These results clearly confirm the mechanism summarized by eq 2. A similar mechanism was proposed[10] recently for the rearrangement of diphenylcarbene to fluorene on the basis of methyl labeling experiments. Thus, this process may have considerable generality for aromatic carbenes even though highly strained intermediates such as the bicycloheptatrienes **10** are formally invoked. In fact, the results imply that relatively small energy barriers separate phenylcarbene, cycloheptatrienylidene, and bicycloheptatriene isomers.

Acknowledgment. We thank Dr. P. Green for determining the ^{13}C nmr spectra and Dr. E. B. Whipple for helpful discussions of the nmr data.

[9] It is interesting that the mass spectra of labeled styrene and benzocyclobutene both had 55% ^{13}C-enriched C_6H_6 fragments as evidenced by the intensities at *m/e* 78, 79, and 80, even though the parent ions in both cases indicated a 65% enrichment of ^{13}C. The electron-impact induced fragmentation of these molecules to C_6H_6 must occur with randomization of carbon atoms.

[10] J. A. Myers, R. C. Joines, and W. M. Jones, *J. Amer. Chem. Soc.*, **92**, 4740 (1970).

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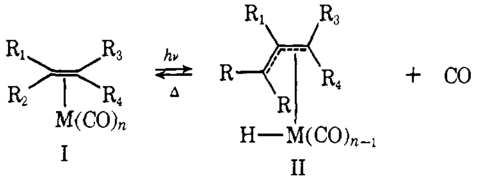
Metal Carbonyl Photoassisted Cis–Trans Isomerization of Stilbene

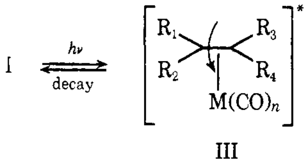
Sir:

Our work[1] and that of others[2,3] has established the fact that irradiation of metal carbonyl–olefin complexes results in reaction of the olefin. However, the nature of the excited intermediates is in doubt. Two extreme possibilitities exist for intermediates responsible for the cis trans isomerization of olefins complexed to metals: (1) the metal π-allyl hydride (II) formed photochemically as in eq 1 may lead to isomerization *via* thermal reversibility or (2) irradiation of I may produce an



(1)

excited state which features relatively free rotation about the olefinic bond as in eq 2. Metal-π-allyl hy-



(2)

dride intermediates have received a great deal of attention,[4–7] especially as metal hydrides are well-known thermal catalysts for olefin isomerizations.[7] Excited intermediates such as III have been proposed to account for ligand photoisomerization in metalloporphyrin complexes.[8,9] In this communication we present a report of $M(CO)_6$-photoassisted isomerization of the stilbenes. The results suggest strongly that an intermediate similar to III is responsible for the cis–trans photoisomerization of olefins complexed to metal carbonyls.

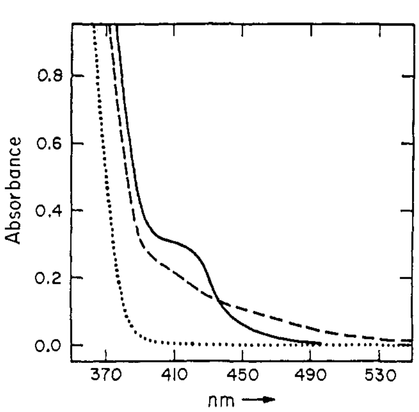


Figure 1. Spectral changes in the uv-visible region due to photochemical formation of $[W(CO)_5(\textit{cis}\text{-stilbene})]$ ( ) and $[W(CO)_5(\textit{trans}\text{-stilbene}]$ (———) from 366-nm irradiation of $(WCO)_6$ (· · ·).

Isomerization of the stilbenes has been observed when solutions of either $W(CO)_6$ or $Mo(CO)_6$ and either *cis*- or *trans*-stilbene are irradiated at 366 nm.[10] Olefin isomerization did not occur in the absence of the metal hexacarbonyl. Spectral changes in the uv-visible region occurred upon irradiation, with the solutions turning a greenish yellow. The spectral changes are illustrated in Figure 1. Partial thermal bleaching of the colored solutions occurred when irradiation was terminated. In the initial stages of the photoreaction no significant changes were detected in the ir spectra, but after prolonged or intense irradiations we noted disappearance of the hexacarbonyl and concomitant appearance of ir bands attributable to metal carbonyl–stilbene compounds.[13] In contrast to the $W(CO)_6$-photoassisted isomerization of the conjugated dienes,[1] the stilbenes can be equilibrated photochemically with either $W(CO)_6$ or $Mo(CO)_6$. In Figure 2 we follow the $W(CO)_6$-photocatalyzed equilibration of *cis*- and *trans*-stilbene, starting with solutions of varying initial stilbene compositions.

To determine whether irradiation of the complex results in the cis–trans isomerization, we irradiated at wavelengths where only the metal carbonyl–stilbene

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[1] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, **92**, 6068 (1970).

[2] W. Jennings and B. Hill, *ibid.*, **92**, 3199 (1970).

[3] E. K. von Gustorf and F. Grevels *Fort. Chem. Forsch.*, **13**, 366 (1969), and references cited therein.

[4] T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

[5] L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, **87**, 5502 (1965).

[6] G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

[7] M. Orchin, *Advan. Catal. Relat. Subj.*, **16**, 1 (1966).

[8] D. G. Whitten, P. D. Wildes, and I. G. Lopp, *J. Amer. Chem. Soc.*, **91**, 3393 (1969).

[9] P. D. Wildes and D. G. Whitten, *ibid.*, **92**, 7609 (1970).

[10] Well-degassed solutions of $\sim 10^{-2}$ *M* stilbene and $\sim 10^{-3}$ *M* $M(CO)_6$ in hydrocarbon solvents were irradiated at 366 nm in a merry-go-round apparatus[11] at room temperature. Light intensity was monitored by benzophenone–piperylene actinometry.[12] Stilbene analysis was by vpc with a 6-ft × 1/8-in. UCW-98 column at 180°. The spectral data were obtained with a Cary 14 spectrometer or with a Perkin-Elmer 225 grating infrared spectrometer.

[11] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

[12] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[13] Metal carbonyl–stilbene complexes have been noted previously: (a) I. W. Stolz, H. Haas, and R. K. Sheline, *J. Amer. Chem. Soc.*, **87**, 716 (1965); (b) G. Drefahl, H. H. Hörhold, and K. Kühne, *Chem. Ber.*, **98**, 1826 (1965); (c) R. Ercoli, F. Calderazzo, and A. Alberola, *Chim. Ind. (Milan)*, **41**, 975 (1959).

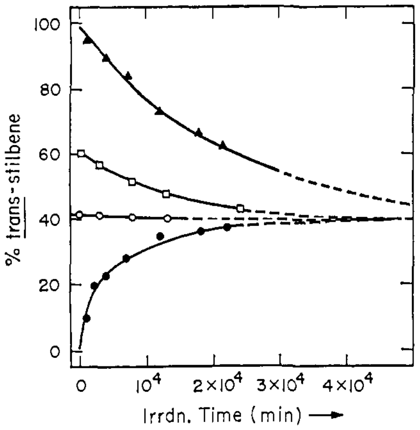


Figure 2. Per cent *trans*-stilbene as a function of 366-nm irradiation time using $W(CO)_6$ as the photocatalyst.

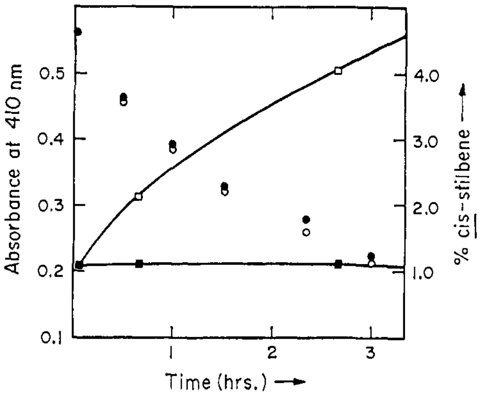


Figure 3. Thermal bleaching of $[W(CO)_5$(*trans*-stilbene)] in irradiated (>380 nm) samples (●) and in nonirradiated samples (○) and concurrent trans → cis isomerization of stilbene in nonirradiated (■) and irradiated (□) tubes.

complex absorbs ($\lambda \geq 380$ nm). Samples were initially irradiated at 366 nm to produce the metal carbonyl–stilbene complex. The disappearance of the complex was followed by uv–visible absorption spectra in the irradiated samples and in samples not irradiated at $\lambda \geq 380$ nm. In Table I we present some representative isomerization data, and Figure 3 shows the bleaching rate for irradiated and nonirradiated tubes. The data clearly show that irradiation of the complex results in isomerization but that the rate of thermal bleaching is virtually unaffected by irradiation. During the thermal bleaching in nonirradiated tubes, no isomerization of the stilbene occurred.[14]

Table I. Irradiation of $[W(CO)_5$ (stilbene)] Using ≥380-nm Light

Time,[a] min, at 366 nm	Time, min, at ≥380 nm	% trans → cis
0	136	0.00
74	0	0.91
74[b]	136	1.35

[a] Time irradiated. [b] This sample was irradiated first at 366 nm to produce the complex and then at ≥380 nm.

In Table II we present observed initial relative rates of isomerization using $Mo(CO)_6$ and $W(CO)_6$. Chromium hexacarbonyl was found to be ineffective in photoassisting the isomerization of stilbene. This metal effect may be rationalized as due to large differences in the ability to bind the olefin and marked differences[15] in the first uv absorption band of the hexacarbonyls. The first uv absorption band has been assigned as a singlet → triplet d–d transition and, as would be expected, its intensity increases dramatically with increasing weight of the central metal.[15] The overall quantum efficiencies for cis–trans isomerizations are of the order of 0.01.

Table II. Observed Initial Relative Rates of Isomerization of the Stilbenes[a]

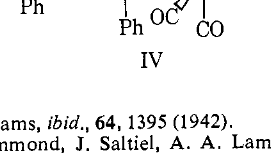
Metal carbonyl	Cis → trans	Trans → cis
$W(CO)_6$	1.000[b]	0.18
$Mo(CO)_6$	0.049	0.073
$Cr(CO)_6$		0.000

[a] 366-nm irradiation, 5.83×10^{-10} einstein/sec. [b] Corresponds to observed quantum efficiency of 0.11.

Qualitatively, *cis*- and *trans*-stilbene behave similarly, but we have noted that solutions containing the cis isomer tend to form multiple-substitution metal carbonyl products under high-intensity irradiation. The uv–visible spectra of $[W(CO)_n$(*cis*-stilbene)] and $[W(CO)_n$(*trans*-stilbene)] are also different (Figure 1). However, starting with either stilbene isomer or with mixtures of both isomers the same trans/cis ratio is found at the photostationary state (Figure 2).

Photoisomerization of the olefins while complexed to the metal followed by olefin–olefin exchange as recently proposed[1] is strongly indicated. Two key factors persuade us to suggest that the most likely intermediate is similar to III. First, stilbene contains no easily abstractable allylic hydrogens to form the metal–π-allyl hydride complex and second, the stationary-state trans/cis ratio is significantly different from the thermodynamic ratio for the stilbenes.[16] The stationary state implicates excited-state intermediates either for the isomerization or for the exchange. We rule out any major contribution from photoexchange, as the bleaching rate is unaffected by irradiation (Figure 3). The photostationary state established using $W(CO)_6$ is close to that obtained using high-energy triplet sensitizers.[17] This resemblance must be fortuitous since clearly both the excitation and decay ratios of the metal–olefin complex will differ from the ratios of the triplet-sensitized case.

We propose that excited-state isomerization proceeds through an intermediate (IV) which is characterized by



IV

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(14) The thermal bleaching process is probably regeneration of the $M(CO)_6$ and is accompanied by thermal exchange of the olefin bound to the complex with the free olefin in the medium.[1]

(15) N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5713 (1968).

(16) R. B. Williams, *ibid.*, **64**, 1395 (1942).

(17) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

a metal–carbon σ bond with free rotation about the olefinic bond. Thermal *cis*- ⟶ *trans*-stilbene isomerization catalyzed by $Fe(CO)_5$ or metal carbonyl thermally catalyzed isomerization of 1,2-dichloroethylene[4] may proceed through a similar intermediate. Very recent work has also implicated the formation of σ-bonded olefins in the thermal decomposition of $(trans\text{-}CF_3\text{-}CH{=}CHCF_3)Fe(CO)_4$ and related compounds.[18] The difference in the photoassisted isomerization is that the isomerizing configuration is achieved *via* electronic excitation by absorption of light. As pointed out above, the transition responsible for the lowest observed uv absorption of the hexacarbonyls has substantial singlet-to-triplet character. Thus the olefin complex may reach a triplet configuration by direct absorption as well as by intersystem crossing from a singlet. The large spin–orbit coupling of the heavy metal atom facilitates intersystem crossing; in fact, in the case of tungsten, spin–orbit effects could be so large that it becomes meaningless to talk about discrete singlet and triplet excited states. Nonradiative decay from the electronic state achieved in absorption may take the form of intramolecular rearrangement leading to intermediate IV with two unpaired electrons and free rotation about the olefinic bond. Decay to yield a metallocyclopropane intermediate (singlet) would not be expected to result in efficient isomerization.

Acknowledgment. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF OSR-71-1958), and the National Science Foundation.

[18] R. Fields, G. L. Godwin, and R. N. Haszeldine, *J. Organometal. Chem.*, 26, C70 (1971), and references cited therein.

[19] National Institutes of Health Trainee.

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New Aquo Ions of Molybdenum

Sir:

The aquo ion $Cr(H_2O)_6^{3+}$, by virtue of its slowness to undergo substitution, has attracted special attention in the past two decades. By contrast, little effort has been devoted to its congener $Mo(H_2O)_6^{3+}$, despite the fact that the higher oxidation states of molybdenum are more stable than those of chromium, and $Mo(H_2O)_6^{3+}$ thus would seem to offer some unusual opportunities for exploring redox behavior. Hartmann and Schmidt[1] purport to have measured the ligand-field spectrum of $Mo(H_2O)_6^{3+}$ in 4 *M* HCl, 4 *M* HBr, and 4 *M* H_2SO_4, and describe the ion as being green. It is difficult to understand why $Mo(H_2O)_6^{3+}$ as a member of the second-row transition series should show strong absorption in the region of 600 nm, and, in view of the results we report here, it appears unlikely that Hartmann and Schmidt were actually dealing with $Mo(H_2O)_6^{3+}$.

When K_3MoCl_6 is dissolved in acidified water, absorption bands are observed initially at 520 (ε 45.3), 416 (61.6), and 308 nm (213). In 6 *M* HCl, the absorption characteristics remain unchanged over a period of 2 days, but when the medium is 1 *M* trifluoromethylsulfonic acid (HTFMS) or 1 *M p*-toluenesulfonic acid (HPTS)[2] the red solution changes to yellow, and after 1.5 days absorption in the visible spectral region has disappeared, but a strong band (ε 6.0 × 10^2) develops at 293 nm.

The solution of Mo(III) in HPTS was placed on a cation-exchange column 50W-X2. Analysis of the liquid which passed through, and of the wash water, showed that more than 5 mol of Cl^- had been set free for each mole of Mo(III). By using 0.5 *M* HPTS, a yellow band was eluted from the column, and with 1 *M* HPTS a second band, lighter in color, was slowly eluted. The solution containing the light yellow species was collected. Analysis showed that the average oxidation state of molybdenum was still 3+, and that the solution was free from Cl^-. The analytical evidence and the elution behavior indicate that we have the ion $Mo(H_2O)_6^{3+}$ in hand. By following the procedure outlined, about 90% of the total molybdenum is obtained as Mo^{3+}. The conclusion that we have the aquo ion is supported by the measurement of the absorption characteristics. There is no significant absorption in the visible, but strong bands appear at 293 (6.0 × 10^2) and 253 nm (7.2 × 10^2) (*cf.* Figure 1.) The same spectrum is obtained if the solution in 1.5 *M* HTMS is kept under argon for 2 days. This indicates that aquation of a dilute solution of $MoCl_6^{3-}$ is virtually complete at equilibrium.

When solutions containing Mo(III) are stored for a time (see below), a green color develops. Earlier efforts[4] to produce $Mo(H_2O)_6^{3+}$ by reduction of Mo(VI) also yielded green solutions. (Those described by Hartmann and Schmidt were obtained by reduction.) It seems likely that the green species is a condensation product of Mo(III).

We turn now to describe a method for the preparation of the aquo ion of Mo(II), which, in contrast to Cr(II), exists in the dimeric form. Attempts to prepare Mo_2^{4+}(aq), reducing $MoCl^{2+}$(aq) by the method[5] which yielded Rh_2^{4+}, were only partially successful. A solution containing $MoCl^{2+}$(aq)[6] and dilute Cr^{2+} shows mainly the color of Cr^{2+}, but turns green after a few days. The same color change takes place even without Cr^{2+}. When EDTA is added to a mixture of $MoCl^{2+}$ and Cr^{2+}, immediate reaction occurs, producing a reddish brown solution and a precipitate of the same color. Taking note of the color, we surmise that some Mo_2^{4+} is formed by this method, but it is clear that the reaction is by no means quantitative. An alternative method (to be described) of preparing Mo_2^{4+} showing promise, we gave up further work attempting to reduce $MoCl^{2+}$(aq). It should be noted that a method for preparing Mo_2^{4+} which is dependent on cation-exchange separation, as is the case with the

[1] H. Hartmann and H. J. Schmidt, *Z. Phys. Chem.* (*Frankfurt am Main*), 11, 234 (1957).

[2] It has been shown[3] that when a solution of $Cr(H_2O)_6^{3+}$ is made 6 *M* in HTFMS, complex formation is negligible. There is no reason to believe that Mo(III) will have a higher affinity for $TFMS^-$ than does Cr(III), and our experience indicates that even with PTS^-, which is expected to be somewhat more nucleophilic than $TFMS^-$, complex formation at the 1 *M* level is negligible.

[3] A. Scott and H. Taube, *Inorg. Chem.*, 10, 62 (1971).

[4] A. B. Hoffman and H. Taube, unpublished observations.

[5] F. Maspero and H. Taube, *J. Amer. Chem. Soc.*, 90, 2361 (1968).

[6] The species $MoCl^{2+}$(aq) is separated by cation exchange from a solution of K_3MoCl_6 in 1 *M* TFMS which had been allowed to aquate for *ca.* 12 hr.