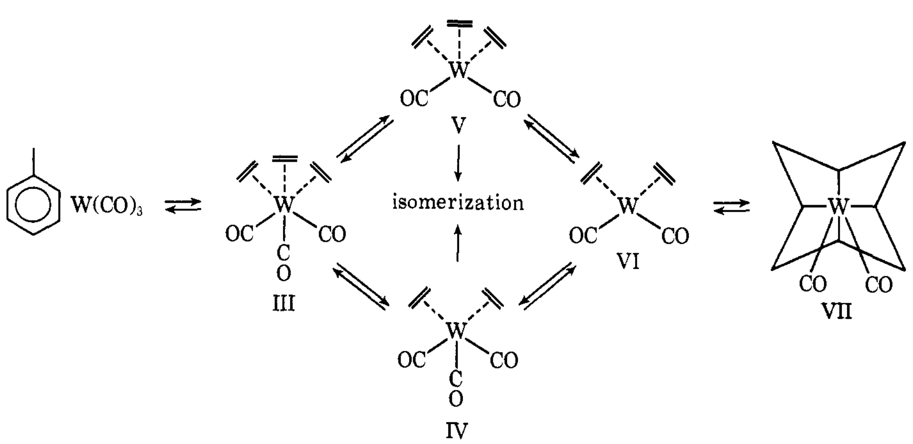

(2)

therefore be proposed (eq 2). Replacement of toluene by olefin generates the trisolefin–W(CO)$_3$ complex III which, upon loss of olefin or CO, would generate the bisolefin–W(CO)$_3$ IV or the trisolefin–W(CO)$_2$ V, respectively. Further loss of olefin from V would provide the bisolefin–W(CO)$_2$ species VI in which the two olefinic ligands can now undergo disproportionation *via* the tetramethylene–W(CO)$_2$ complex VII.

Results of the reaction of 4-nonene with toluene–W(CO)$_3$ under a variety of conditions are listed in Table I. These data are clearly consistent with the scheme depicted in eq 2. The principal features of the data are summarized below.

Table I. Distribution of Products from Reaction of 4-Nonene with Toluenetungsten Tricarbonyl

Conditions[a]	mmol of 4-nonene	% dispropor-tionation[b]	% isomeri-zation[c]
1. Open system	0.258	28	6
2. Closed system[d]	0.258	0	<1
3. Open system, excess olefin	7.00	2	5
4. Closed system, excess olefin	7.00	0	<1
5. Open system, excess toluene[e]	0.258	2	~0

[a] All reactions were conducted for 24 hr at 98° in the presence of 0.070 mmol of toluenetungsten tricarbonyl in 0.95 ml of heptane. The starting nonene was a mixture of cis–trans isomers. [b] The maximum theoretical per cent disproportionation is ~50%. After about 20% conversion, secondary disproportionation products began to appear. [c] Due to the possibility that our vpc column could not separate all the isomers of nonene, the yields of isomerization reported represent minimum yields of isomerization. [d] Results obtained after 17 hr at 98°. After an additional 48 hr at 120°, there was still observed no disproportionation although 33% isomerization was found. [e] Excess toluene (0.48 ml, 4.52 mmol) and less heptane (0.47 ml) were employed.

When 4-nonene is treated with toluene–W(CO)$_3$ in heptane at 98° in an open system, disproportionation of nonene to octenes plus decenes occurs, together with a little isomerization, and both toluene and CO are found in the reaction products (line 1). When the same reaction is conducted in a closed system, thus preventing the escape of CO, no disproportionation of nonene occurs, but isomerization is observed (line 2). Toluene is again produced as a reaction product. The fact that isomerization still proceeds under these conditions is readily accounted for by the scheme shown in eq 2. The pathway available for isomerization of olefins by metal carbonyls involves reversible transformation of a coordinated olefin to a π-allyl metal hydride VIII, eq 3.[10] In proceeding from the olefin to the π-allyl system VIII the number of donor electrons increases by only 2; hence the bisolefin–W(CO)$_2$ species IV can still effect isomerization in the closed system. When the reaction is conducted in an open system (line 3) in the presence of excess nonene the reaction proceeds but leads to a very much increased ratio of isomerization as compared to disproportionation; that is consistent with the formation of the complex V and inhibition of its conversion to VI. When the reaction is conducted in a closed system in the presence of a relatively large excess of nonene, then toluene is liberated but neither disproportionation nor significant isomerization occurs (line 4); this again is in full accord with the equilibria shown in eq 2. These latter conditions favor the formation of the trisolefin–W(CO)$_3$ complex III which of course is not a catalyst for either reaction. The addition of toluene (line 5) also inhibits both isomerization and disproportionation as would be expected from the mechanistic scheme.

(3)

Results analogous to those reported for nonene have been obtained for reactions of 2-pentene, styrene, and 1,7-octadiene.

These data are clearly in accord with the hypothesis that both toluene and carbon monoxide must be removed from the arene–W(CO)$_3$ before two coordinated olefinic molecules are able to undergo disproportionation as required by the scheme outlined in eq 2.

Acknowledgment. We thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support.

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Photochemically Induced Reversible Color Changes in Cholesteric Liquid Crystals

Sir:

The very sensitive dependence of the pitch of cholesteric liquid crystals on weak external physical perturba-

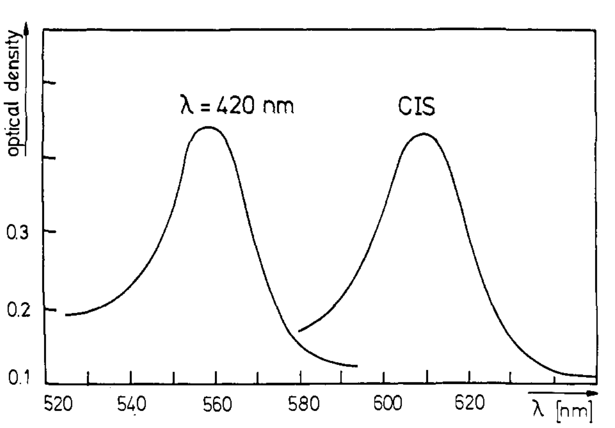

Figure 1. Transmission spectra of an oriented cholesteric mixture of cholesteryl chloride (CC) and cholesteryl nonanoate (CN) (35:65 by weight) containing azobenzene at a concentration of 0.35 *M*. The light beam was directed parallel to the screw axis of the cholesteric phase. The right spectrum with a maximum at λ_{max} 610 nm (cis) was taken with pure *cis*-azobenzene as solute. The left spectrum with λ_{max} 560 (λ 420) is obtained after irradiation of this sample at 420 nm for 3 min.

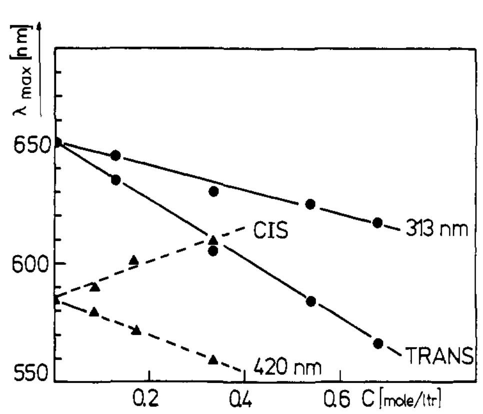

Figure 2. Dependence of the wavelength of maximum reflectivity λ_{max} on the concentration *c* of dissolved azobenzene isomers. The experimental curves denoted by TRANS (——) and CIS (----) were obtained with solutions of pure *trans*- and *cis*-azobenzene, respectively. The straight lines denoted by 313 and 420 nm were obtained from the corresponding solutions of the pure isomers after irradiation with light of 313 and 420 nm in the photostationary equilibrium. The weight ratio CC:CN in the experiments with pure *trans*- (*cis*-) azobenzene was 25:75 (35:65).

tions as temperature, pressure, and electric and magnetic fields has led to a number of technological applications of cholesteric phases as devices for temperature measurement,[1] pressure measurement,[2] and optical display systems.[3,4]

The pitch of cholesteric phases may also be changed by dissolved molecules: Fergason[5,6] reported color changes of cholesteric phases by traces of dissolved gases. Haas, *et al.*,[7] observed color changes of cholesteric phases induced by photochemical decomposition of cholesterol derivatives. The cholesteric–nematic transition induced by mixing two components of opposite twisting power is another example of the sensitive dependence of the pitch on chemical contaminations.[8–10] In this communication, we report on reversible color changes in cholesteric phases induced by photochemical cis–trans isomerization of dissolved molecules.

It is shown that the change of the pitch can be used to determine the composition of mixtures of isomers quantitatively.

Oriented samples of the cholesteric phases were prepared by sandwiching the liquid-crystal solutions between flat quartz plates separated by 20 to 50 μm. The pitch *P* was measured by transmission experiments performed with a Cary spectrometer. The light beam was directed parallel to the screw axis. The wavelength of maximum reflectivity is then given by[11] $\lambda_{max} = 2nP$. The mean refractive index *n* has a value of $n \approx 1.5$ for cholesterol derivatives.[11] Mixtures of cholesteryl chloride (CC) and cholesteryl nonanoate (CN)[12] were used as cholesteric solvent. The components do not absorb above 270 nm and therefore photochemical solvent decomposition[7] can be ruled out. The temperature was kept constant within a range of ±2° during the measurement (at 25°) and thermally induced pitch changes were negligibly small.

trans-Azobenzene was purified chromatographically and the cis isomer was prepared according to Woelm Information No. 13. A trans–cis (cis–trans) conversion can be accomplished by irradiation with light of 313 nm (420 nm).[13]

In Figure 1 the transmission spectra of a 0.35 *M* solution of *cis*-azobenzene in the cholesteric phase is presented and the effect of the irradiation at 420 nm is demonstrated. The wavelength of maximum reflectivity (λ_{max}) changes from 610 to 560 nm after irradiation and a dramatic color change from red to green is observed. In Figure 2 the dependence of λ_{max} on the concentration of pure *cis*- and *trans*-azobenzene is presented, as well as the change of λ_{max} obtained in the photostationary equilibrium (about 3 min of irradiation). It is found (Figure 2) that λ_{max} decreases (increases) linearly with increasing concentration of *trans*- (*cis*-) azobenzene. If $\lambda_{max}{}^{t}$ ($\lambda_{max}{}^{c}$) is the maximally reflected wavelength of a solution of pure *trans*- (*cis*-) azobenzene and $\lambda_{max}{}^{0}$ is the corresponding wavelength of the pure solvent, the following relations hold (c = concentration, *M*)

$$\begin{aligned} \lambda_{max}{}^{t} &= \lambda_{max}{}^{0} + q_t c_t \\ \lambda_{max}{}^{c} &= \lambda_{max}{}^{0} + q_c c_c \end{aligned} \tag{1}$$

q_t and q_c do not depend on the composition of the liquid crystal.

From Figure 2, $q_t = -125$ and $q_c = +75$ (nm l.)/mol are obtained.

If a solution of a pure isomer is irradiated at a definite wavelength, the same photostationary composition is obtained[13] regardless of the intensity and concentration. The observed change of λ_{max} ($\Delta\lambda_{max}$) after irradiation of a solution of a pure isomer is linearly depen-

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dent on the initial concentration c_0 (Figure 2). Therefore, the following relation between the change of $\lambda_{\max}$ and the composition of the isomer mixture can be deduced

$$\Delta\lambda_{\max} = \lambda_{\max} - \lambda_{\max}{}^0 = q_t c_t + q_c(c_0 - c_t) \quad (2)$$

Using eq 2, the composition of a mixture of the two isomers can be determined. Defining y_c as the fraction of the cis isomer, we find $y_c{}^{313} = 0.4$ and $y_c{}^{420} = 0.3$. The corresponding values found by Zimmermann, *et al.*,[13] are $y_c{}^{313} = 0.8$ and $y_c{}^{420} = 0.2$. The last value is in reasonable agreement with our result; the first value, however, is much larger. This discrepancy is most probably due to the large band width of our solution filter.

The cholesteric–isotropic transition temperature T_{iso} depends on the composition of the isomer mixture. A pure 35:65 by weight mixture of CC and CN has a transition temperature of 76°. T_{iso} is lowered to 63 and 50° for 0.27 and 0.54 *M* solutions of *cis*-azobenzene, respectively. However, T_{iso} is lowered to 52 and 35° for the corresponding concentrations of the trans isomer.

By dissolving *trans*-stilbene, $\lambda_{\max}$ increases with increasing concentration (q_t = 200 (nm l.)/mol). A shift of $\lambda_{\max}$ to shorter wavelength is observed when a trans–cis isomerization is induced by irradiation with light of λ 313 nm.

By the method described in this paper, selective uv irradiation produced sharp colored images without decomposing the liquid-crystal solvent. The image formation is reversible.

Since the change of *n* by the solute molecules is very small, it must be concluded that the change of the pitch is due to an intrinsic twisting power[10] of the solute molecules which do not have an asymmetric center.

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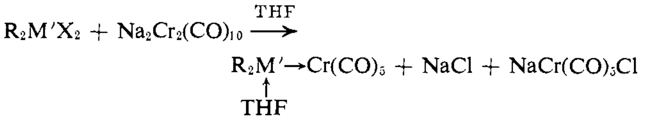
Dialkylgermylene- and -stannylene-Pentacarbonylchromium Complexes

Sir:

A great deal has been learned about chemically interesting, highly reactive molecules by studying their more accessible transition metal complexes.[1] Not only are the chemical and physiochemical properties of the complex informative as to the nature of the highly reactive species, but the complex may also serve as a convenient source for generation of the species. Divalent group IV radicals constitute an area in which there is considerable interest[2] and recently, the coordination compounds of divalent carbon have received much attention.[3] Also, a platinum complex of dichlorosilylene has been reported.[4] We wish to communicate here our synthetic results on pentacarbonylchromium complexes of dialkylgermylenes and -stannylenes,[5] R_2Ge and R_2Sn, and to report some of the more interesting properties of these new complexes. This study represents the first reported synthesis of such coordination compounds.[6] Since these are directly related to pentacarbonylchromium–carbene complexes, which have been subjected to extensive chemical, spectroscopic, and structural examination,[3a,b] they are of special interest for comparative purposes, as part of a homologous series.

The low-temperature (−78°) reaction of $Na_2Cr_2(CO)_{10}$[7] in tetrahydrofuran with dialkylgermanium and -tin dihalides yields pentacarbonylchromium complexes of dialkylgermylenes and -stannylenes.



$$\mathrm{R_2M'X_2 + Na_2Cr_2(CO)_{10} \xrightarrow{THF} \underset{\overset{\uparrow}{THF}}{R_2M'}\rightarrow Cr(CO)_5 + NaCl + NaCr(CO)_5Cl}$$

Ia, R = CH_3; M′ = Ge
b, R = CH_3; M′ = Sn
c, R = *t*-C_4H_9; M′ = Sn

These complexes are isolated by crystallization from hexane solutions at −78° as extremely air-sensitive, pale-yellow, tetrahydrofuran adducts.[8] All attempts to carry out the reaction in noncoordinating solvents or to remove the tetrahydrofuran without decomposition of the complexes have failed. The approximate order of thermal stability of the complexes is Ic > Ib > Ia; only Ic is stable for any length of time at room temperature, hence it has so far proven the most amenable to complete purification and characterization.[9] *Anal.* Calcd for $C_{17}H_{26}O_6CrSn$: C, 41.07; H, 5.28; Cr, 10.46; mol wt, 497. Found: C, 40.98; H, 5.38; Cr, 11.08; mol wt, 475 (cryoscopic in benzene); pale yellow crystals;[10] mp,

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(1) An elegant example is Pettit's study of cyclobutadiene complexes: P. Reeves, T. Devon, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5890 (1969), and references therein.

(2) (a) P. L. Timms, *Prep. Inorg. React.*, **4**, 59 (1968); (b) J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, **4**, 145 (1971); (c) J. D. Donaldson, *Progr. Inorg. Chem.*, 8, 287 (1667); (d) W. H. Atwell and R. D. Weyenberg, *Angew. Chem., Int. Ed. Engl.*, 8, 469 (1969); (e) W. P. Neumann, *ibid.*, 2, 165 (1963); (f) W. P. Neumann and K. Kühlein, *Justus Liebigs Ann. Chem.*, 683, 1 (1965), and references therein; (g) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

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(8) (a) Reactions with dialkylsilicon dihalides yield only $Cr(CO)_6$ as the final hydrocarbon-soluble metal carbonyl product. Reactions with diarylgermanium and -tin dihalides are considerably more complex and will be discussed at a later date. (b) Contamination by unstable THF–$Cr(CO)_5$[8c,d] considerably complicates purification. (c) W. Strohmeier and K. Gerlach, *Chem. Ber.*, **94**, 398 (1961). (d) T. J. Marks, unpublished results.

(9) (a) In refluxing benzene, Ic reacts with triphenylphosphine to produce $(C_6H_5)_3PCr(CO)_5$. (b) The ^{19}Sn Mössbauer spectrum of Ic (IS = 2.11, QS = 4.14 mm/sec; we thank Professor J. J. Zuckerman for this measurement) is quite unlike spectra of Sn(IV)–transition metal compounds[9c] and will be discussed in detail at a later date. (c) J. J. Zuckerman, *Advan. Organometal. Chem.*, **9**, 22 (1970). (d) Though we have not yet obtained complete analytical data for less stable Ib and Ia, the great similarity in spectral properties leads us to believe that Ia, Ib, and Ic have essentially the same structures.

(10) An X-ray study is in progress.