data for compounds in this synthesis (6 pages). Ordering information is available on any current masthead.

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[11] McKillop, A.; Young, D. W. *Synthesis* **1979**, 401.

[12] This epoxide is a chiral synthon for other 1,5-methyl substituted compounds. (a) Pine sawfly pheromone: Ade, E.; Helmchen, S.; Heligenmann, G. *Tetrahedron Lett.* **1980**, *21*, 1175. (b) Tsetse fly pheromone: Baker, R.; Winton, P. M. *Ibid.* **1980**, *21*, 1137.

[13] Acker, R. D. *Tetrahedron Lett.* **1977**, 3407.

[14] Valentine, D.; Chan, K. K.; Scott, C. G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 4145.

[15] Rinehart, K. L.; Shield, L. S. *Prog. Chem. Org. Nat. Product* **1976**, *33*, 231.

[16] (a) Corey, E. J.; Hase, T. *Tetrahedron Lett.* **1979**, 335. (b) Corey, E. J.; Schmidt, G. *Ibid.* **1979**, 2317. (c) Nagaoka, H.; Rutsch, W.; Schmid, G.; Iio, H.; Johnson, M. R.; Kishi, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7962. (d) Iio, H.; Nagaoka, H.; Kishi, Y. *Ibid.* **1980**, *102*, 7965.

New Tungstophosphates: $Cs_6W_5P_2O_{23}$, $Cs_7W_{10}PO_{36}$, and $Cs_7Na_2W_{10}PO_{37}$

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Received December 1, 1980

We wish to report the facile preparations of three new tungstophosphates and crystal-structure determinations on two of them. These preparations depend on the use of cesium as a counterion and emphasize the important role that counterions can play in determining solid-state heteropolyanion structure.

The three new tungstophosphates are $Cs_6W_5P_2O_{23} \cdot 7.5H_2O$, $Cs_7W_{10}PO_{36} \cdot 7H_2O$, and $Cs_7Na_2W_{10}PO_{37} \cdot 8H_2O$. The first is prepared by adding cesium hydroxide to tungstic acid (15 g) in water (100 mL) until pH 13 is reached. Phosphoric acid is then added to lower the pH to 7, and the solution is chilled. Crystalline $Cs_6W_5P_2O_{23} \cdot 7.5H_2O$ separates in 60% yield. The infrared spectrum is quite similar to that of $Na_6Mo_5P_2O_{23}$,[1] and structure determination reveals that $W_5P_2O_{23}{}^{6-}$ is indeed isostructural with $Mo_5P_2O_{23}{}^{6-}$ (Figure 1).

$Cs_6W_5P_2O_{23} \cdot 7.5H_2O$ can be recrystallized from water if the solution is not heated beyond 60 °C. Above this temperature, and most rapidly at 100 °C, aqueous solutions of $Cs_6W_5P_2O_{23}$ separate the relatively insoluble salt $Cs_7W_{10}PO_{36} \cdot 7H_2O$. The crystallographically determined structure of $Cs_7W_{10}PO_{36} \cdot 7H_2O$ (Figure 2) can be derived from the Keggin structure[2] by a 60° rotation of each of two W_3O_{13} sets and removal of the two octahedra that become edge shared as a result of these rotations. This structure is particularly interesting, because 60° rotations of two W_3O_{13} sets in the Keggin structure give one of the proposed, but as yet unreported, Baker–Figgis isomers;[3] furthermore, Pope[4]

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[1] (a) Lyhamm, L. *Chem. Scr.* **1977**, *12*, 153–161. (b) Strandberg, R. *Acta Chem. Scand.* **1973**, *27*, 1004–1018.

[2] Keggin, J. F. *Proc. R. Soc. London, Ser. A.* **1934**, *144*, 75.

[3] Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* 1970, *92*, 3794–3797.

[4] Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2008.

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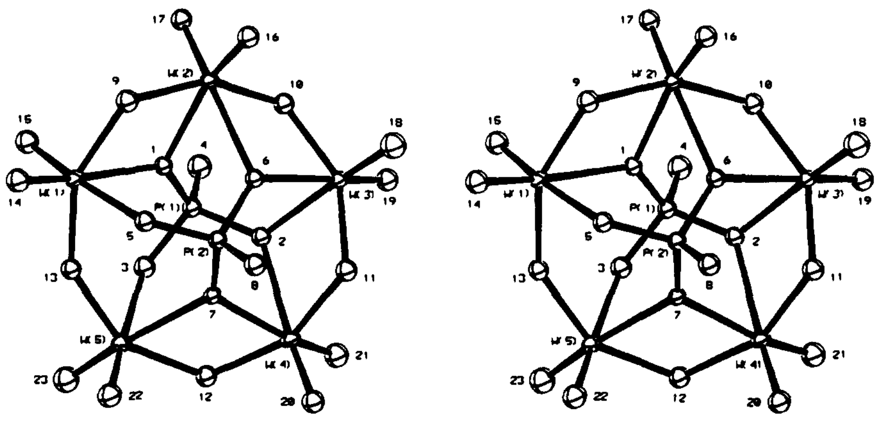


Figure 1. $W_5P_2O_{23}{}^{6-}$:[8] The P–O–W bond lengths are quite variable. P(1)–O(1), 1.576; P(1)–O(2), 1.579; P(1)–O(3), 1.526; P(1)–O(4), 1.498; P(2)–O(5), 1.546; P(2)–O(6), 1.566; P(2)–O(7), 1.548; P(2)–O(8), 1.502; W(1)–O(1), 2.303; W(1)–O(5), 2.164; W(2)–O(1), 2.200; W(2)–O(6), 2.320; W(3)–O(2), 2.233; W(3)–O(6), 2.293; W(4)–O(2), 2.313; W(4)–O(7), 2.194; W(5)–O(3), 2.175; W(5)–O(7), 2.414 Å (esd's are all 0.003 Å). The W–O(bridging)–W and W–O(terminal) distances are each quite uniform; the average W–O bond lengths are 1.925 and 1.738 Å, respectively.

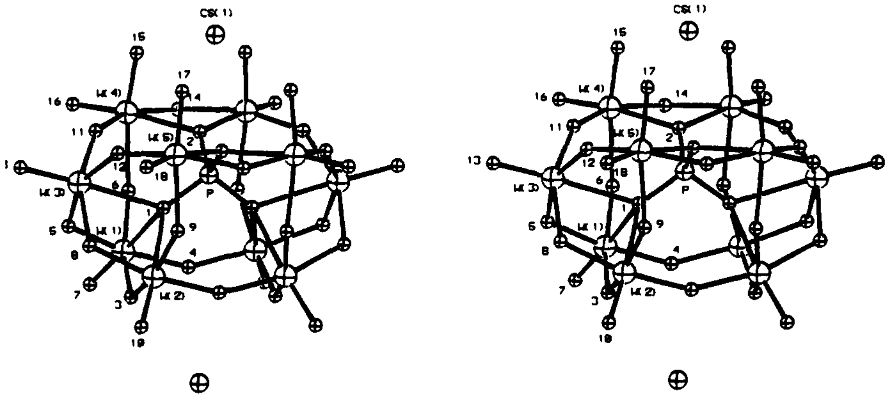
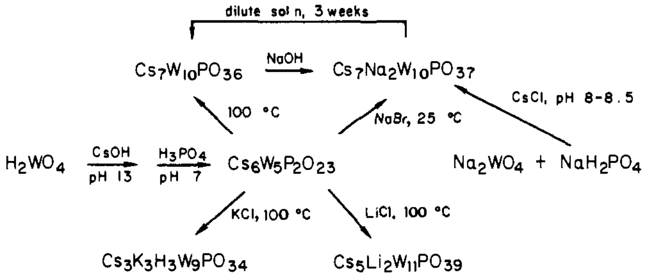


Figure 2. $W_{10}PO_{36}{}^{7-}$:[9] The anion has crystallographic two-fold symmetry and is capped at both ends by cesium cations, namely Cs(1) and its translational (z-axis) equivalent. The dimensions of the atoms are not related to the refined thermal parameters but are, for aesthetic reasons, artifical. Selected bond distances are given in Table I.

Scheme I[a]



[a] All reactions were run in water.

Table I. Selected Bond Distances (Å) with Estimated Standard Deviations for $Cs_7W_{10}PO_{36}\cdot 7H_2O$

P–O(1)	1.541 (12)	W(3)–O(13)	1.694 (13)
P–O(2)	1.574 (12)	W(4)–O(2)	2.294 (13)
W(1)–O(1)	2.398 (11)	W(4)–O(6)	2.146 (13)
W(1)–O(3)	1.956 (11)	W(4)–O(11)	1.907 (13)
W(1)–O(4)	1.894 (12)	W(4)–O(14)	1.955 (12)
W(1)–O(5)	1.916 (14)	W(4)–O(15)	1.749 (13)
W(1)–O(6)	1.830 (12)	W(4)–O(16)	1.769 (14)
W(1)–O(7)	1.698 (13)	W(5)–O(2)'	2.326 (12)
W(2)–O(1)	2.397 (11)	W(5)–O(9)	2.157 (13)
W(2)–O(3)	1.961 (11)	W(5)–O(12)	1.933 (13)
W(2)–O(4)'	1.917 (12)	W(5)–O(14)'	1.953 (13)
W(2)–O(8)	1.948 (13)	W(5)–O(17)	1.723 (13)
W(2)–O(9)	1.809 (13)	W(5)–O(18)	1.724 (12)
W(2)–O(10)	1.705 (12)	Cs(1)–O(2)	3.219 (12)
W(3)–O(1)	2.466 (12)	Cs(1)–O(3)'	3.143 (12)
W(3)–O(5)	1.945 (13)	Cs(1)–O(4)'	3.319 (11)
W(3)–O(8)	1.951 (12)	Cs(1)–O(15)	3.128 (14)
W(3)–O(11)	1.942 (13)	Cs(1)–O(17)	3.143 (13)
W(3)–O(12)	1.909 (12)		

has suggested that this isomer is unstable relative to the Keggin structure or its known β isomer,[3,5] because it contains one more pair of edge-shared octahedra than do the latter structures. This leads to additional electrostatic repulsions within the system. Obviously, removing this pair of edge-shared octahedra removes this additional electrostatic repulsion, and the stability of $W_{10}PO_{36}{}^{7-}$ can be partly rationalized on this basis.

The third new tungstophosphate, $Cs_7Na_2W_{10}PO_{37}$, can be prepared directly from sodium tungstate, sodium dihydrogen phosphate, and cesium chloride, or by the reaction of sodium bromide with $Cs_6W_5P_2O_{23}$ or sodium hydroxide with $Cs_7W_{10}PO_{36}$ (Scheme I). Dilute solutions of $Cs_7Na_2W_{10}PO_{37}$ separate $Cs_7W_{10}PO_{36}$ in low conversion after standing for several weeks. Although $Cs_7Na_2W_{10}PO_{37}$ is highly crystalline, crystals suitable for structure determination have not yet been obtained. Its composition is inferred from analysis[6] and supported by its formation from $Cs_7W_{10}PO_{36}$ and sodium hydroxide.

Counterions are very important in these syntheses; the replacement of cesium hydroxide by potassium hydroxide in the $Cs_6W_5P_2O_{23}$ preparation described above gives $W_9PO_{34}{}^{9-}$[7] rather

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(5) Yamamura, K.; Sasaki, Y. *J. Chem. Soc., Chem. Commun.* **1973**, 648–649.

(6) Anal. Calcd for $Cs_7Na_2W_{10}PO_{37}\cdot 8H_2O$: Cs, 25.97; Na, 1.28; O, 20.10; P, 0.86; W, 51.33; H_2O, 4.02. Found: Cs, 26.31; Na, 0.98; O, 20.17; P, 0.98; W, 50.78; H_2O, 3.71.

(7) Massart, R.; Contant, R.; Fruchart, J.; Ciabrini, J.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916–2921.

than $W_5P_2O_{23}^{6-}$. Similarly, the replacement of sodium tungstate and sodium dihydrogen phosphate by potassium tungstate and potassium dihydrogen phosphate in the reaction with cesium chloride to form $Cs_7Na_2W_{10}PO_{37}$ does not give $Cs_7K_2W_{10}PO_{37}$; salts of $W_9PO_{34}^{9-}$ are obtained instead. Some effects of counterions on the chemistry of $Cs_6W_5P_2O_{23}$ are shown in Scheme I. The importance of counterions in determining solid-state structure raises the question of whether these new tungstophosphate structures persist in solution. The fact that all of the new salts can be successfully recrystallized from water cannot be regarded as conclusive evidence. Solutions of these salts each exhibit a single ^{31}P resonance ($Cs_6W_5P_2O_{23}$, −2.4 ppm; $Cs_7W_{10}PO_{36}$, −10.5 ppm; $Cs_7Na_2W_{10}PO_{37}$, 1.2 ppm) which suggests at least that they each form only one species in solution. We can speculate that the structures persist in solution for a finite time, perhaps stabilized by ion pairing. We hope to obtain more meaningful information on this point from future ^{183}W NMR studies.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters and structure amplitudes (63 pages). Ordering information is given on any current masthead page.

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(8) **Crystal structure information**: Monoclinic, space group $P2_1/c$; at −100 °C, a = 13.009 (2), b = 15.974 (3), c = 17.087 (3) Å; β = 98.93 (1)°; V = 3508 Å^3; Z = 4. Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, ω scans of 1.0°, $4 < 2\theta < 50°$, 6172 reflections. An empirical absorption correction based on ψ-scan data was applied; the "transmission factors" ranged from 0.475 to 0.996. The structure was refined by full-matrix, least-squares techniques: 5201 reflections with $I > 2\sigma(I)$, 240 variables (W and Cs with anisotropic thermal parameters, P and O with isotropic paramters, no hydrogen atoms included), R = 0.038, R_w = 0.037. The three water molecules labeled OW(7), OW(8), and OW(9) originally showed up in a difference Fourier with magnitudes which were half those of the other water oxygen atoms. It appears that the area is occupied half the time by two water molecules, OW(7) and OW(9), and half the time by just one, OW(8). The final difference map showed only residues of the W and Cs atoms, the largest of which had a magnitude of 1.2 e Å^{-3}. The mathematical and computational details may be found in ref 10.

(9) **Crystal structure information** (where different from ref 8): Orthorhombic, space group $P2_12_12$; at −100 °C, a = 12.401 (3), b = 18.948 (4), c = 9.636 (2) Å; V = 2264 Å^3; Z = 2 (the heteropolyanion sits on a crystallographic twofold axis). Reflections (2952) were measured in the range $4 < 2\theta < 55°$. "Transmission factors" ranged from 0.428 to 0.994. Refinement information: 2665 reflections with $I > 3\sigma(I)$, 166 variables, R = 0.047, R_w = 0.054 (the enantiomeric structure refined to R = 0.057). All of the major residual peaks in the final difference, 1.4–1.8 e Å^{-3}, were associated with the W atoms.

(10) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030–2032.

Photogeneration of an Active Formate-Decomposition Catalyst

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Received September 15, 1980

Simple group 6 metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) have been shown to be active homogeneous catalysts for the water gas shift reaction under basic conditions.[1] These catalysts are of particular interest in view of their high sulfur tolerance.[2] Recent mechanistic studies[3,4] strongly suggest that these catalysts function through the decomposition of an intermediate formatopentacarbonylmetallate anion $HCO_2M(CO)_5^-$ (M = Cr, Mo, W) produced by formate ion addition to $M(CO)_5$ resulting from the reversible CO dissociation of corresponding $M(CO)_6$ species as summarized in the following equations:

$$CO + OH^- \rightarrow HCO_2^- \tag{1}$$

$$M(CO)_6 \rightleftharpoons M(CO)_5 + CO \tag{2}$$

$$M(CO)_5 + HCO_2^- \rightarrow HCO_2M(CO)_5^- \tag{3}$$

$$HCO_2M(CO)_5^- \rightarrow HM(CO)_5^- + CO_2 \tag{4}$$

$$HM(CO)_5^- + H_2O \rightarrow H_2M(CO)_5 + OH^- \tag{5}$$

$$H_2M(CO)_5 \rightarrow M(CO)_5 + H_2 \tag{6}$$

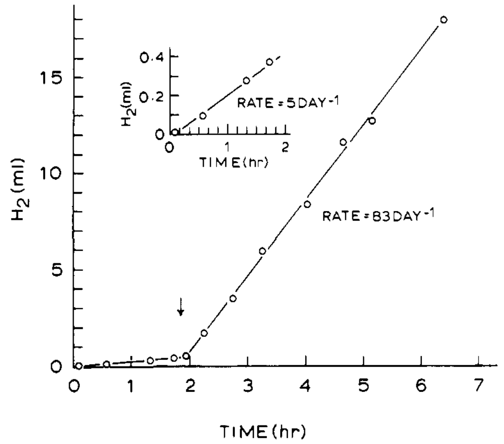

Figure 1. Hydrogen production (mL at 1 atm, 25 °C) from the catalytic decomposition of formate ion as a function of time. Catalyst solution: $W(CO)_6$ (0.039 mmol), $NaHCO_2$ (40 mmol), 200 mL (25:75 H_2O–2-ethoxyethanol); T = 75 °C. The arrow indicates the time at which the formerly dark solution is illuminated by sunlight.

It is well-known that group 6 metal hexacarbonyls are readily photolyzed by visible light to produce the same $M(CO)_5$ species as shown resulting from the thermal dissociation of $M(CO)_6$ indicated in eq 2.[5] This suggests the photochemical dissociation of $M(CO)_6$ to produce $M(CO)_5$ can be substituted for the thermal dissociation step involved in the above sequence of reactions. This could provide facile entry into the main part of the catalytic cycle (eq 3–6), thereby leading to enhanced catalytic activity at relatively low temperatures. This communication describes preliminary observations on the decomposition of formate ion by eq 3–6 (M = W) using photolysis to generate the required $W(CO)_5$ intermediate.

Figure 1 shows hydrogen production as a function of time over 200 mL of a solution [25:75 water-2-ethoxyethanol (v/v)] containing sodium formate (0.20 M) and 0.039 mmol of $W(CO)_6$ maintained under an atmosphere of CO (P_{CO} = 1 atm) at 75 °C.[6] The nearly horizontal portion of the data represents hydrogen production from this solution made up and maintained under extremely low-light conditions. This colorless solution containing dissolved $W(CO)_6$ exhibits a very low level of thermal catalytic activity at 75 °C which is shown in the inset of Figure 1 to

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(1) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2925.

(2) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Chem. Soc., Chem. Commun.* **1980**, 529.

(3) King, R. B.; King, A. D., Jr.; Yang, D. B. *ACS Symp. Ser.*, in press.

(4) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.*, in press.

(5) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(6) The photocatalytic experiments described here were carried out in 250-mL Schlenk tubes fitted with an arrangement of glass tees such that one septum and four rubber bulbs were maintained in contact with the gas phase (100 mL) contained over the solution (200 mL) within the tube. This arrangement provided for expansion during gas production so that GLC analysis could be easily effected using Pressure-Loc syringes for gas sampling. Hydrogen analyses were performed by using a 8-ft column of 13X molecular sieve with argon as a carrier gas at 50 °C. CO_2 and CO analyses were carried out by using a Fisher Model 1200 gas partitioner fitted with the standard Columnpak PQ and 13X molecular sieve columns at 50 °C, using helium as the carrier gas. Prior determined external sensitivity factors were used to convert GLC peaks to gas sample volumes. Simultaneous heating and illumination was accomplished by using an electrical heating mantle connected to an Omega Model 49 proportioning controller with the thermocouple sensor held tightly against the external surface of the Schlenk flask below the liquid level with electrical tape. When insulated with glass wool, this arrangement provided adequate temperature control for these experiments (±1 °C).