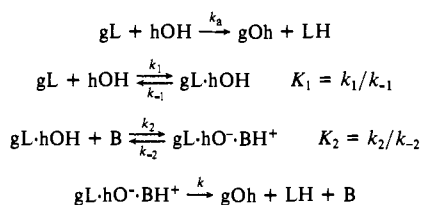*uncomplexed* U(AU)$_2$BOH with that of *uncomplexed* **6** toward *uncomplexed* ester. The much greater rates of reaction of U-(AU)$_2$BOH compared to **6** are interpreted in terms of all effects associated with U(AU)$_2$BOH complexing CH$_3$CH(CO$_2$R)NH$_3^+$ in its transition state for transacylation (both NH$_3^+$···O and O-C-O$^-$ as binding sites) as compared to **6** complexing CH$_3$CH(CO$_2$R)NH$_3^+$ (only O-C-O$^-$ as a binding site) in its transition state for transacylation. The rate factor estimated in runs 6 and 8 is $\approx 10^{11}$. Although this value is approximate and subject to uncertainties,[11] there is no doubt that the rate factor associated with all of the effects of complexation is very large indeed, probably within a few powers of ten of that estimated. The high magnitude of this value provides an indication of the importance of collection and orientation[12] by complexation to the rate accelerations. The crystal structure of the complex U-(AUCH$_2$)$_2$A·(CH$_3$)$_3$CNH$_3^+$ClO$_4^-$ indicates it to be highly structured by three N$^+$—H···O=C hydrogen bonds in a nearly perfect tripod-type arrangement.[5] In molecular models a similar structure for U(AU)$_2$BOH·CH$_3$CH(CO$_2$R)NH$_3^+$ places the

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(11) Calculation of the rate factors of Table I involve the following definitions and reasonable assumptions about mechanistic schemes. The reaction of CH$_3$CH(CO$_2$C$_6$H$_4$-*p*-NO$_2$)NH$_3$ClO$_4$ (gL) with **3** (hOH) to give **5** (gOh) and *p*-NO$_2$C$_6$H$_4$OH (HL) is presumed to involve an overall bimolecular rate constant k_a but to go by the following mechanism in which [B] is the concentration of R$_3$N:

$$\text{gL} + \text{hOH} \xrightarrow{k_a} \text{gOh} + \text{LH}$$

$$\text{gL} + \text{hOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{gL·hOH} \qquad K_1 = k_1/k_{-1}$$

$$\text{gL·hOH} + \text{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{gL·hO}^-\text{·BH}^+ \qquad K_2 = k_2/k_{-2}$$

$$\text{gL·hO}^-\text{·BH}^+ \xrightarrow{k} \text{gOh} + \text{LH} + \text{B}$$

Experimentally [hOH] and [B] are constant, K_1 is very high valued, and k_{-1} is expected to be $> k$. Thus, the observed first-order kinetics (k_{obsd}) for the appearance of LH can be decribed by eq 1. With the reasonable assumption

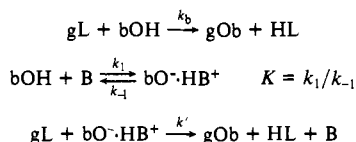$$k_{obsd} = [\text{B}]K_2 k \text{ m}^{-1} \qquad (1)$$

$$k_a = [\text{B}]K_1 K_2 k \text{ M}^{-1} \text{ m}^{-1} \qquad (2)$$

$$k_a = K_1 k_{obsd} \text{ M}^{-1} \text{ m}^{-1} \qquad (3)$$

that $k_{-1} > k_2[\text{B}]$, the second-order rate constant (k_a) for acylation of hOH by gL can be expressed by eq 2, which when combined with eq 1 gives eq 3. The value of K_1 for CH$_3$CH(CO$_2$C$_6$H$_4$-*p*-NO$_2$)NH$_3$ClO$_4$ complexing **3** is presumed to be within a few orders of magnitude of K_1 for CH$_3$NH$_3$ picrate complexing **3** (2×10^9 M^{-1}). This assumption is supported by the following facts. With chorand hosts, *t*-BuNH$_3$ClO$_4$ gave K_1 values ~60 times those of *t*-BuNH$_3$ picrate (Moore, S. S.; Tarnowski, T. L.; Newcomb, M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6398–6405). The K_1 values for **3** complexing Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$, CH$_3$NH$_3^+$, and *t*-BuNH$_3^+$ picrates vary only from extremes of 10^8 to 10^{11} M^{-1}, suggesting that the value for the alanyl ester picrate should fall in this range.

The reaction of gL with 3-phenylbenzyl alcohol (bOH) to give acylated product gOb and HL is presumed to involve an overall bimolecular rate constant k_b and to go by the following mechanism:

$$\text{gL} + \text{bOH} \xrightarrow{k_b} \text{gOb} + \text{HL}$$

$$\text{bOH} + \text{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{bO}^-\text{·HB}^+ \qquad K = k_1/k_{-1}$$

$$\text{gL} + \text{bO}^-\text{·HB}^+ \xrightarrow{k'} \text{gOb} + \text{HL} + \text{B}$$

With [bOH] $>$ [gL] and [B] constant, [mO$^-$·HB$^+$] is constant, and the reaction should follow the first-order kinetics (k_{obsd}^b) of eq 4. Equation 5

$$k_{obsd}^b = k'[\text{mO}^-\text{·HB}^+] \text{ m}^{-1} \qquad (4)$$

$$k_b = [\text{B}]k_1 k'/(k' + k_{-1}) \text{ M}^{-1} \text{ m}^{-1} \qquad (5)$$

$$k_b = k_{obsd}^b/[\text{bOH}] \text{ M}^{-1} \text{ m}^{-1} \qquad (6)$$

$$k_a/k_b = K_1 k_{obsd}[\text{bOH}]/k_{obsd}^b \qquad (7)$$

expresses k_b as a function of k_1, k_{-1}, k', and [B]. Since $k_{-1} > k_1$, eq 5 reduces to eq 6. The rate factor due to all effects of complexation is k_a/k_b, whose values at constant [M] can be estimated through eq 7. We warmly thank Professors R. L. Schowen and F. A. L. Anet for very helpful suggestions regarding this kinetic treatment.

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CO$_2$R carbonyl group of the guest beautifully oriented for attack by the CH$_2$O$^-$ group of the host. This high rate acceleration further confirms the validity of combining the techniques of host design, synthesis, crystal structure determination, and kinetic studies of structural recognition in complexation.[13]

Sodium ion in a concentration equal to that of **3** acted as a competitive inhibitor of complexation and, therefore, of acylation in run 9. The estimated acceleration rate factor fell by 2 orders of magnitude in run 9 as compared to run 6, in which Na$^+$ was absent. This degree of inhibition is consistent with expectations based on the $-\Delta G°$ values of binding of 15.0 kcal mol^{-1} by U-(AU)$_2$BOH for Na$^+$ vs. 12.7 kcal mol^{-1} for CH$_3$NH$_3^+$.

We were encouraged to do this work by the success of our first use of a thiol chorand as a host for transacylation of amino ester salts[14] and by the subsequent findings by others that two other thiol chorand hosts behaved similarly.[15] Unlike the earlier studies, the current one involves an incremental approach to serine protease-mimicking host systems. Compounds **1** and **2** in molecular models contain what in principle are all the features needed to approach the catalytic activities of the enzymes, but their syntheses represent a substantial effort. Accordingly, the synthesis of hemispherand U(AUCH$_2$)$_2$A was developed, it was found to bind CH$_3$NH$_3^+$ and Na$^+$ much better than the chorands, and its complexes were found to provide the anticipated structures.[5] In U(AU)$_2$BOH (**3**) described herein, the binding site and nucleophile are combined and are found to act cooperatively. In future studies, the imidazole and carboxylates of **1** and **2** will be added sequentially to **3** in the hope of making the proton transfers intramolecular, which with **3** are intermolecular parts of the transacylation processes.

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Dimerization and Cycloaddition Reactions of a Carbomethoxy-Substituted Cyclopropene

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Suitably substituted cyclopropenes suffer the ene reaction[1-3] and also readily undergo dimerization,[4] cycloaddition[5] and complexation with transition metals[6] as a means of releasing strain. During the course of our studies dealing with the excited-state behavior of cyclopropenes, we have uncovered a novel dimerization reaction that differs significantly from previously reported examples.[7] We report here the results of these studies.

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†John Simon Guggenheim Memorial Fellow, 1981–1982.

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(2) Weigert, F. J.; Barid, R. L.; Shapley, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 6630.

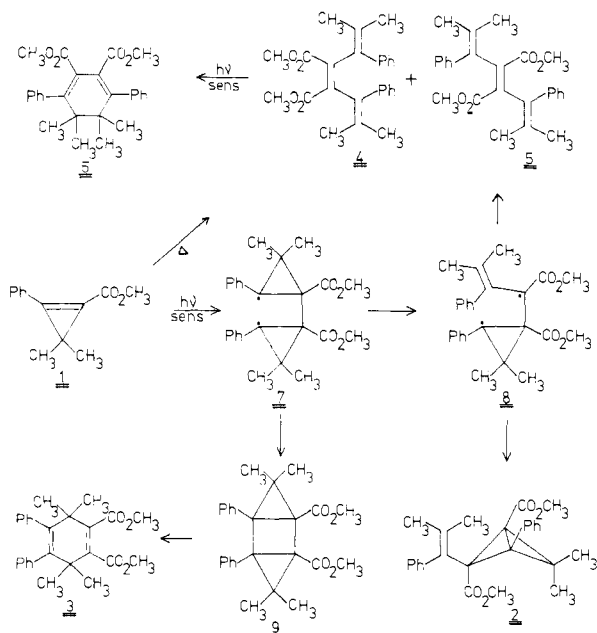(3) Padwa, A.; Reiker, W. *J. Am. Chem. Soc.* **1981**, *103*, 1859.

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Scheme I

Scheme II

The sensitized irradiation of 1-phenyl-2-carbomethoxy-3,3-dimethylcyclopropene (1) in benzene (thioxanthone) afforded a mixture of two products (ratio 5:1). The identity of the major photoproduct 2 was based on its characteristic NMR spectrum (90 MHz, CDCl$_3$) which showed four distinct methyl signals at δ 1.23, 1.58, 1.69, and 2.20 and two methoxy singlets at δ 3.54 and 3.87 as well as an aromatic multiplet (δ 6.86–7.49). Unequivocal proof of this assignment derives from a single-crystal X-ray structure analysis. Crystals of 2 were monoclinic with space group $P2_1/C$ and with a = 14.951 (3) Å, b = 10.402 (3) Å, c = 14.075 (3) Å, β = 90.36 (2)°, Z = 4, d_c = 1.227 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares analysis with isotropic thermal parameters. Convergence was achieved with R = 0.058 for 943 observations and 121 variables. The structure of the minor photodimer 3 was assigned on the basis of its straightforward spectral data[8] (NMR (CDCl$_3$, 90 MHz) δ 1.31 (s, 12 H), 3.77 (s, 6 H), 6.80–7.13 (m, 10 H)). Thermolysis of dimer 2 resulted in the formation of two new products (4 and 5 (1:1)), whose structures were deduced from their spectroscopic properties.[9] These same two compounds were also formed by heating cyclopropene 1 at 175 °C for 72 h. Structures 4 and 5 could be readily interconverted by thermolysis or sensitized photolysis. Extended irradiation of the mixture produced cyclohexadiene 6 as the exclusive photoproduct.[10] This photochemistry is summarized in Scheme I.
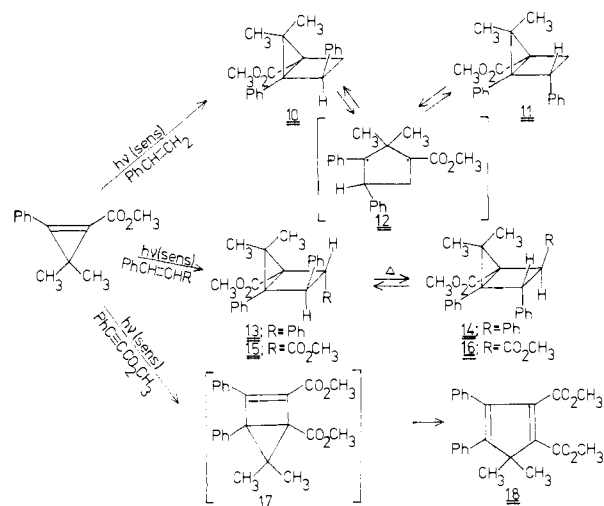
An attractive rationalization for the formation of the photoproducts is that bond formation occurs in a stepwise fashion to generate diradical 7. Simple collapse of 7 with carbon–carbon bond formation furnishes tricyclohexane 9 which undergoes a subsequent cycloreversion to give 3. In addition, diradical 7 can undergo cyclopropyl ring opening to give 8 which subsequently cyclizes to give bicyclobutane 2. The diradical formed from 1,2,3-trisubstituted cyclopropenes rapidly couples before it has a chance to undergo cyclopropyl ring opening, and consequently only tricyclohexane dimers are found in the triplet-sensitized irradiation of these systems.[7] No sign of dimers 2–6 could be found in the direct photolysis of cyclopropene 1. The major products produced under these conditions correspond to 1-carbomethoxy-2-phenyl- and 1-phenyl-2-carbomethoxy-4-methyl-1,3-pentadiene. Thus, the formation dimer 2 from the sensitized photolysis cannot be explained in terms of vinylcarbene generation from the singlet state (i.e., light leakage) followed by a subsequent cycloaddition to the cyclopropene π-bond.

We have also found that cyclopropene 1 undergoes photochemical (2 + 2) cycloaddition to several alkenes in high yield. The cycloadditions are carried out by using a slight excess of the olefinic acceptor in the presence of thioxanthone as the triplet sensitizer. These conditions almost completely suppress the formation of dimers 2 and 3 which are formed in high yield in the absence of a trapping agent. The structures of the cycloadducts rests largely upon the interpretation of the ^{13}C and ^1H NMR spectra [11] and by analogy with the earlier work of Arnold[12] and Farid.[13] The regiochemistry encountered in the cycloaddition of 1 with styrene (Scheme II) can be rationalized in terms of a stepwise addition to give the most stable diradical intermediate. Cycloadducts 10 and 11 were readily interconverted by heating in benzene at 125 °C. This isomerization involves cleavage of the central bond to give diradical 12, which undergoes ring-flipping followed by subsequent ring closure.[14]

Interestingly, only a single photoadduct is obtained when *trans*-stilbene or methyl cinnamate are used as the trapping agents. Heating the initial photoadduct produces an isomeric product (ca. 1:1 ratio) via the ring-flipping mechanism. The exclusive formation of 13 and 15 from the sensitized irradiation indicates that the photocycloaddition is sensitive to steric factors. The reactants approach each other in a fashion that minimizes steric interactions. Thus, the π-center bearing the R substituent (R = Ph or CO$_2$CH$_3$) attacks the cyclopropene π bond from the least hindered exo face. Coupling of the initially produced diradical will occur so as to give a cycloadduct with the most stable (trans) relationship of the substituent groups. This explanation is perfectly consistent with the exclusive formation of cycloadducts 13 and 15 as well

(8) Satisfactory spectral and analytical data were obtained for each new compound. Complete spectroscopic details will be provided in a later publication.

(9) 4: NMR (CDCl$_3$, 90 MHz) δ 1.63 (s, 6 H), 1.78 (s, 6 H), 3.43 (s, 6 H), 7.18 (m, 10 H). 5: NMR (CDCl$_3$, 90 MHz) δ 1.23 (s, 6 H), 1.51 (s, 6 H), 3.64 (s, 6 H), 7.11 (m, 10 H).

(10) 6: NMR (CDCl$_3$, 90 MHz) δ 1.03 (s, 12 H), 3.23 (s, 6 H), 7.23 (m, 10 H).

(11) 10: NMR (CDCl$_3$, 90 MHz) δ 1.08 (s, 3 H), 1.20 (s, 3 H), 2.16 (dd, 1 H, J = 11.0, 5.0 Hz), 3.12 (dd, 1 H, J = 11.0 Hz), 3.64 (s, 3 H), 3.97 (dd, 1 H, J = 11.0, 5.0 Hz), 6.94–7.57 (m, 10 H). 11: NMR (CDCl$_3$, 90 MHz) δ 1.07 (s, 3 H), 1.53 (s, 3 H), 2.24 (dd, 1 H, J = 12.0, 6.0 Hz), 2.62 (dd, 1 H, J = 12.0, 4.0 Hz), 3.22 (dd, 1 H, J = 6.0, 4.0 Hz), 3.75 (s, 3 H), 6.85–7.17 (m, 10 H). 13 NMR (CDCl$_3$, 90 MHz), δ 1.20 (s, 3 H), 1.30 (s, 3 H), 3.20 (s, 3 H), 3.71 (d, 1 H, J = 5.0 Hz), 4.22 (d, 1 H, J = 5.0 Hz), 7.0–7.9 (m, 15 H). 14 NMR (CDCl$_3$, 90 MHz) δ 1.24 (s, 3 H), 1.27 (s, 3 H), 3.50 (s, 3 H), 3.71 (d, 1 H, J = 5.0 Hz), 4.80 (d, 1 H, J = 5.0 Hz), 7.0–7.9 (m, 15 H). 15 NMR (CDCl$_3$, 90 MHz) δ 1.02 (s, 3 H), 1.20 (s, 3 H), 3.40 (s, 3 H), 3.50 (d, 1 H, J = 5.0 Hz), 3.62 (s, 3 H), 4.36 (d, 1 H, J = 5.0 Hz), 7.0–7.7 (m, 15 H). 16 NMR (CDCl$_3$, 90 MHz) δ 1.22 (s, 3 H), 1.40 (s, 3 H), 3.58 (s, 3 H), 3.61 (s, 3 H)3.81 (d, 1 H, J = 5.0 Hz), 4.22 (d, 1 H, J = 5.0 Hz), 7.10–7.73 (m, 10 H). 18 NMR (CDCl$_3$, 90 MHz) δ 1.40 (s, 6 H), 3.73 (s, 3 H), 3.80 (s, 3 H), 7.0–7.5 (m, 10 H).

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as the isolation of a mixture of stereoisomers (i.e., **10** and **11**) when styrene is used as the trapping agent. Aryl-substituted alkenes are effective substrates, whereas simple or electron deficient olefins fail to react with the electronically excited triplet state. Finally, the triplet-induced photolysis of **1** in the presence of methyl phenylpropiolate was also studied and was found to give cyclopentadiene **18** as the exclusive photoproduct. The formation of **18** is most readily accommodated by a (2 + 2) cycloaddition followed by an electrocyclic ring opening of the initially generated bicyclo[2.1.0]pentene intermediate (see Scheme II).

Further studies on the scope and mechanism of these cycloadditions are in progress and will be reported in due course.

Supplementary Material Available: Structure and table of fractional coordinates for nonhydrogen atoms of 1,4-dicarbomethoxy-2,2-dimethyl-3-phenyl-4-(1′-phenyl-2′-methylprop-1′-enyl)bicyclo[1.1.0]butane (**2**) (9 pages). Ordering information is given on any current masthead page.

Figure 1. Structure of the Mo(S₂C₂(COOCH₃)₂)₃²⁻ anion, showing atom labeling scheme, and the MoS₆C₆ core illustrating the trigonal prismatic geometry. Thermal ellipsoids are drawn by ORTEP (Johnson, C. K., ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) and represent the 50% probability surfaces.

Reaction of MoS₉²⁻ with Bis(carboxymethyl)acetylene. Crystal and Molecular Structure of (Ph₄P)₂Mo[S₂C₂(COOMe)₂]₃: A Trigonal Prismatic Complex with a New Dithiolene Ligand
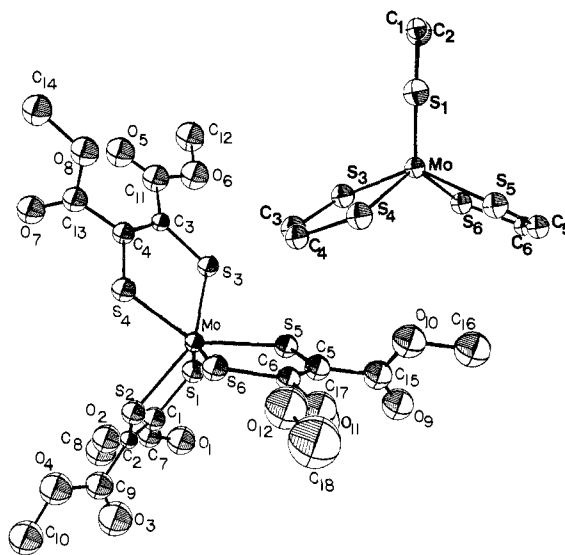
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The hydrodesulfurization of organosulfur compounds in petroleum distillates is catalyzed by alumina-supported "sulfided" molybdenum and cobalt salts.[1] The mechanism of the hydrodesulfurization reaction and the structure of the catalyst are not known; however, it has been proposed that the active sites are located on the molybdenum sulfide surfaces.[2] In the absence of primary information, essential for an understanding of the hydrodesulfurization reaction, we have initiated studies on the reactivity of specific binary Mo–S complexes toward organic molecules that may or may not contain sulfur. Thus far our studies have shown that the (MoS₉)²⁻,[3,4] (Mo₂S₁₀)²⁻,[4,5] and (Mo₂S₁₂)²⁻[4] complexes react readily with CS₂, and two of the isolated, structurally characterized products, [(CS₄)₂MoS]²⁻ and [(CS₄)₂Mo₂S₄]²⁻, contain the S–S chelating perthiocarbonate ligand.[6]

In this communication we report on the reaction of dimethyl 2-butynedioate (DMA) with the [(S₄)₂MoS]²⁻ anion in CH₃CN and on the crystal and molecular structure of one of the products, (Ph₄P)₂[Mo(S₂C₂(COOCH₃)₂)₃]·DMF·C₆H₆ (I; DMF = dimethyl formamide).

The reaction of (Ph₄P)₂[(S₄)₂MoS][6] with excess DMA, under dinitrogen, in warm (50–60 °C) acetonitrile solution proceeds

Table I. Selected Distances and Angles in [Mo(S₂C₂(COOMe)₂)₃]²⁻

	n^a	mean value^b	range
		Bond Lengths (Å)	
Mo–S	6	2.393 (5)	2.385 (6)–2.399 (5)
C–S	6	1.74 (2)	1.72 (2)–1.76 (2)
C=C	3	1.34 (5)	1.28 (2)–1.38 (2)
C–O	6	1.32 (2)	
O–CH₃	6	1.46 (2)	
C=O	6	1.19 (2)	
C–C	6	1.50 (3)	
S–S$_{intra}$^{c}	3	3.09 (2)	
S–S$_{inter}$^{d}	6	3.18 (6)	
		Angles (deg)	
S–Mo–S$_{intra}$^{c}	3	80.5 (5)	80.1 (2)–81.1 (2)
S–Mo–S$_{inter}$^{d} (cis)	6	83 (2)	81.4 (2)–85.9 (2)
S–Mo–S$_{inter}$^{d} (trans)	6	135 (8)	125.0 (3)–143.9 (3)
Mo–S–C	6	109 (1.5)	107.1 (6)–110.9 (6)

^{a} Number of independent measurements. ^{b} The standard deviations of the averages were taken as the larger of the individual standard deviations or the standard deviation from the mean $\sigma = [\Sigma_i^n(x_i^2 - n\bar{x}^2)/(n-1)]^{1/2}$. ^{c} Intraligand. ^{d} Interligand.

readily. Addition of diethyl ether to the green solution results in the deposition of a green solid which can be recrystallized from dimethyl formamide–benzene mixtures. The green crystals retain a molecule of both benzene and DMF of solvation. Anal. Calcd for (Ph₄P)₂Mo[S₂C₂(COOMe)₂]₃·DMF·C₆H₆ (I; C₇₅H₇₁S₆P₂O₁₃NMo): C, 58.71; H, 4.63; S, 12.52; Mo, 6.26. Found: C, 58.50; H, 4.53; S, 12.15; Mo, 6.36. The electronic spectrum of I in CH₂Cl₂ is characterized by absorptions at 650 nm (ε 5800), 450 (sh), and 356 (ε 11 500). In the infrared spectrum, two overlapping bands at 1710 and 1730 cm⁻¹ are assigned tentatively to the C=O stretching vibrations of the ligand and the DMF molecule of solvation respectively.

Single-crystal X-ray diffraction and intensity data on I[7] were collected on a Nicolet P3 automatic diffractometer by using an ω scan technique. The data corrected for Lorentz, polarization, and absorption effects were used for the solution of the structures by direct methods. Refinement by full-matrix least-squares

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(7) Crystal and refinement data for (Ph₄P)₂[Mo(S₂C₂(COOMe)₂)₃]·DMF·C₆H₅: a = 22.907 (14) Å, b = 14.619 (9) Å, c = 43.746 (21) Å, β = 95.34(5)°; space group $C_{2/c}$, z = 8; $2\theta_{max}$ 35° (Mo radiation); $F^2 \geq 3\sigma(F^2)$, 2637 reflections used; 389 parameters.