experimentally.[7,20,21] Figure 1 shows the pertinent region of the gas-phase photoelectron spectra[22] of II and IV and illustrates the "peak-matching" technique used to measure the a_2 IP's given in Table II. At minimum the results in Table II demonstrate that it becomes progressively easier to remove an electron from a localized π orbital of a phenyl group attached to a carbyne carbon as the number of cobalt atoms per carbyne carbon in the cluster increases. Based on our earlier work and the data in Table I, we suggest that these IP's also demonstrate increasing negative charge on the carbyne carbon as the a_2 IP decreases. This suggestion is in accord with the decreasing trend in C–C bond order for I, II, and III as reflected by the measured C–C distances.[4] It is also in accord with Mulliken charge analyses of extended Hückel calculations on I, II, III, and IV.[23] These are given in Table II, where it is seen that there is a smooth increase in the relative carbyne carbon negative charge as the number of cobalt atoms per carbyne carbon increases.[24]

The generally accepted model for coordination of acetylene to a transition metal involves $\pi \rightarrow M$ and $M \rightarrow \pi^*$ charge transfer.[26] A net transfer of electron density either from or to the acetylene ligand will cause an increase in the C–C bond distance (and reduction in bond order) due to either a net depopulation of the bonding π orbital or a net population of the antibonding π^* orbital. The results of this work on I, II, and III demonstrate that for cobalt there is a net back-donation into the π^* orbital of the ligand, which increases as the number of metal atoms to which the acetylene is bound increases. The measurement on IV suggests that the highest negative charge on carbon is achieved by cleaving the C–C bond thereby increasing the proportion of metal nearest neighbors to the carbon. Insofar as the behavior of these clusters model the interactions of acetylene with a metal surface, the results suggest that the fairly facile cleavage of alkynes on metals is due to charge transfer from the metal to carbon,[27] and those sites permitting the greatest number of metal–carbyne carbon interactions will be the most effective in carrying out the cleavage.

The measured work function changes on adsorption of acetylene on various metals are negative and have been interpreted as involving ligand to metal charge transfer.[1,28] However, it has been pointed out that there exist conditions where even the adsorption of an electronegative atom on a metal surface can yield a negative work-function change.[29] Assuming the carbonyl cobalt clusters studied here do model an important aspect of surface bonding, we suggest that acetylene as an admolecule also produces a paradoxical change in the metal work function. Work on related systems is underway, and a complete account of this work will appear elsewhere.

Acknowledgment. The support of the National Science Foundation under Grant CHE 79-15220 is gratefully acknowledged. We thank the University of Notre Dame Computing Center for providing computing time and Professor R. L. DeKock for helpful discussions.

Registry No. I, 536-74-3; II, 12154-91-5; III, 12568-53-5; IV, 20756-47-2; $C_6H_5CH_2CH_3$, 100-41-4; $C_6H_5CH_2NH_2$, 100-46-9; $C_6H_5CH_2OH$, 100-51-6.

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High Optical Yields in a Photochemical Cycloaddition. Lack of Cooperativity as a Clue to Mechanism

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High optical yields in photochemical asymmetric induction through 2 + 2 cycloaddition can be obtained when the conformations leading to chiral products are rigidly enforced. Most commonly such conformations are enforced by maintaining the cycloaddends in a chiral crystal lattice,[1] although optical yields up to 86% have been obtained in solution by enforcing the conformation with an intervening chiral chain connecting the cycloaddends.[2] The extensive π overlap and resulting rigidity apparent in the exciplex of *trans*-stilbene and dimethyl fumarate (**1**), which produces almost exclusively dimethyl μ-truxinate (**2**) despite the greater stability of the all trans isomer dimethyl δ-truxinate (**3**) (see Figure 1),[3] suggested this system as a model in solution for the geometry imposed by the crystal state. Furthermore, the possibility of alternative reaction paths, one involving stepwise bond formation, the other concerted bond formation, made available a further application of the principle of cooperativity in asymmetric induction.[4]

The stereoselectivity of dimethyl μ-truxinate formation requires an intimate relationship between the phenyl groups and carboxyalkyl groups of the cycloaddends (see Figure 2). We reasoned that fumarate derivatives with chiral alcohols as prosthetic groups should exhibit substantial selectivity for one prochiral face of the stilbene excited state, leading to exciplex formation, and that the resulting cycloadduct should exhibit a large enantiomeric excess.[5] In order to test this hypothesis, we synthesized methyl *l*-bornyl fumarate (**4**), di-*l*-bornyl fumarate (**5**),[6] methyl (*R*)-2-methyl-1-butyl fumarate (**6**), and bis((*R*)-2-methyl-1-butyl) fumarate (**7**) and investigated the unsensitized photocycloaddition to stilbene. The resulting cycloadducts were produced in high optical yields, in one case reaching 90–94%.

Irradiations of 0.06 M benzene solutions of *trans*-stilbene in the presence of the optically active esters (0.06 M) were carried out with a 450-W medium-pressure mercury lamp with Corex filter. The reactions were monitored by gas chromatography and

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[6] Methyl *l*-bornyl fumarate, a colorless liquid, was synthesized from *l*-borneol and the monomethyl ester of fumaryl chloride. Di-*l*-bornyl fumarate, mp 106–108 °C, was synthesized from *l*-borneol and fumaryl chloride. Methyl (*R*)-2-methyl-1-butyl fumarate and bis((*R*)-2-methyl-1-butyl) fumarate were similarly prepared as colorless liquids. All new compounds gave satisfactory elemental analyses.

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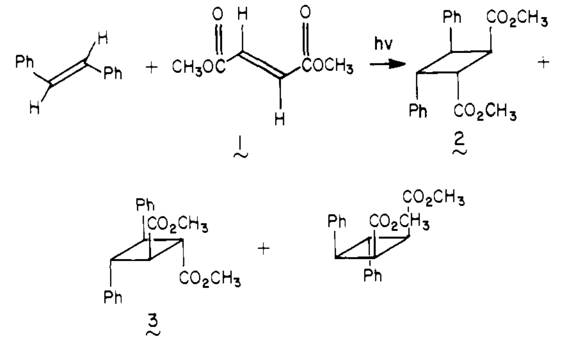

Figure 1. Products of dimethyl fumarate–stilbene cycloaddition.

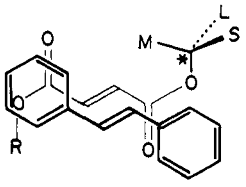

Figure 2. Steric approach of stilbene and dialkyl fumarate.

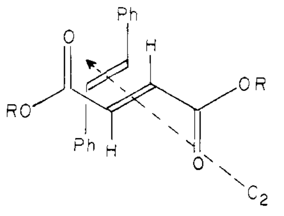

Figure 3. Symmetry of concerted pathway.

stopped at ca. 90% conversion. The rather complex reaction mixture exhibited substantial (>80%) isomerization of stilbene and also significant maleate formation. After solvent removal the resulting esters were hydrolyzed with aqueous hydrochloric acid (1:2), the acidic products removed by washing with base, and the neutralized acids reesterified with methanol under acidic conditions. By this method the cycloadducts were converted to the corresponding dimethyl esters, which were separated by preparative high-pressure liquid chromatography and compared with authentic materials (see Table I).[3,7] The methyl bornyl fumarate produced the μ-truxinate as the major product. The colorless crystals, mp 85–95 °C and $[\alpha_D] = -76.5°$, reached a constant melting point of 89–92 °C and a constant rotation of −85.0° upon further recrystallization from methanol. Thus the initial cycloadduct was produced in 94% enantiomeric excess. For dibornyl fumarate, which produced no μ-truxinate, the major product was the δ-truxinate derivative. This was also a minor product from methyl bornyl fumarate. In both cases isolation by conversion to the dimethyl esters and silica gel chromatography produced oils giving identical rotations of −1.8°, which from literature values indicated an enantiomeric excess of 16%.[8] In contrast, use of the sterically less demanding (*R*)-2-methyl-1-butyl esters **6** and **7** gave both μ- and δ-truxinates, although in greatly reduced optical yield (see Table I). The mixtures were further characterized by using a chiral shift reagent, tris[((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III).[9] Although dimethyl μ-truxinate showed no resolution with this shift reagent, potassium *tert*-butoxide/tetrahydrofuran epimerization yielded the more stable δ-truxinate. Resolution of the enantiomerically distinct methyl groups for this isomer was readily achieved. In this manner all of the optical purities were determined and are listed in Table I.[10]

Table I. Quenching Constants and Yields of Cyclobutane Products

	products, %^{a}				
fumarate	μ-truxinate	δ-truxinate	$k_q\tau$, L mol^{-1}	QY (rel)^c	λ_m (exciplex)^d
1	50 (0.0)	2 (0.0)	8.3^b	1.0	520
5		10 (20.0)	11.3	0.011	500
4	20 (90.4)	5 (20.0)	11.6	0.035	505
7	30 (20.0)	20 (0.0)	12.7		
6	35 (19.5)	5 (0.0)	12.8		

^{a} Enantiomeric excesses, determined by using chiral shift reagent, in parentheses. ^{b} This value compares with the published value of 7.6.^{3b} ^{c} Quantum yield based on *total* cyclobutane products. ^{d} Uncalibrated.

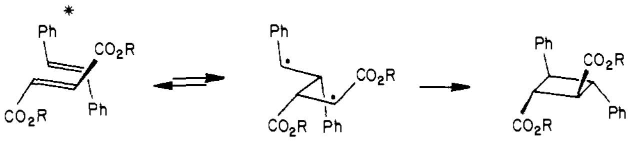

Figure 4. Partition of 1,4-diradical intermediate.

The production of high optical yields in one product but not in the other presents some interesting contrasts. First, the lack of μ-truxinate formation in the case of dibornyl ester cycloaddition is probably a case of steric hindrance. Suppression of μ-truxinate formation is also reflected in a marked decrease in relative quantum yield as a function of increased alkyl substitution (see Table I). Second, the high optical yield from methyl bornyl fumarate cycloaddition to yield μ-truxinate is clearly in accord with experimental and theoretical evidence for a highly ordered exciplex intermediate.[3] The weak emission of the dimethyl fumarate–stilbene exciplex, which can be observed at 520 nm, is remarkably sensitive to substitution of the fumarate and exhibits both a decrease in intensity and a shift to shorter wavelengths upon substitution, indicating less efficient overlap (see Table I). Third, the lack of cooperativity in asymmetric induction for the doubly chiral esters, as evinced by no increase in optical yield of the truxinate derivatives in replacing a methyl group with a second chiral group, is evidence for the existence of asymmetry in the formation of this cycloadduct. Our rationale is as follows. Asymmetric induction is a relative rate effect, and for a photochemical reaction the relative diastereomer ratio will be reflected in the relative quantum yield. From Lewis's model and assumption of irreversible exciplex formation,[3b] the quantum yield for cyclobutane formation is given by

$$\phi = \left(\frac{k_a}{k_a + k_{ed}}\right)\left(\frac{\tau k_e[F]}{1 + \tau k_e[F]}\right)$$

where k_a is the rate of product formation from the exciplex or intermediate, k_{ed} is the rate of decay of the exciplex to ground state, k_e is the rate of exciplex formation, τ is the stilbene singlet lifetime, and [F] is the concentration of fumarate. The degree of asymmetric induction will be reflected by the ratio of two such quantum yields. [F] and τ are independent of the identity or steric approach of the fumarate. The rate of exciplex formation k_e is generally associated with the rate of fluorescence quenching k_q. Least-squares Stern–Volmer treatment of the data obtained from concentration studies of quenching of stilbene fluorescence by the various fumarates used in this study are given in Table I. The $k_q\tau$ values so obtained are similar and reflect quenching at or near diffusion-controlled rates. Thus variations in k_e apparently are not responsible for the induction. The degree of asymmetric induction must be reflected in the partition between product

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(7) We thank Professor F. D. Lewis for a generous gift of dimethyl μ-truxinate.

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(11) Ground-state complexes as intermediates are excluded both on the basis of concentrations used and the occurrence of efficient trans → cis stilbene isomerization, which is inefficient when the complex is irradiated.[3a]

formation k_a and decay of the exciplex k_{ed}. We note that a concerted 2 + 2 mechanism requires a C_2 axis during the course of the cycloaddition, and therefore, the effect on the transition-state energy between the two deactivation pathways will be additive and the effect on the asymmetric induction will be multiplicative. The fact that the additional chiral group leads to no increase in optical yield indicates that only one of the prosthetic groups is involved in the rate-determining step.

Still unanswered is the question of how the partition between decay and product formation is affected by chiral substitution. The most plausible nonconcerted mechanism involves the intervention of a 1,4-biradical either as an exciplex or after its decay to the ground-state energy surface (see Figure 4). We would expect bonding for the methyl bornyl fumarate to occur at the least crowded site of the fumarate moiety, i.e., at the methyl end. This should also lead to the least asymmetric induction, since the chiral group is farther away from the reaction center and decay would be relatively unaffected. In fact the opposite is the case. All the asymmetric induction occurs with the first chiral group. This apparent contradiction is resolved if we equate k_a with the formation of the second bond. Thus asymmetric induction is controlled by the rate at which the 1,4-biradical intermediate progresses to product. As far as we know, this is the first evidence that a biradical or unsymmetrical intermediate can give rise to stereospecific products, a possibility first suggested by Michl several years ago,[12] and is consistent with theories requiring close approach between ground and excited states for efficient decay to ground state.[12,13] Thus we have additional evidence that cooperativity effects can give significant mechanistic information even in the presence of rather complex reaction mixtures.

Acknowledgment. Support by the National Science Foundation through Grant CHE-80-24644 is gratefully acknowledged.

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(12) Michl, J. *Pure Appl. Chem.* **1975**, *41*, 507.

(13) More precisely, k_a competes not with k_{ed} but with that fraction of k_{ed} that involves return to ground state. The results on asymmetric induction, therefore, provide indirect evidence that formation of the 1,4-biradical is in fact the method of deactivation of the exciplex.

Synthesis, Structure, and Properties of $[Co_8S_6(SC_6H_5)_8]^{4-}$ Containing an Octanuclear Co_8S_6 Rhombic Dodecahedron Related to That of Cobalt Pentlandite

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The chemistry of the iron-sulfide-thiolate clusters $[Fe_nS_n(SR)_4]^{2-,3-}$ (n = 2, 4; R = alkyl, aryl) has been developed in considerable detail.[2-8] As yet a comparably extensive chemistry of other discrete homonuclear metal–sulfide–thiolate clusters has not emerged. In particular, attempts to prepare analogous cluster species with other first-transition-series ions, employing corresponding synthetic procedures, have repeatedly failed in our hands. However, the recent syntheses of $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$,[9] $[Fe_6S_8(PEt_3)_6]^{2+}$,[10] and $[Ni_9S_9(PEt_3)_6]^{2+}$ [11] and the presence of recognizable (but nondiscrete) clusters in sulfide minerals[12] are considered to presage a rich chemistry of metal–sulfide clusters having core structural features different from those of $[Fe_nS_n(SR)_4]^{2-,3-}$. For this reason Co(II)/S^{2-}/RS^- reaction systems, among others, are being further explored.

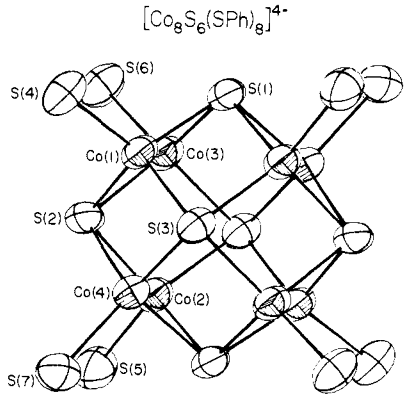

Figure 1. Structure of centrosymmetric $[Co_8S_6(SPh)_8]^{4-}$, with inequivalent atoms labeled, 50% probability ellipsoids given, and phenyl rings omitted.

Table I. Structural Parameters of $[Co_8S_6(SPh)_8]^{4-}$ and Cobalt Pentlandite (Co_9S_8)

dist (Å)/ angle (deg)	$[Co_8S_6(SPh)_8]^{4-}$ anion 1	anion 2	Co_9S_8 ^{a}
Co···Co	2.636 (2)–2.682 (2)	2.634 (2)–2.679 (2)	
	2.662 (16)^b	2.653 (19)^b	2.505 (1)
Co–S	2.214 (3)–2.244 (3)	2.214 (3)–2.236 (3)	
	2.230 (10)^c	2.225 (7)^c	2.227 (1)
Co–S(Ph)	2.228 (3)–2.250 (3)	2.239 (3)–2.246 (3)	
	2.241 (9)^d	2.243 (3)^d	
Co–S–Co^e	72.3–74.1	72.6–74.0	
	73.3^c	73.2^c	68.44 (6)
S–Co–S	105.5–107.6	105.7–107.6	
	106.5^c	106.6^c	111.4 (5)

^{a} Data from ref 21. ^{b} Mean of six values. ^{c} Mean of 12 values. ^{d} Mean of four values. ^{e} Co–Co–Co: anion 1, 89.2–91.1°; anion 2, 89.7–90.5°.

In one Co(II)/S^{2-}/PhS^- system, containing ~1:1:6 mol ratio of reactants in methanol, a copious intractable black solid was formed together with a soluble product, isolable in slight yield as its n-Pr_4N^+ salt. Subsequently a reaction system (eq 1) containing excess methoxide[9] was found to afford the latter product in improved and reproducible yield (10%) after purification.

$$\mathrm{8CoCl_2 + 8Li_2S + 13LiSPh \xrightarrow[MeOH,\ N_2]{16LiOMe} Li_4[Co_8S_6(SPh)_8] + 2Li_2S + 5LiSPh + 16LiCl} \quad (1)$$

Following separation of the usual black precipitate, addition of n-Pr_4NBr to the intense red-brown filtrate and recrystallization of the resultant solid (acetonitrile/ether) gave black air-sensitive crystals of composition $(n\text{-}Pr_4N)_4[Co_8S_6(SPh)_8]\cdot MeCN$.[13] Further experimentation led to reaction 2. Here treatment of

$$\mathrm{2[Co_4(SPh)_{10}]^{2-} + 6HS^- \rightarrow [Co_8S_6(SPh_8)]^{4-} + 6PhS^- + 6PhSH} \quad (2)$$

5 mmol of $(n\text{-}Pr_4N)_2[Co_4(SPh)_{10}]$[14] in 200 mL of acetone with a small excess (20 mmol) of NaHS resulted in separation of microcrystalline $(n\text{-}Pr_4N)_4[Co_8S_6(SPh)_8]$ in 50% yield after several hours.

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