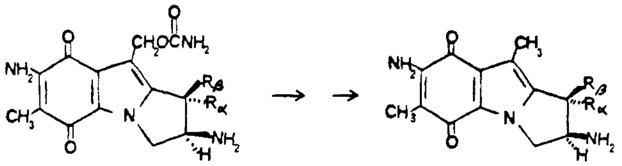
nol.[22,23] In both cases, the new carbon 10 methyl products **6a,b**



5a, R_β = H; R_α = OH
b, R_β = OH; R_α = H

6a, R_β = H; R_α = OH
b, R_β = OH; R_α = H

were readily identified by their spectroscopic properties. Of particular note, was the absence of the carbamate absorption at 1708 cm^{-1} in the infrared spectrum of **6a** and the appearance of a singlet at $\sim\delta$ 2.25 in the ^1H NMR spectra of **6** for the carbon 10 methyl group.

Two mechanisms are likely for the formation of **6a,b**. One pathway (Scheme II) involves the tautomerization of **4** to **7** in the absence of an external nucleophile, followed by proton loss to produce the oxidized adduct **6**. Alternatively, catalytic hydrogenolysis of the carbamate group in **2** should generate the carbon 10 methyl derivative which then is reoxidized during the workup to yield **6**. This latter route is precedented since benzylic carbamates are readily hydrogenated to give the corresponding toluene derivatives.[24]

Substantiation for the first mechanism (Scheme II) was obtained by rerunning each of these reductions under slightly modified conditions. First, D_2 was substituted for H_2 (Table I, entries 1 and 3), while in a second experiment the O-deuterated alcohol (ROD) was used in place of the corresponding protonated solvent (ROH) (Table I, entries 2 and 4). Deuterium incorporation (86–91%) at carbon 10 was observed *only* in the second experiment, establishing solvent as the source of deuterium.[25] Notably, we obtained a similar result in an earlier study concerning the mechanism of carbon 1 ring opening in mitosenes.[7]

These results provide the first evidence for the ambidextrous (i.e., electrophilic[27] and nucleophilic) nature of the carbon 10 methylene unit in mitomycin C. Additional studies in progress are aimed at determining the generality and biological significance of this phenomenon.

Acknowledgment. We thank the National Institutes of Health (ROICA29756) and the National Institutes of Health sponsored Biomedical Research Support Grant Program at the University of Houston for their generous support of our work. We also express our appreciation to Dr. Gary Martin (College of Pharmacy) and Ed Ezell of this department for running the high-field NMR spectra and Dr. Stephen Reynolds (Exxon Research and Engineering Co.) for obtaining the field-desorption mass spectra. Grateful acknowledgment is made to both Dr. W. T. Bradner, Bristol-Myers Laboratories, Syracuse, NY, and Dr. I. Matsubara, Kyowa Hakko Kogyo Co., Ltd., Tokyo, Japan, for gifts of mitomycin C.

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[22] Compound **6b**: HPLC retention time 16.4 min; ^1H NMR (300.1 MHz, CD_3OD) δ 1.75 (s, 3 H, C_6CH_3), 2.27 (s, 3 H, $C_{10}CH_3$), 3.68 (dd, 1 H, J = 8.5, 12.2 Hz, C_3H_β), 3.77–3.86 (m, 1 H, C_2H), 4.44 (dd, 1 H, J = 7.2, 12.2 Hz, C_3H_α), 4.72 (d, 1 H, J = 5.3 Hz, C_1H); UV (MeOH) λ_{max} = 248, 309, 350 (sh), 525 nm.

[23] Reduction of **5b** was run in ethanol (37 °C, 7 min) rather than methanol due to the enhanced solubility of the starting material in the former solvent. Although HPLC analysis indicated that the reaction proceeded cleanly, lower isolated yields for **6b** were observed in these reactions.

[24] Rylander, P. N. "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York, 1967; p 454.

[25] ^1H NMR spectroscopy provided a convenient method to monitor these reactions. Monodeuteration at carbon 10 led to an appearance of a 1:1:1 multiplet ($J_{HD} \sim$ 2.07 Hz) upfield ($\sim$0.02 ppm) from the singlet normally associated with the carbon 10 methyl group. Both the upfield shift and the observed coupling constant are diagnostic of deuterium incorporation at this site.[26]

[26] Batiz-Hernandez, H.; Bernheim, R. A. In "Progress in NMR Spectroscopy"; Pergamon Press: Oxford, 1967; Vol. 3, pp 63–85.

[27] This property should be modulated by the type of substituent present at carbon 7.

Organometallic Derivatives of the Tetrathiometallates: Syntheses, Structures, and Reactions of $MS_4[Rh(COD)]_2$ and $MS_4[(C_5H_5)Ru(PPh_3)]_2$ (M = Mo, W)

Kevin E. Howard and Thomas B. Rauchfuss*

School of Chemical Sciences
University of Illinois at Urbana—Champaign
Urbana, Illinois 61801

Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19711

Received August 1, 1985

We wish to describe experiments which demonstrate that the tetrathiometallate(VI) compounds[1] can function as ligands for reactive low-valent, organometallic complexes.[2] Previous work on the coordination chemistry of MoS_4^{2-} and WS_4^{2-} has focused almost exclusively on their inorganic coordination compounds.

The complex $WS_4Rh_2(COD)_2$ (**1**) (COD = 1,5-cyclooctadiene) was readily prepared by the reaction of stoichiometric quantities of $(Ph_4P)_2WS_4$ with $[Rh(COD)Cl]_2$ in acetonitrile. After 18 h, the product was collected and recrystallized from CH_2Cl_2/CH_3CN to give **1** in 80% yield as dark red crystals (eq 1).[3] The intermediate in this synthesis, $WS_4Rh(COD)^-$, could be isolated as its tetraphenylphosphonium salt by the addition of a second equivalent of $(Ph_4P)_2WS_4$ to $WS_4Rh_2(COD)_2$.[4] $WS_4Ir_2(COD)_2$ and $MoS_4Rh_2(COD)_2$ may also be prepared in an analogous manner, although the $MoRh_2$ complex is somewhat unstable in solution. Compound **1** was further characterized by X-ray diffraction (Figure 1).[5]

$$Rh_2Cl_2(COD)_2 + WS_4^{2-} \rightarrow (COD)RhS_2WS_2Rh(COD) + 2Cl^- \quad (1)$$

Compound **1** is a versatile synthetic intermediate as evidenced by its substitution chemistry (Scheme I). Addition of 4 equiv of PPh_3 to a CH_2Cl_2 solution of **1** results in the formation of a deep purple solution from which we isolated $WS_4Rh_2(PPh_3)_4$ (**2**).[6] Similarly, addition of 2 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) results in the formation of the bis-chelated $WS_4Rh_2(dppe)_2$ (**3**).[7] Although **1** gives intractable products when treated with CO, $WS_4[Rh(PPh_3)CO]_2$ (**4**) could be prepared by carbonylation of **2** or by treatment of **1** with CO in the presence of 2 equiv of

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[1] Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934. Coucouvanis, D. *Acc. Chem. Res.* **1981**, *14*, 201. Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455.

[2] Organometallic derivatives of the tetrathiometallates have been prepared previously (Adam, G. J. S.; Green, M. L. H. *J. Organomet. Chem.* **1981**, *208*, 299. Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1982**, *1*, 400) but only once has their reactivity been examined: Kovacs, J. A.; Bashkin, J. K.; Holm, R. H. *J. Am. Soc.* **1985**, *107*, 1784.

[3] All new compounds were isolated in analytically pure form and were characterized by ^1H and ^{31}P NMR and mass spectrometry. $WS_4Rh_2(COD)_2$: IR (Nujol) 434, 403 cm^{-1}.

[4] $(PPh_4)[WS_4Rh(COD)]$: FAB^- MS 523 ($WS_4Rh(COD)^-$); FAB^+ MS 339 (Ph_4P^+); IR (Nujol) 492, 484, 448 cm^{-1}.

[5] A crystal was obtained by cleavage of a twinned specimen. Systematic absences uniquely defined the space group as $P2_1/c$. Crystal parameters of a = 7.314 (2) Å, b = 10.774 (2) Å, and c = 25.323 (5) Å; β = 91.51 (2)°; V = 1994.8 (9) Å^3; Z = 4 were determined. The data were collected on a Nicolet R3 diffractometer at ambient temperatures with monochromatized Mo Kα (λ = 0.71073 Å) radiation. Of the 3610 reflections collected 2594 unique reflections with $F_c \geq 3\sigma(F_o)$ were used in the structure solution and refinement. The W, Rh, and S atoms were located by direct methods (SOLV-SHELXTL). Anisotropic temperature factors were used for the refinement (blocked cascade) of all non-hydrogen atoms. Hydrogen atoms were refined isotropically. Final structure refinement converged to R_F = 3.6% and R_{wF} = 3.7%.

[6] $WS_4Rh_2(PPh_3)_4$: ^{31}P NMR (all ^{31}P NMR spectra were measured at 101 MHz on CH_2Cl_2 solutions and are quoted in ppm vs. 85% H_3PO_4 external standard) 43.9 (d, $|J(^{103}Rh,^{31}P)|$ = 173 Hz).

[7] $WS_4Rh_2(dppe)_2$: ^{31}P NMR 71.55 (d, $|J(^{103}Rh,^{31}P)|$ = 164 Hz); FAB^+ MS 1316(MH^+).

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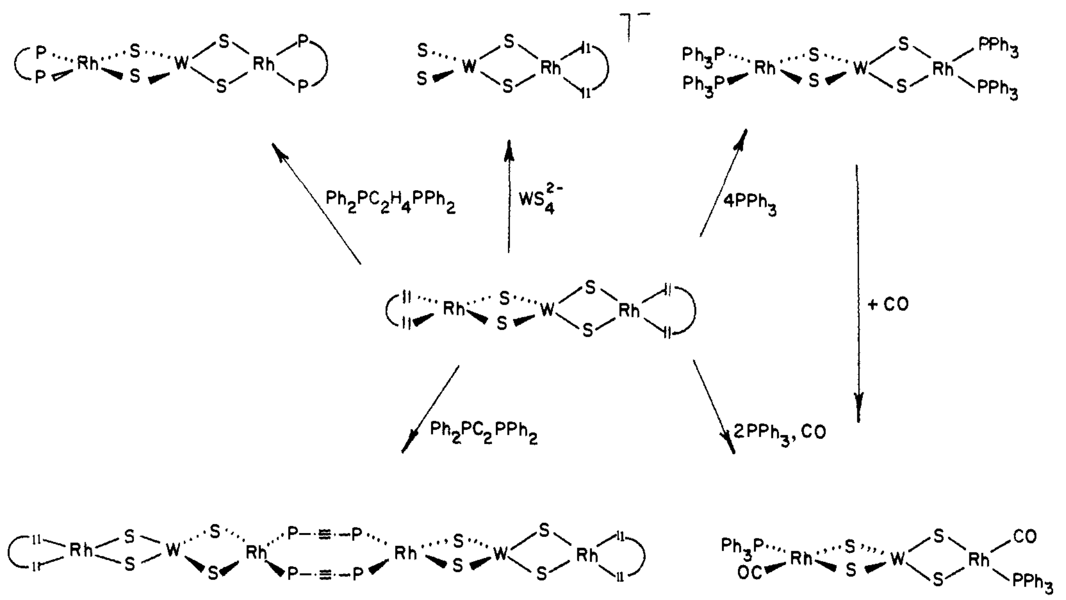
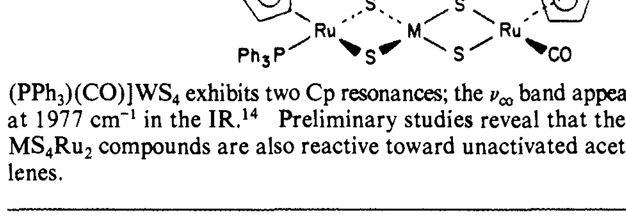
Scheme I



PPh_3.[8] The dicarbonyl diphosphine complex has a ν_{CO} band at 2011 cm^{-1} (CH_2Cl_2 solution).[9] The reaction of **1** with 1 equiv of 1,2-bis(diphenylphosphino)acetylene (DPPA) affords the hexametallic chain complex $Rh_4W_2S_8(DPPA)_2(COD)_2$ (**5**).[10]

The complexes $[(RC_5H_4)Ru(PPh_3)]_2MS_4$ were obtained in good yields from the reaction of $(RC_5H_4)Ru(PPh_3)_2Cl$ (R = H, CH_3)[11] with $(Ph_4P)_2MS_4$ (M = Mo, W) in refluxing acetonitrile.[12,13] The Ru_2M compounds exhibit intense absorptions in their visible spectra giving rise to their green (M = Mo, λ_{max} = 638 nm, ϵ = 5540 M^{-1} cm^{-1}) and red (M = W, λ_{max} = 530 nm, ϵ = 5800 M^{-1} cm^{-1}) colors. The observation of one methyl and four distinct $C_5H_4CH_3$ resonances in the ^{1}H NMR spectrum (CD_2Cl_2 solution[13]) of $[(CH_3C_5H_4)Ru(PPh_3)]_2WS_4$ proves that this chiral compound is configurationally stable on the NMR time scale. The $[(RC_5H_4)Ru(PPh_3)]_2MS_4$ clusters react rapidly with CO (1 atm) to give purple (M = Mo) and orange (M = W) *mono*carbonyl adducts (eq 2). The ^{1}H NMR spectrum of $[(C_5H_5)_2Ru_2(PPh_3)(CO)]WS_4$ exhibits two Cp resonances; the ν_{CO} band appears at 1977 cm^{-1} in the IR.[14] Preliminary studies reveal that these MS_4Ru_2 compounds are also reactive toward unactivated acetylenes.



(2)

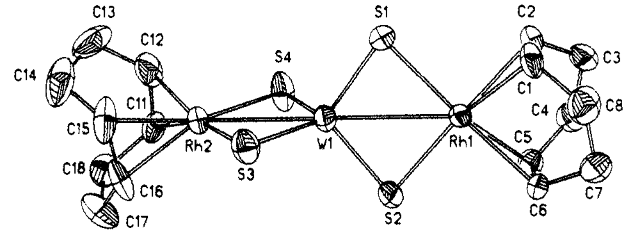


Figure 1. ORTEP plot of the non-hydrogen atoms in $WS_4Rh_2(C_8H_{12})_2$. The thermal ellipsoids are drawn at the 35% probability level. The S(1)-W-S(2) and S(3)-W-S(4) angles are 106 ± 1°; the other S-W-S angles are in the range 110.8 (1)-112.4 (1)°. The S(1)-W-S(2), S-(3)-W-S(4) dihedral angle is 90.72°.

The Ru_2MS_4 clusters all show reversible one-electron redox couples by cyclic voltammetry.[15] The compounds $[(C_5H_5)Ru(PPh_3)]_2MS_4$ (M = Mo, W) exhibit *single* redox couples at 479 and 527 mV, respectively (vs. Ag/AgCl); $(C_5H_5)Ru(PPh_3)_2Cl$ is reversibly oxidized at 590 mV. $[(C_5H_5)_2Ru_2(PPh_3)(CO)]WS_4$ is more difficult to oxidize at 729 mV. A similar trend is observed for $(CH_3C_5H_4)Ru(PPh_3)_2Cl$ (542 mV), $(CH_3C_5H_4)_2Ru_2(PPh_3)_2WS_4$ (472 mV), and $[(CH_3C_5H_4)_2Ru_2(PPh_3)(CO)]WS_4$ (622 mV). These data indicate considerable electron delocalization in these Ru_2MS_4 compounds, particularly since a single wave was observed at lower potential for the $(RC_5H_4)_2Ru_2(PPh_3)_2MS_4$ clusters than for the monoruthenium precursors. Furthermore, the replacement of a triphenylphosphine ligand by carbon monoxide at one metal clearly affects the chemical and electrochemical properties of the entire trimetallic unit.

The experiments described in this report demonstrate that the tetrathiometallates are effective in supporting low-valent metal centers which in turn are reactive toward π-acid ligands. These findings are significant because mixed-metal thiomolybdates have been implicated in the chemistry of π-acidic species such as dinitrogen[16] and thiophene.[17]

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(8) $WS_4Rh_2(CO)_2(PPh_3)_2$: ^{31}P NMR 36.04 (d, $|J(^{103}Rh,^{31}P)|$ = 159 Hz); IR (CH_2Cl_2 solution) ν_{co} = 2011 cm^{-1}.

(9) This data[8] shows that the bridging WS_4 ligand is a good electron acceptor. For comparison, $Rh_2Cl_2(CO)_2(PPh_3)_2$ has ν_{CO} at 1979 cm^{-1} (CsBr) and the *tetra*carbonyl $Rh_2(SPh)_2(CO)_4(PPh_3)_2$ has ν_{CO} at 2062, 2003, and 1995 cm^{-1} (hexadecane). Bonnet, J.-J.; Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1977**, *16*, 1514 and references therein. Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1975**, *14*, 2779.

(10) $W_2S_8Rh_4(DPPA)_2(COD)_2$: ^{31}P NMR 27.73 (d,$|J(^{103}Rh,^{31}P)|$ = 163 Hz).

(11) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601.

(12) $Cp_2Ru_2(PPh_3)_2WS_4$: Anal. C, H, S, P.; ^{1}H NMR 7.50 (?, ~30 H), 4.71 (s, ~10 H); ^{31}P NMR 48.73 (s); FAB$^+$ MS 1170 (MH$^+$). $Cp_2Ru_2(PPh_3)_2MoS_4$: Anal. C, H; FAB$^+$ MS 1082 (MH$^+$).

(13) $(MeCp)_2Ru_2(PPh_3)_2WS_4$: ^{1}H NMR ($CDCl_3$ solution) 7.40 (m, ~30 H), 4.90 (m, 4 H), 4.24 (d, 4 H), 1.60 (d, 6 H); ^{1}H NMR (CD_2Cl_2 solution) 7.40 (m, ~30 H), 4.94 (d, 2 H), 4.90 (d, 2 H), 4.26 (s, 2 H), 4.15 (s, 2 H), 1.59 (s, 6 H); ^{31}P NMR 50.25 (s).

(14) $Cp_2Ru_2(PPh_3)(CO)WS_4$: ^{1}H NMR 7.30 (m, ~15 H), 5.43 (s, 5 H), 4.83 (s, 5 H); ^{31}P NMR 49.82 (s); IR (CH_2Cl_2 solution) ν_{CO} = 1977 cm^{-1}. The $MoRu_2$ compound has very similar properties.

(15) Electrochemical measurements were made with a BAS 100 instrument on 10^{-3} M solutions of the compound in 10^{-1} M Bu_4NClO_4 in CH_2Cl_2 using a Pt disk working electrode, with a scan rate of 200 mV/s.

(16) Stiefel, E. I. "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum"; Climax Molybdenum Co.; Ann Arbor, 1982; p 56. Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Radiochem.* **1983**, *27*, 198.

(17) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. "The Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979. Zdrâzil, M. *Appl. Catal.* **1982**, *4*, 107. Massoth, F. E.; Muralidhar, G. "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum"; Climax Molybdenum Co.: Ann Arbor, 1982; p 343. Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure factors (19 pages). Ordering information is given on any current masthead page.

Electronic Spectroscopy of a Non-Kekulē Isomer of Benzene, 2,4-Dimethylene-1,3-cyclobutanediyl

Gary J. Snyder[1a] and Dennis A. Dougherty*[1b]

Contribution No. 7315, Crellin Laboratory of Chemistry, California Institute of Technology Pasadena, California 91125

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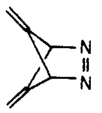
Non-Kekulē molecules are intrinsically novel structures that have been of considerable interest recently because of their potential usefulness as models for photochemical excited states and reacton transition states and their possible incorporation into materials with novel optical, electronic, or magnetic properties. ESR spectroscopy is the most powerful tool for unambiguously identifying the high spin states (triplet, quintet, ...) of such structures. Once such an assignment has been made, the potentially quite informative techniques of electronic absorption and emission spectroscopy can be implemented.[2] We report herein the absorption and emission spectra of triplet biradical **1**, a

1

non-Kekulē isomer of benzene. We also describe a novel technique that could be generally applicable to the often vexing problem of correlating an observed optical spectrum with an ESR spectrum.

Irradiation (334 ± 10 nm) of diazene **2** at 77 K in a 2-



2

methyltetrahydrofuran (MTHF) matrix produces a bright yellow-orange color. A sample prepared in this manner exhibits an ESR spectrum which has been previously assigned to triplet **1**,[3] as well as the electronic absorption and emission spectra presented in Figure 1. An excitation spectrum, measured by monitoring the emission at 552 nm, faithfully reproduced the absorption spectrum, establishing that the same species is responsible for both spectra of Figure 1.

The fine structure of the optical spectra in Figure 1 can be readily analyzed in terms of a single electronic transition with two independent vibrational modes. Frequency $\tilde{\nu}_2$ (Figure 1) is ca. 620 cm^{-1} in both spectra, but $\tilde{\nu}_1$ varies slightly, with frequencies in the ground and excited states of 1550 and 1500 cm^{-1}, respectively. The mirror-image relationship between the absorption and emission spectra, along with the small (150 cm^{-1}) Stokes' shift and the prominence of the 0–0 bands, implies nearly identical geometries for the ground and excited states.

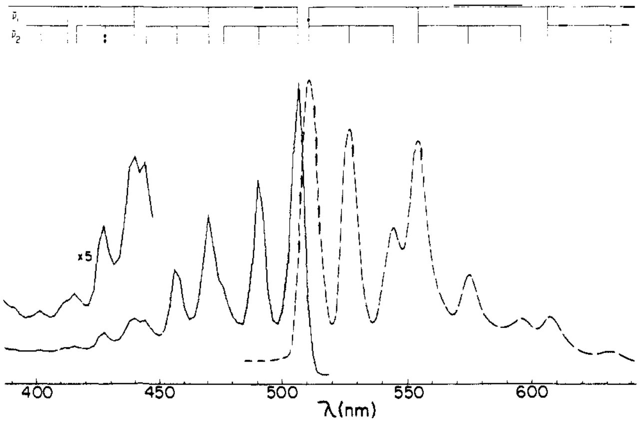


Figure 1. Absorption (—) and fluorescence (---; λ_{ex} = 440 nm) spectra of triplet **1** in MTHF at 77 K, with λ_{max} = 506 and 510 nm, respectively. The fluorescence spectrum is not corrected for the ca. 40% decomposition of the sample that occurred during the scan from 500 to 700 nm.

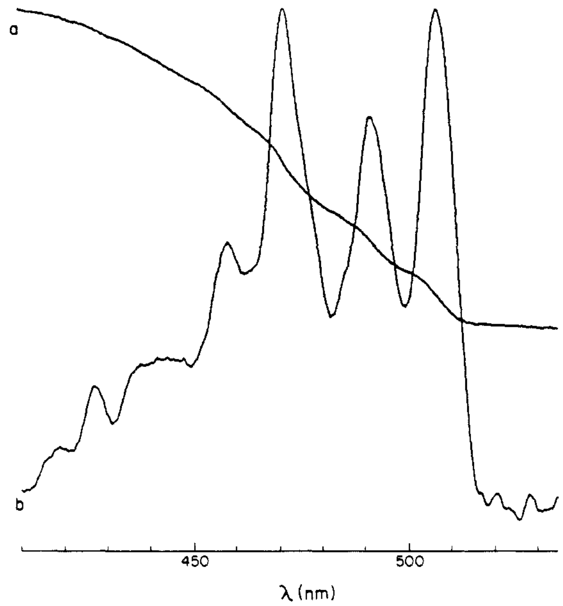


Figure 2. (a) ESR signal intensity of triplet **1** vs. wavelength of irradiation (see text). The final is ca. half the initial intensity. (b) $(1/I)$ $(-dI/d\lambda)$ vs. λ after quadratic least-squares smoothing.[6]

Both the ESR signal of triplet **1** and the absorption spectrum of Figure 1 decay slowly at 77 K and with the same unimolecular rate constant.[4] We have also correlated the ESR and absorption spectra in a novel way by taking advantage of the previously reported[3] photochemical lability of **1**. Figure 2a shows the decrease in the ESR signal intensity (I) of **1** at 4 K as a function of irradiation wavelength, which was increased at a constant rate. Curve b, which represents $(1/I)$ $(-dI/d\lambda)$, is effectively equivalent to a plot of ϵ vs. λ for the ESR signal carrier.[5] The similarity of this photochemical "action spectrum" and the absorption spectrum (Figure 1) is evident.

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(1) (a) NSF Predoctoral Fellow, 1981–1984. (b) Fellow of the Alfred P. Sloan Foundation, 1983–1985; Camille and Henry Dreyfus Teacher Scholar, 1984–1989.

(2) (a) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400–7404. (b) Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629–1630. Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216–2218. (c) Turro, N. J.; Mirbach, M. J.; Harrit, N.; Berson, J. A.; Platz, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 7653–7658. (d) Roth, W. R.; Biermann, M.; Erker, G.; Jelich, K.; Gerhartz, W.; Görner, H. *Chem. Ber.* **1980**, *113*, 586–597.

(3) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774–1775.

(4) The decay is nonexponential due to a distribution of matrix sites and has a half-life of ca. 30 h at 77 K. The most probable rate constant derived from a ln I vs. $t^{1/2}$ plot is 7 × 10^{-7} s^{-1}. Doba, T.; Ingold, K. U.; Siebrand, W. *Chem. Phys. Lett.* **1984**, *103*, 339–342. Doba, T.; Ingold, K. U.; Siebrand, W.; Wildman, T. A. *J. Phys. Chem.* **1984**, *88*, 3165–3167.

(5) Monochromatic light (ca. 5-nm band-pass) from a 1000-W Xe arc lamp was used. The increased intensity of the 470-nm peak (Figure 2b) can be attributed to a local maximum in lamp output (P(470 nm) $\simeq$ 1.5 P(506 nm)).

(6) Savitsky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, *36*, 1627–1639.

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