this structure lacks the symmetry indicated by the NMR data. We have also considered the possibility that the bridging carbene might isomerize rapidly between the four possible isomeric forms. However, given the observation of diastereotopic methylene hydrogens, such a process would have to occur with retention of stereochemistry at the carbene carbon. It is difficult to see why this would be the case. Therefore, we currently favor structure **3**, an iodoalkyl complex, which best fits all of the data in hand. **3** could be imagined to arise via initial displacement of iodide by EDA, followed by loss of nitrogen and recombination of iodide at carbon. Alternatively, a direct insertion mechanism is not out of the question.[10,11] Assuming rapid rotation about the metal–alkyl bond, structure **3** is consistent with all of the spectroscopic data and rationalizes both the lack of carbene transfer to styrene and the observation of a vacant coordination site available for olefin π-complex formation. To date, we have not been able to obtain an X-ray crystal structure of adduct X to confirm this hypothesis. These efforts are continuing.

We have recently discovered that X is not the kinetic product of the reaction between EDA and the rhodium porphyrin. Mixing these species at −40 °C rather than room temperature produces a different compound that isomerizes to X above −20 °C. Studies directed toward further characterizing these interesting organometallic porphyrin complexes and elucidating their potential roles in the catalytic cyclopropanation reaction are underway.

Acknowledgment. We thank the Texas Advanced Research Program for support. T.K. also acknowledges the American Cancer Society for providing a Junior Faculty Research Award.

Supplementary Material Available: Figures showing the ^{13}C and 2-D COSY ^{1}H NMR spectra of X and the ^{1}H NMR spectrum of X + styrene (3 pages). Ordering information is given on any current masthead page.

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(10) This would presumably require cis coordination sites, which are generally assumed not to be available in metalloporphyrin complexes. However, some complexes with two ligands on the same face of the macrocycle are known: Lecomte, C.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1976**, 434. Ledon, H.; Bonnet, M. *J. Chem. Soc., Chem. Commun.* **1979**, 702. Mentzen, B. F.; Bonnet, M. C.; Ledon, H. J. *Inorg. Chem.* **1980**, *19*, 2061.

(11) There is precedent for apparent insertion of organic moieties into a rhodium porphyrin–halide bond: Ogoshi, H.; Setsune, J.-I.; Nanbo, Y.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 329.

Photochemically Enhanced Carbon–Carbon Bond-Forming Reaction between CS_2 and $[W(CO)_5CH_3]^-$. X-ray Structure of $[PPN][W(CO)_4(\eta^2\text{-}S_2CCH_3)]$

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Summary: The reaction between carbon disulfide and $[W(CO)_5CH_3]^-$ has been found to be greatly accelerated in the presence of UV light, with the quantitative formation of $[W(CO)_4(\eta^2\text{-}S_2CCH_3)]^-$. This complex is prepared alternatively by photolysis of the $[W(CO)_5S_2CCH_3]^-$ complex, which was prepared from the thermal reaction of $[W(CO)_5CH_3]^-$ and CS_2. The chelating dithioacetate derivative of tungsten has been characterized as its $[PPN]^+$ salt by single-crystal X-ray diffraction. A rapid photochemical reaction between carbon dioxide and $[W(CO)_5CH_3]^-$ has been observed as well, but with the exclusive production of the formate complex $[W(CO)_5O_2CH]^-$.

The carboxylation of transition-metal alkyls to yield the corresponding metal carboxylates is an important reaction in the reduction chemistry of carbon dioxide (eq 1).[1] It has previously been established that the carboxylation of metal alkyls or aryls has a much higher barrier to reaction than insertion of CO_2 into metal–hydride bonds.[2] Indeed when both phenyl and hydride functionalities appear on the same metal center, carboxylation occurs exclusively at the hydride bond (eq 2).[3]

$$[MR]^- + CO_2 \rightarrow [MO_2CR]^- \qquad (1)$$

$$trans\text{-}(H)Ni(Ph)(PCy_3)_2 + CO_2 \rightarrow trans\text{-}(HCO_2)Ni(Ph)(PCy_3)_2 \qquad (2)$$

Relevant to efforts aimed at enhancing the rate of CO_2 insertion into metal–carbon bonds, Cooper and Johnston have communicated the first photochemically activated CO_2 insertion into a transition-metal–carbon bond (eq 3).[4]

$$(Cp)_2Ti(CH_3)_2 + CO_2 \xrightarrow{h\nu} (Cp)_2Ti(CH_3)(O_2CCH_3) \qquad (3)$$

Although reaction 3 does not take place at ambient temperature in the absence of light, it does occur at elevated temperatures.[5] Similarly, Sullivan and Meyer have reported the photoinduced insertion of CO_2 into the metal–hydride bond of *fac*-Re(2,2′-bipyridine)$(CO)_3H$ to provide *fac*-Re(2,2′-bipyridine)$(CO)_3O_2CH$.[6] The reaction period for the analogous thermal process is reduced from 5 h to 10 min with irradiation. Others have reported the

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(1) (a) Walther, D. *Coord. Chem. Ref.* **1987**, *79*, 135. (b) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; Reidel: Dordrecht, The Netherlands, 1983; p 169. (c) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79. (d) Darensbourg, D. J.; Kudaroski, R. *Adv. Organomet. Chem.* **1983**, *22*, 129. (e) Ito, T. T.; Yamamoto, A. In *Organic and Bioorganic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodonsha: Toyoko, Japan, 1982; p 79. (f) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (g) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 225. (h) Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev. (Engl. Transl.)* **1978**, *47*, 334. (i) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (j) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, West Germany, 1988; p 26.

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(3) Darensbourg, D. J.; Darensbourg, M. Y.; Goh, L. Y.; Ludvig, M.; Wiegreffe, P. *J. Am. Chem. Soc.* **1987**, *109*, 7539.

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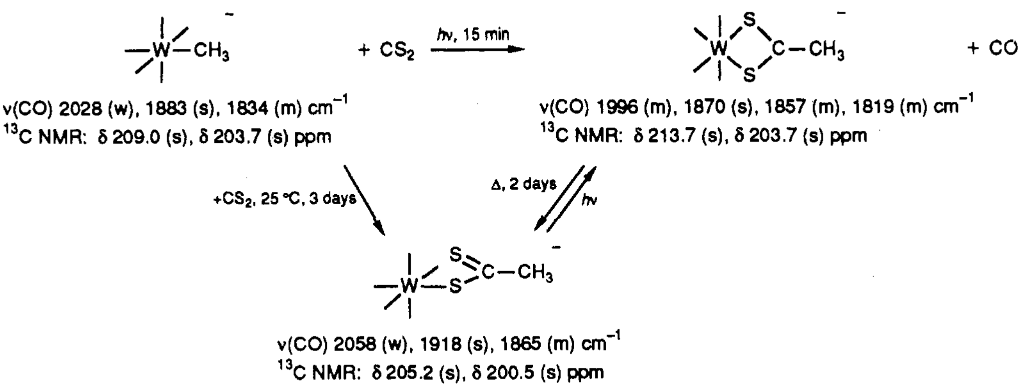
Scheme I



use of light to photodissociate H_2 from $[MoH_4(dppe)_2]$[7] and $[ReH_3(diphos)_2]$,[8] thereby generating reactive metal–hydride species that react with CO_2 to yield $[Mo(dppe)_2H(O_2CH)]$ and $[Re(O_2CH)(diphos)_2]$, respectively.

In this communication, we report the results of our studies on the thermal and photochemical reactions of CS_2 with $[PPN][W(CO)_5CH_3]$. The thermal reaction of CS_2 and $[W(CO)_5H]^-$ to afford $[W(CO)_5S_2CH]^-$ occurs readily at ambient temperature,[9] whereas the corresponding process involving $[W(CO)_5CH_3]^-$ has not been reported previously. Indeed, the insertion of carbon dioxide into the W–CH_3 bond of $[W(CO)_5CH_3]^-$ is quite slow at 1 atm of CO_2 pressure, with a rate constant of 8.32×10^{-7} s^{-1} at 23 °C in THF.[2] *It is noteworthy that thermal* CO_2 *insertion into the W–C bond of* $[W(CO)_5CH_3]^-$ *is not inhibited by excess carbon monoxide; hence, CO dissociation is not a prerequisite step in the insertion mechanism.* In like fashion we have observed the insertion of CS_2 into $[W(CO)_5CH_3]^-$ to yield $[W(CO)_5S_2CCH_3]^-$ to be extremely slow, occurring over a 3-day period in excess CS_2 at ambient temperature accompanied by significant decomposition. The product has IR ν(CO) stretching frequencies corresponding to a molecule of C_{4v} symmetry (2058 (w), 1918 (s), 1865 (m) cm^{-1}) and the ^{13}C NMR spectrum of the ^{13}CO-enriched product consists of resonances at 205.2 and 200.5 ppm of intensity ratio approximately 1:4. Consistent with the reported $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ chemistry of the acetate ligand,[10] the photolysis of this complex yields the chelated derivative $[W(CO)_4(\eta^2\text{-}S_2CCH_3)]^-$ on the basis of its C_{2v} ν(CO) IR band pattern: 1996 (m), 1870 (s), 1857 (m), 1819 (m) cm^{-1}. Thermal reaction of this η^2-dithioacetate derivative with CO led to regeneration of the η^1 species.

During our investigation of the reaction between CS_2 and $[W(CO)_5CH_3]^-$ we have found that this process is greatly accelerated by photolysis. That is, when a THF solution of $[W(CO)_5CH_3]^-$ and CS_2 is photolyzed for 15 min, $[W(CO)_4(\eta^2\text{-}S_2CCH_3)]^-$ is identified as the major product (>90%) by its IR and ^{13}C NMR spectra. This expeditious and near-quantitative production of $[W(CO)_4(\eta^2\text{-}S_2CCH_3)]^-$ photochemically is a considerable improvement over the thermal preparation described above.[11]

Additionally, we have been able to grow crystals of this complex and confirm its structure by X-ray crystallography.[12] Crystals of $[PPN][W(CO)_4(\eta^2\text{-}S_2CCH_3)]$ were grown from a THF/ether/hexane mixture at −20 °C. The complex crystallized in the $P\bar{1}$ space group with two independent cations and two independent anions in the unit cell. The anion consists of a tungsten atom coordinated to four carbonyl ligands and two sulfur atoms of the bidentate thiocarboxylate ligand in a distorted octahedron (Figure 1). The S(1)–W(1)–S(2) and the S(1)–C(1)–S(2) bond angles are 67.0 and 113.4°, respectively. A repre-

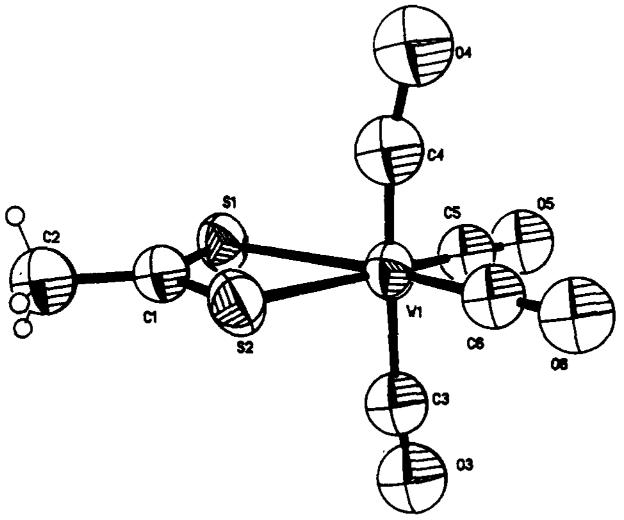


Figure 1. ORTEP representation of the anion of $[PPN][W(CO)_4(\eta^2\text{-}S_2CCH_3)]$.

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(10) (a) Darensbourg, D. J.; Wiegreffe, H. P. *Inorg. Chem.* **1990**, *29*, 592. (b) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. W. *J. Am. Chem. Soc.*, in press.

(11) Anal. Calcd (found) for $[PPN][W(CO)_4S_2CCH_3]$: C, 54.49 (54.07); H, 3.59 (3.72).

(12) Crystallographic data for $[PPN][W(CO)_4(\eta^2\text{-}S_2CCH_3)]$: Examination and data collection of a yellow plate (0.08 mm × 0.30 mm × 0.32 mm, formula $C_{84}H_{66}N_2O_8P_4S_4W_2$, formula weight 1852.2) were performed on a Nicolet R3m/V X-ray diffractometer (oriented graphite monochromator; Mo Kα (λ = 0.710 73 Å) radiation); triclinic, $P\bar{1}$ (No. 2), a = 10.253 (3) Å, b = 13.101 (4) Å, c = 28.879 (8) Å, α = 89.81 (2)°, β = 85.35 (2)°, γ = 89.29 (2)°, V = 3866 (2) Å^3, D_{exptl} = 1.590 g cm^{-3}, ν = 3.278 mm^{-1}, Z = 2, F(000) = 1840 e. Data were collected for $4.0° \le 2\theta \le 40.0°$ (ω (Wyckoff scans), $-9 \le h \le 9$, $-12 \le k \le 12$, $0 \le l \le 27$) at 193 K. The scan range for data collection was 1.60° plus the Kα separation, with a variable scan rate of 1.50–15.00° min^{-1}. Lorentz and polarization corrections were applied to 7089 reflections. A total of 5850 unique reflections (R_{int} = 0.09), with $|I| \ge 2.0\sigma(I)$, were used in further calculations. The structure was solved by Patterson synthesis (SHELXS, SHELXTL-PLUS program package, by G. M. Sheldrick, 1988). Full-matrix least-squares anisotropic refinement for W(1), W(2), S(1), S(2), S(3), and S(4) and isotropic refinement for all remaining non-hydrogen atoms (SHELXLS, SHELXTL-PLUS program package, by G. M. Sheldrick, 1988; number of least-squares parameters 448; quantity minimized $\sum w(F_o - F_c)^2$; $w^{-1} = \sigma^2F + gF^2$, g = 0.00001) yielded R = 0.063, R_w = 0.068, and S = 4.44 at convergence (largest Δ/σ 0.0246; mean Δ/σ 0.0001; largest positive peak in the final Fourier difference map −3.12 e Å^{-3}). The extinction coefficient χ (where $F^* = Fc/[1 + 0.002\chi F_c^2/(\sin 2\theta)]^{0.25}$) was refined to 0.000 073 (14). Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral atom scattering factors and anomalous scattering correction terms were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for the [PPN][$W(CO)_4(\eta^2\text{-}S_2CCH_3)$] Complex[a]

Bond Lengths			
W(1)-S(1)	2.557 (5)	S(2)-C(1)	1.71 (2)
W(1)-S(2)	2.565 (5)	C(1)-C(2)	1.47 (3)
W(1)-C(3)	1.99 (2)	C(3)-O(3)	1.17 (2)
W(1)-C(4)	1.93 (2)	C(4)-O(4)	1.19 (2)
W(1)-C(6)	1.94 (2)	C(5)-O(5)	1.21 (2)
W(1)-C(5)	1.91 (2)	C(6)-O(6)	1.17 (2)
S(1)-C(1)	1.67 (2)		
Bond Angles			
S(1)-W(1)-S(2)	67.0 (1)	S(1)-W(1)-C(4)	95.3 (6)
S(2)-W(1)-C(3)	90.7 (6)	S(1)-C(1)-S(2)	113.4 (10)

[a] The values listed are for only one of the two molecules that crystallized in the unit cell.

sentative listing of bond lengths and bond angles is presented in Table I.

[$W(CO)_4(\eta^2\text{-}S_2CCH_3)$]$^-$ was found to react with added CO to yield the pentacarbonyl species, although the reaction is much slower than the corresponding reaction involving [$W(CO)_4(\eta^2\text{-}O_2CCH_3)$]$^-$.[10] Whereas the latter reacts with CO at ambient temperature to yield the monodentate species in a few minutes, after 2 days the reaction between [$W(CO)_4(\eta^2\text{-}S_2CCH_3)$]$^-$ and CO has not gone to completion. The slower reactivity of the sulfur analogues is anticipated on the basis of ring strain and bond strength considerations. The thermal and photochemical reactions of [$W(CO)_5CH_3$]$^-$ and CS_2 are summarized in Scheme I.

The photoenhanced carbon–carbon bond-forming reaction of CS_2 with [$W(CO)_5CH_3$]$^-$ is most likely initiated by W–CH_3 homolysis (Scheme II)[13] and not CO photodissociation. Consistent with this proposal, an analogous photolyzed reaction of [$W(CO)_5CH_3$]$^-$ in THF in the presence of an excess of CH_2Cl_2 quantitatively afforded [$W(CO)_5Cl$]$^-$. Hence, radical pathways initiated by light analogous to those seen in SO_2 insertion reactions with alkyl cobaloximes may be operative.[14] Of more importance to our primary interest is the analogous behavior of CO_2 toward [$W(CO)_5CH_3$]$^-$ in the presence of light. Indeed, we have observed that the reactivity of [$W(CO)_5CH_3$]$^-$ toward carbon dioxide is greatly enhanced upon photolysis. However, in this instance the product is not the acetate complex but instead the product of hydrogen atom abstraction; i.e., the formate derivative [$W(CO)_5O_2CH$]$^-$ was afforded in good yield.[15] It is apparent from these preliminary findings that the photophysics and photochemistry of group 6 metal alkyls with CO_2, and the analogous heteroallene CS_2, warrant thorough investigation.

Scheme II

$$CH_3W(CO)_5^- \overset{h\nu}{\rightleftharpoons} CH_3^\bullet + {}^\bullet W(CO)_5^-$$

$${}^\bullet W(CO)_5^- + CS_2 \rightarrow (CO)_5WCS_2^{\bullet -}$$

$$(CO)_5WCS_2^{\bullet -} + CH_3W(CO)_5^- \rightarrow (CO)_4WS_2CCH_3^- + {}^\bullet W(CO)_5^- + CO$$

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 88-17873) and the Robert A. Welch Foundation is greatly appreciated.

Supplementary Material Available: Tables of refined anisotropic thermal parameters, final fractional coordinates, and thermal parameters for hydrogen atoms (5 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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(13) For reports of photolytic homolysis of the closely related $RMn(CO)_5$ derivatives, see e.g.: (a) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1974**, 966. (b) Hudson, A.; Lappert, M. F.; Lednor, P. W.; Macquitty, J. J.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* 1981, 2159. (c) Young, K. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 157.

(14) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013.

(15) The formate complex was conclusively identified in solution by infrared spectroscopy and, more importantly, ^{13}C NMR spectroscopy, where the $-O_2CH$ resonance was found at 168.8 ppm, W-CO (cis) at 201.4 ppm, and W-CO (trans) at 206.5 ppm in acetone.[8] In addition the formate proton signal was observed at 7.90 ppm in THF.

Formation of Acetylplatina(IV)cyclobutane: Methodology for the Synthesis of Platina(IV)cyclobutane Complexes Bearing Electrophilic Substituents

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Summary: A methodology for the syntheses of platina(IV)cyclobutanes bearing an electron-withdrawing keto group has been achieved. This method, which involves protection of cyclopropyl methyl ketone, platinum insertion, and subsequent deprotection, yields acetylplatinacyclobutane.

Metallacyclobutane complexes range from proposed transition states to stable entities and are considered to be important pathway components in several organic transformations.[1-4] Platina(IV)cyclobutanes are among the most stable and studied. Formation of platinacyclobutanes is easily accomplished by the insertion (oxidative addition) of platinum into the carbon–carbon bond of a cyclopropane. However, until now the ring-bearing substitutions were unfortunately *limited* to alkyl and aryl groups. *The presence of strong electron-withdrawing substituents prevented insertion and thus exploration of potentially rich chemistry*[5] (eq 1). We now wish to report

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