

Figure 2. $\ln(A_{\infty} - A_t)$ vs. time plot for the $\text{Co}(\text{CN})_5\text{OH}_2^{2-}\text{-N}_3^-$ reaction at 40.0 °C, $[\text{N}_3^-] = 0.403 \text{ M}$, pH 6.86, $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ prepared from $\text{Co}_2\text{O}_2(\text{CN})_{10}^{6-}$.

sumably the polymeric pentacyanocobaltate(III) produced on heating concentrated solutions of the monomer.^{5,6} The lower molar absorbance of $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ solutions prepared from $\text{Co}_2\text{O}_2(\text{CN})_{10}^{6-}$ as compared to $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ solutions prepared from $\text{Co}(\text{CN})_5\text{Cl}^{3-}$ is indicative of the presence of the polymeric species.⁵ The tailing noted above would not have been observed in the earlier¹ work (if indeed such tailing obtained) because a manual spectrophotometer and a point-sampling technique were utilized: five to six samples were withdrawn during the first 2 half-lives, the "infinity" absorbance was measured after 8–10 half-lives, and the slopes of the $\ln(A_{\infty} - A_t)$ vs. t plots were estimated by a graphic procedure. In fact, if the present measurements are processed by a similar procedure, namely, least-squares fitting of $\ln(A_{\infty} - A_t)$ vs. t data during 2 half-lives utilizing a fixed A_{∞} value measured after 8–10 half-lives, excellent first-order plots are obtained (Figure 2). The slopes of these plots give k_{obsd} values (listed in column 4 of Table I) in agreement with those reported earlier.¹ (Compare the open circles, present work, with the open squares, earlier work, in Figure 1.)

Although the earlier results¹ can be reproduced if the same preparations and methods for treating the data are followed, the present data obtained with samples of $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ prepared from $\text{Co}(\text{CN})_5\text{Cl}^{3-}$ and the new results⁴ obtained with $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ prepared from $\text{Co}(\text{CN})_6^{3-}$ almost certainly represent the intrinsic $\text{Co}(\text{CN})_5\text{OH}_2^{2-}\text{-N}_3^-$ reaction. Therefore, it must be concluded, as Burnett and Gilfillan⁴ did, that the reaction is first order in azide. Presumably, the deviations from first-order behavior in azide observed in the earlier work¹ and in the present work with samples prepared from $\text{Co}_2\text{O}_2(\text{CN})_{10}^{6-}$ are associated with the presence of the polymeric pentacyanocobaltate(III) species in the reacting solutions. However, there are some unanswered questions. Even with samples of $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ prepared by photolysis of $\text{Co}(\text{CN})_6^{3-}$, a procedure that appears to produce pure samples,^{7–10} both first-order⁴ and less than first-order³ kinetics with respect to azide ion have been reported. Moreover, the reaction of $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ with SCN^- studied with samples prepared

from either $\text{Co}_2\text{O}_2(\text{CN})_{10}^{6-}$ or from $\text{Co}(\text{CN})_6^{3-}$ exhibits in both cases the functional dependence of eq 1.¹¹ Evidently, additional work is necessary. However, since the functional dependence given by eq 1 for the $\text{Co}(\text{CN})_5\text{OH}_2^{2-}\text{-N}_3^-$ reaction was of *essence* in the assignment of an $\text{S}_{\text{N}}1$ mechanism to substitution reactions of pentacyanocobaltate(III) complexes,¹ with the finding of a first-order reaction with respect to N_3^- , the question of the mechanism of these reactions must be regarded as unsettled by the kinetic measurements. On the basis of measurements of volumes of activation¹² and of linear free energy considerations,⁴ it seems clear that a dissociative mechanism obtains, but whether a genuine, long-lived penta-coordinate intermediate is present in the spontaneous substitution reactions remains an open question. Intermediates are apparently present in the assisted^{13,14} substitution reactions of $\text{Co}(\text{CN})_5\text{N}_3^{3-}$ (by H^+ and by NO^+), but preliminary measurements of competition ratios suggest different intermediates for different reactions. Still different intermediates appear to be formed in the photochemical reactions of $\text{Co}(\text{CN})_6^{3-}$ ^{7,15} and $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$.^{5,7} In this context, it is noteworthy that a common penta-coordinate intermediate has been excluded in the spontaneous aquations of pentamminecobalt(III) complexes¹⁶ and that the question of a common intermediate in their assisted aquations is highly controversial.^{17–19}

Registry No. $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$, 14842-83-2; N_3^- , 14343-69-2.

- (11) For thiocyanate, there exists the additional complication associated with the formation of N- and S-bonded linkage isomers and their possible interconversion during reaction.
- (12) Palmer, D. A.; Kelm, H. Z. *Anorg. Allg. Chem.* **1979**, *450*, 50.
- (13) Haim, A.; Wilmarth, W. K. *Inorg. Chem.* **1962**, *1*, 583.
- (14) Haim, A.; Grassi, R.; Wilmarth, W. K. *Adv. Chem. Ser.* **1965**, No. 49, 31.
- (15) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 5254.
- (16) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647.
- (17) Buckingham, D. A.; Edwards, J. D.; Lewis, T. W.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 892.
- (18) Reynolds, W. L.; Hafezi, S.; Kessler, A.; Holly, S. *Inorg. Chem.* **1979**, *18*, 2860.
- (19) Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001.

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Dinuclear, Metal–Metal-Bonded Platinum(III) Compounds. 1. Preparation and Structure of $\text{K}_2[\text{Pt}_2(\text{SO}_4)_4(\text{OSMe}_2)_2] \cdot 4\text{H}_2\text{O}$

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In recent years it has become evident that there is a class of dinuclear compounds of platinum(III) containing metal–metal bonds comparable to those of rhodium(II),¹ although it is not yet clear whether this class of Pt^{III}_2 species will be as extensive as the rhodium group. Thus far only a few have been identified conclusively by X-ray crystallography. These are $\text{K}_2[\text{Pt}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]^{2-}$ (1), $[\text{Pt}_2(\text{O}_2\text{CCF}_3)_2(\text{CH}_3)_4(p\text{-CH}_3\text{C}_5\text{H}_4\text{N})_2]^{2-}$ (2), $[(\text{H}_2\text{O})(\text{NH}_3)_2\text{Pt}(\text{C}_5\text{H}_4\text{NO})_2\text{Pt}(\text{NH}_3)_2]^{2-}$

- (6) Similar polymerization effects and tailing in the absorbance vs. time traces are observed with aged solutions of $\text{Fe}(\text{CN})_5\text{OH}_2^{2-}$: Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 2080. Jwo, J. J.; Haim, A. *J. Am. Chem. Soc.* **1976**, *98*, 1172.
- (7) Adamson, A. W.; Chiang, A.; Zinato, E. *J. Am. Chem. Soc.* **1969**, *91*, 5467.
- (8) Moggi, L.; Bolletta, F.; Balzani, V.; Scandola, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2589.
- (9) Wrighton, M.; Bredesen, D. *Inorg. Chem.* **1973**, *12*, 1707.
- (10) However, note that molar absorbances 301 and 260 $\text{M}^{-1} \text{cm}^{-1}$ at 380 nm are reported for $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ prepared by photolysis of $\text{Co}(\text{CN})_6^{3-}$: ref 4. Nishazawa, M.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 294.

- (1) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; Chapter 8.
- (2) Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl Akad. Nauk SSSR* **1976**, *226*, 76.
- (3) Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938.

Table I. Crystallographic Data

space group	$P2_1/n$
a , Å	9.573 (2)
b , Å	10.738 (4)
c , Å	14.041 (4)
β , deg	116.37 (2)
V , Å ³	1293.2 (8)
Z	2
fw	1080.96
density (calcd), g cm ⁻³	2.776
range of 2θ , deg	0–60
total unique observns	2337
no. of observns with $F^2 > 3\sigma(F^2)$	2306
no. of variables	163
unwtd R factor	0.034
wtd R factor	0.044
error in an observn of unit wt	1.036
largest parameter shift/esd	0.01

(NO₃)](NO₃)₃·2H₂O⁴ (3), and Na₂[Pt₂(HPO₄)₄(H₂O)₂]⁵ (4).

The previous report² on the sulfato compound provided little in the way of details, and nothing further has appeared in the following 6 years. We have been able to repeat the preparation of the compound using essentially the method published,⁶ but we found the compound to have inconveniently low solubility and to be, apparently, rather unstable in solution. We noted, however, that a dimethyl sulfoxide (Me₂SO) adduct could be easily obtained and, further, that this appeared to be more stable and formed beautiful crystals. We therefore determined the crystal structure, and it is reported here.

Experimental Section

Preparation. K₂[Pt₂(SO₄)₄(H₂O)₂] was prepared in an analogous manner to that previously reported.⁶ A 2.0-g (4.4-mmol) sample of K₂Pt(NO₃)₄ in 30 mL of 9 M H₂SO₄ was heated at 100 °C for 5 h. The color of the solution during this time changed from blue to green to brown with copious evolution of NO gas. The resulting solution and yellow precipitate were cooled, and the product was collected via suction filtration on a fine glass frit. The precipitate was washed with small portions of ice water, ethanol, and ether.

The dimethyl sulfoxide adduct was formed by adding 2 mL of Me₂SO to a solution of 0.1 g of K₂[Pt₂(SO₄)₄(H₂O)₂] in 20 mL of water. The resulting compound is more soluble in water and displays a higher degree of stability in solution. Crystals suitable for X-ray crystallography were grown by slow evaporation of the solvent in air.

X-ray Crystallography. A crystal measuring 0.5 × 0.2 × 0.1 mm was coated with epoxy cement and mounted on a glass fiber. Data were collected on a Syntex PI four-circle diffractometer equipped with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. Lorentz, polarization, and absorption corrections were applied for the 2306 reflections with $I > 3\sigma(I)$.

The heavy atom position was determined from the Patterson function and subsequent difference Fourier maps revealed the remaining nonhydrogen atoms. Full-matrix least-squares refinement converged to final R factors of $R = 0.034$ and $R_w = 0.044$ where

$$R = \frac{\sum ||F_o| - |F_c||}{\sum F_o} \quad R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

$$w = 1/\sigma^2(F_o)$$

A final difference map revealed no peaks except for some extremely close to the Pt positions over $e/\text{Å}^3$.

Results and Discussion

Table I gives the crystallographic data for K₂[Pt₂(SO₄)₄(OS(CH₃)₂)₂]₂·4H₂O. Final atomic coordinates are shown on Table II. Table III gives selected bond distances and angles. Other results are available as supplementary material, as specified in the paragraph at the end of this paper.

- (4) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761.
 (5) Cotton, F. A.; Falvello, L. R.; Han, S. *Inorg. Chem.* **1982**, *21*, 1709.
 (6) Muraveiskaya, G. S.; Orlova, V. S.; Evstaf'eva, O. N. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1974**, *19*, 1030.
 (7) All calculations were done on the PDP 11/60 computer equipped with the Enraf-Nonius structure determination package at B. A. Frenz and Associates, Inc., College Station, TX.

Table II. Final Positional Parameters^a

atom	x	y	z
Pt(1)	0.14200 (3)	0.01277 (2)	0.03184 (2)
K(1)	0.2974 (2)	-0.0934 (2)	0.3701 (2)
S(1)	0.0217 (2)	0.1111 (2)	0.1878 (1)
S(2)	-0.0536 (2)	0.2373 (2)	-0.0967 (1)
S(3)	0.5019 (3)	-0.0059 (2)	0.1919 (2)
O(1)	0.1629 (6)	0.0585 (5)	0.1762 (4)
O(2)	0.1070 (6)	0.1929 (5)	-0.0133 (4)
O(3)	0.1207 (6)	-0.0338 (5)	-0.1122 (4)
O(4)	0.1774 (6)	-0.1670 (5)	0.0762 (4)
O(5)	0.3839 (6)	0.0423 (6)	0.0808 (4)
O(6)	-0.0006 (7)	0.2412 (5)	0.1581 (5)
O(7)	0.0467 (7)	0.0840 (6)	0.2933 (4)
O(8)	-0.0743 (7)	0.2122 (6)	-0.2019 (4)
O(9)	-0.0623 (8)	0.3662 (5)	-0.0715 (5)
O(1w)	0.1041 (12)	-0.1555 (10)	0.4644 (7)
O(2w)	-0.2993 (12)	0.3756 (12)	0.0487 (8)
C(1)	0.651 (1)	0.112 (1)	0.2341 (10)
C(2)	0.600 (1)	-0.130 (1)	0.1620 (9)

^a Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Selected Bond Distances (Å) and Angles (Deg)^a

Distances			
Pt–Pt	2.471 (1)	S(1)–O(7)	1.421 (6)
Pt–O(1)	2.007 (5)	S(2)–O(2)	1.537 (6)
Pt–O(2)	2.017 (5)	S(2)–O(4)	1.536 (6)
Pt–O(3)	2.004 (5)	S(2)–O(8)	1.426 (7)
Pt–O(4)	2.010 (5)	S(2)–O(9)	1.440 (6)
Pt–O(5)	2.126 (6)	S(3)–O(5)	1.554 (6)
S(1)–O(1)	1.540 (6)	S(3)–C(1)	1.800 (11)
S(1)–O(3)	1.546 (6)	S(3)–C(2)	1.789 (11)
S(1)–O(6)	1.446 (6)		

Angles			
Pt–Pt–O(1)	89.6 (2)	O(2)–S(2)–O(4)	107.4 (3)
Pt–Pt–O(2)	89.4 (2)	O(2)–S(2)–O(8)	111.2 (4)
Pt–Pt–O(3)	90.3 (2)	O(2)–S(2)–O(9)	105.0 (3)
Pt–Pt–O(4)	90.7 (2)	O(4)–S(2)–O(8)	109.7 (4)
Pt–Pt–O(5)	177.0 (2)	O(4)–S(2)–O(9)	107.0 (4)
O(1)–S(1)–O(3)	106.1 (3)	O(8)–S(2)–O(9)	116.1 (4)
O(1)–S(1)–O(6)	110.3 (4)	Pt–O(5)–S(3)	118.5 (4)
O(1)–S(1)–O(7)	106.6 (3)	O(5)–S(3)–C(1)	102.4 (5)
O(3)–S(1)–O(6)	110.4 (4)	O(5)–S(3)–C(2)	103.7 (5)
O(3)–S(1)–O(7)	107.1 (4)	C(1)–S(3)–C(2)	100.2 (6)
O(6)–S(1)–O(7)	115.7 (4)		

^a Estimated standard deviations in the least significant digits are shown in parentheses.

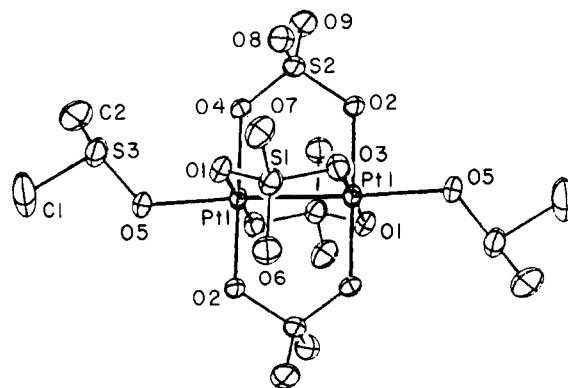


Figure 1. ORTEP drawing of the [Pt₂(SO₄)₄(OSMe₂)₂]²⁻ ion. Each atom is represented by its ellipsoid of thermal vibration at the 40% probability level and the atom numbering scheme is defined.

The main feature of the structure is the short Pt–Pt bond length, 2.471 (1) Å. This is not significantly different from the bond distance in the [Pt₂(SO₄)₄(H₂O)₂]²⁻ ion² (2.466 Å) although the report on this gives no error estimates. The Pt–O(SO₄) bonds make angles with the Pt–Pt axis that av-

erage 90.0 [6]^o and have a mean length of 2.010 [6] Å.⁸ The axially coordinated oxygen atom of the dimethyl sulfoxide is essentially collinear, 177.0 (2)^o, with the Pt-Pt bond at a bond distance of 2.126 (6) Å. In the sulfate groups the average S-O(coord) distance is 1.540 [5] Å, whereas the average S=O(terminal) bond length is 1.433 [12] Å. The difference, 0.107 [13] Å, is highly significant. Each sulfur atom is bent out of the O-Pt-Pt-O plane in the ring to which it belongs, and these bends are all in the same rotational sense about the Pt-Pt axis. Thus, while the central Pt₂O₈ unit has essentially *D*_{4h} symmetry, the entire Pt₂(SO₄)₄ unit has only *C*_{4h} symmetry. The structure of the central Pt₂(SO₄)₄ unit, with its *C*_{4h} symmetry, is very similar to what has been found previously in Re₂(SO₄)₄,⁹ Mo₂(SO₄)₄,¹⁰ Mo₂(HPO₄)₄,¹¹ and Pt₂(HPO₄)₄⁵ moieties.

The Me₂SO ligand is coordinated through oxygen. While its dimensions are generally similar to those of free Me₂SO itself,¹² there is one striking difference, namely, the length of the S-O bond, which is now 1.554 (6) Å, as compared to 1.513 (5) Å in the uncoordinated molecule. This significant elongation, 0.041 (8) Å, is considerably greater than the very slight elongation, 0.012 (6) Å, observed in Rh₂(O₂CCF₃)₄-(Me₂SO)₂.¹³ This is not unexpected since the Pt atom in the present case is doubtless a more positively charged and less polarizable acceptor.

The potassium ions occupy a fourfold general position and have a coordination number of 8. Seven of the potassium ligands are oxygen atoms of the sulfate ions. Two of these, belonging also to the platinum coordination shell, make an average distance of 2.93 [1] Å to potassium, and the remaining five, peripheral sulfate oxygen atoms, contact the potassium ion at an average distance of 2.79 [1] Å. One set of water molecules also serve as ligands to the potassium ions, with a K-O distance of 2.79 (1) Å. The second set of water molecules form hydrogen bonds to the first set, at an O...O distance of 2.86 (2) Å, and also to sulfate oxygen O(6), at a distance of 2.953 (8) Å. All of the K-O and O...O distances are available in a supplementary table.

Concluding Remarks. The Pt-Pt distance found here, 2.471 (1) Å, is not significantly different from that reported for the [Pt₂(SO₄)₄(H₂O)₂]²⁻ ion, 2.466 Å, with the assumption that the esd for the latter, which was not stated,² is 0.001 or 0.002 Å. While the Pt-Pt distance in the [Pt₂(HPO₄)₄(H₂O)₂]²⁻ ion, 2.486 [2] Å,⁵ is slightly lower in a statistically significant way, it is unlikely that the difference, 0.015 Å, has any chemical significance. The Pt-Pt bonds in these species with four bridging anions are distinctly shorter than those in the two compounds with only two bridging groups, viz., **2** and **3**, mentioned in the introduction, where the distances are respectively 2.557 (1) and 2.539 (1) Å.

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Registry No. K₂[Pt₂(SO₄)₄(OSMe₂)₂·4H₂O], 81602-75-7; K₂[Pt₂(SO₄)₄(H₂O)₂], 58807-43-5.

Supplementary Material Available: Tables of structure factors, bond lengths and angles, thermal parameters, root-mean-square amplitudes, and noncovalent close contacts (Table IV) (17 pages). Ordering information is given on any current masthead page.

(8) A number in parentheses is an esd for a given individual value while a number in brackets is equal to $[\sum \Delta_i^2 / (n - 1)]^{1/2}$, where Δ_i is the deviation of the *i*th value in a set of *n* such values from the arithmetic mean of the *n* values.

(9) Cotton, F. A.; Frenz, B. A.; Shive, L. W. *Inorg. Chem.* **1975**, *14*, 649.

(10) Cotton, F. A.; Frenz, B. A.; Pedersen, E.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 391.

(11) Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 3562.

(12) Thomas, R.; Shoemaker, C. B.; Eriks, K. *Acta Crystallogr.* **1966**, *21*, 12.

(13) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 2347.

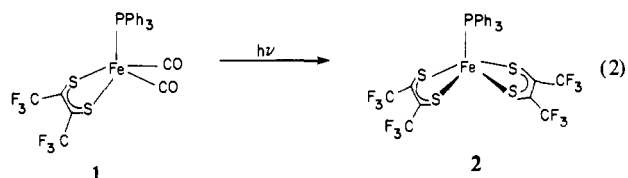
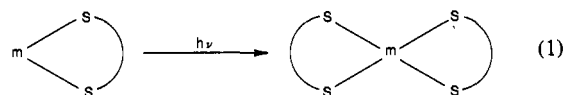
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Photoinduced Bimolecular Bidentate Ligand Migration. A New Photoinduced Reaction Pathway

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In the last decade there has been an upsurge of interest in the photochemistry of inorganic and organometallic substances.²⁻⁸ In this area, photoinitiated reactions of transition-metal carbonyl complexes are best characterized, but only a few generic reactions, namely, unimolecular ligand photo-substitution and intramolecular photorearrangement (isomerizations) have been well documented.³ Herein, we describe a previously uncharacterized *photoinduced bimolecular bidentate ligand migration reaction*, eq 1, as observed for various 1,2-dithiolene complexes,⁹ for example, eq 2.



Because of the inherent low symmetry and, consequently, uncharacterized electronic structure of **1** and **2**,¹⁰ it was decided to find an alternative species that undergoes the same type photoreaction to serve as a model compound for the study of the reaction mechanism.

Careful study of the literature¹¹ revealed that the photogeneration of $M(\text{CO})_n(\text{S}_2\text{C}_2\text{R}_2)_{3-n/2}$ ($n = 0, 2, 4$; $M = \text{W}, \text{Mo}$) from $M(\text{CO})_6$ and $\text{Ni}(\text{S}_2\text{C}_2\text{R}_2)_2$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$)¹² occurs (Scheme I). Assuming that it proceeds by the same mechanism as (2), we studied the photochemical transformation of $\text{W}(\text{CO})_2(\text{S}_2\text{C}_2\text{Me}_2)_2$ (**3**) to $\text{W}(\text{S}_2\text{C}_2\text{Me}_2)_3$ (**4**) as a function of wavelength, solvent, and concentration. Herein we report our preliminary results.

Experimental Section

Authentic samples of trigonal-prismatic $\text{W}(\text{CO})_2(\text{S}_2\text{C}_2(\text{CH}_3)_2)_2$ ¹² (red-violet; λ_{max} 641 (ϵ 850 M⁻¹ cm⁻¹), 507 (15660), 347 nm (5520); ν_{CO} 2027, 1982 cm⁻¹ (CHCl₃)) and $\text{W}(\text{S}_2\text{C}_2(\text{CH}_3)_2)_3$ ¹³ (blue-green;

(1) To whom correspondence should be addressed at the Occidental Research Corp., P.O. Box 19601, Irvine, CA 92713.

(2) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401-430. Wrighton, M. S.; Geoffroy, G. L. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(3) Gustorf, E. K.; Grevels, F.-W. *Fortschr. Chem. Forsch.* **1969**, *13*, 366-450.

(4) Ford, P. C.; Petersen, J. D.; Hintze, R. E. *Coord. Chem. Rev.* **1974**, *14*, 67-105.

(5) Strohmeier, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730-737.

(6) Adamson, A. W.; Waltz, W. L.; Zinato, E. J.; Watts, D. W.; Fleischauer, P. D.; Lindholm, R. D. *Chem. Rev.* **1968**, *68*, 541-585.

(7) Adamson, A. W.; Fleischauer, P. D., Eds. "Concepts of Inorganic Photochemistry"; Wiley: New York, 1975.

(8) Balzani, V.; Carassitti, V., Eds. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.

(9) Other reactions we observed include the following: $(\text{F}_3\text{C})_2\text{C}_2\text{S}_2\text{Fe}(\text{P}(\text{OCH}_3)_3)_3$, $(\text{Fe}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2)_2 + \text{W}(\text{CO})_6$, and $\text{Ni}(\text{S}_2\text{C}_4\text{H}_6)_2^f + \text{W}(\text{CO})_6$ ($z = 2-, 1-$).

(10) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1971**, *10*, 1410-1415. Balch, A. L. *Ibid.* **1967**, *6*, 2518; **1971**, *10*, 276.

(11) E.g.: Burns, R. P.; McAuliffe *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303-348. MacCleverty; J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. Schrauzer; G. N. *Transition Met. Chem. (N.Y.)* **1968**, *4*, 299.

(12) Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. J. *Am. Chem. Soc.* **1966**, *88*, 5174-5179.