Table VI

orbital		H_{ii}, eV	ζ_1	ζ_2	C_1[a]	C_2[a]
Nb	5s	−10.10	1.89			
	5p	−6.86	1.85			
	4d	−12.10	4.08	1.64	0.6401	0.5516
Cl	3s	−26.30	2.183			
	3p	−14.20	1.733			
P	3s	−18.60	1.750			
	3p	−14.00	1.300			

[a] Coefficients in the double-ζ atomic wavefunction.

best regarded as metallacyclopropenes. Future papers will report the redox and halide substitution chemistry of $[CpMCl_2(CO)_2]_2$.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grants CHE-8305235 and CHE-8619864) for support of this research. J.R. thanks the U.S.-Spanish Joint Comittee for Cultural and Educational Cooperation for a fellowship. We are grateful to Dr. W. M. Butler for assistance with the crystallographic studies.

Appendix

In the EHMO calculations, the parameters (ζ and H_{ii}) used for C and H were standard ones contained in the ICON8 program. Those for Nb, Cl, and P are given in Table VI. The bond distances employed were Nb–C(Cp) = 2.34 Å, Nb–C(alkyne) = 2.10 Å, Nb–Cl = 2.36 Å, C–C(Cp) = 1.43 Å, C–C(alkyne) = 1.30 Å, Nb–P = 2.50 Å, P–H = 1.44 Å, and C–H = 1.10 Å. For $CpNbCl_2(HCCH)$, angles were taken from the structure of **1a**, while for $CpNbCl_2(PH_3)_2$, the pertinent angles are Nb–P–H = 116° and CT–Nb–Cl = CT–Nb–P = 110° (CT = centroid of the Cp ring), and the dihedral angle between all CT–Nb–Cl and CT–Nb–P planes was 45°.

Registry No. 1, 95765-11-0; **1a**, 95784-23-9; **2**, 95784-24-0; **3a**, 120411-06-5; **3b**, 120411-07-6; **3c**, 95765-12-1; **3d**, 120411-08-7; **3e**, 120411-09-8; **4a**, 103148-33-0; **4b**, 103148-32-9; **5**, 112968-60-2; **6**, 120411-10-1; **7a**, 120411-11-2; **7b**, 120411-12-3; **7c**, 120411-13-4; DPPE, 1663-45-2; $CpNbCl_4$, 33114-15-7; $Cp'NbCl_4$, 62927-89-3; $CpTaCl_4$, 62927-98-4; $CpNbCl_2(CO)DPPE$, 112942-54-8; $Cp^*TaCl_2(CO)_2(THF)$, 98688-40-5; $Cp^*TaCl_2(C_4H_6)$, 95251-00-6; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $H_2C{=}CHCOOMe$, 96-33-3; $H_2C{=}CHCOOEt$, 140-88-5; $H_2C{=}CHCOOBu$, 141-32-2; di-*p*-tolylacetylene, 2789-88-0; diphenylacetylene, 501-65-5; 3-hexyne, 928-49-4; acetylene, 74-86-2; *cis*-polyacetylene, 25768-70-1; *trans*-polyacetylene, 25768-71-2; 1,3,5-triphenylbenzene, 612-71-5; 1,2,4-triphenylbenzene, 1165-53-3; trimethylphosphine, 594-09-2.

Supplementary Material Available: Tables VIIS and VIIIS, thermal parameters for **1a** and **3c**, and Tables IXS and XS, bond distances and angles for **1a** and **3c** (4 pages); Tables XIS and XIIS, F_o vs F_c for **1a** and **3c** (15 pages). Ordering information is given on any current masthead page.

Mechanism of the Photochemical Cis–Trans Isomerism of (η^5-C_5Me_5)$Re(CO)_2X_2$ (X = Me, Cl, Br, I)

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Photolysis of *cis*-(η^5-C_5Me_5)$Re(CO)_2Me_2$ leads to the isomerism to *trans*-(η^5-C_5Me_5)$Re(CO)_2Me_2$. The mechanism of this reaction has been studied by FTIR spectroscopy at low temperature. It has been determined that photolysis of *cis*-(η^5-C_5Me_5)$Re(CO)_2Me_2$ at 13 K in methylcyclohexane, methylcyclohexene, or (1,2-epoxyethyl)benzene results in extrusion of a carbonyl ligand and the production of (η^5-C_5Me_5)$Re(CO)Me_2$. This molecule undergoes reaction with the photoproduced CO at 100 K to yield only *trans*-(η^5-C_5Me_5)$Re(CO)_2Me_2$. Photolysis of the trans isomer yields the same unsaturated photoproduct. The mechanism of the photochemically induced cis–trans isomerism for the analogous series of dihalides, *cis*-(η^5-C_5Me_5)$Re(CO)_2X_2$ (X = Cl, Br, I) in (1,2-epoxyethyl)benzene, has also been investigated and found to occur by the same sequence of reactions as described above.

Introduction

We wish to report the results of a study dealing with the mechanism of the photochemical cis–trans isomerism of (η^5-C_5Me_5)$Re(CO)_2X_2$ (X = Me, Cl, Br, I). Our interest in the dimethyl complex was initially to see if the photochemical reaction was CO loss, as expected from various studies of metal carbonyls,[1] or reductive elimination as one may expect from the analogous photoreaction of molecules containing cis one-electron ligands. Reductive elimination has been implicated in the photoreactions of a variety of molecules containing cis one-electron groups, such as (η^5-C_5Me_5)$IrPMe_3H_2$,[2] (η^5-C_5Me_5)$IrPMe_3H(R)$,[2] (η^5-C_4H_4)$Fe(CO)_2H(SiEt_3)$,[3] and (η^5-C_5H_5)$Mn(CO)_2H(SiEt_3)$.[4] It is notable that the latter two undergo reductive elimination of the cis groups rather than CO loss. Photochemical reductive elimination of methyl groups also has some precedent in the literature.[5] Other possible reactions of the metal alkyl groups include radical cleavage[6] and alkyl group transfer to a ring carbon as was observed in the photoreaction of (η^5-C_5Me_5)$Fe(CO)_2R$ (R = Me, benzyl).[7] This last example is interesting in that the photoreaction of the alkyl group occurred in competition with CO loss.

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(3) Hill, R. H.; Wrighton, M. S. *Organometallics* **1985**, *4*, 413.

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In contrast, preliminary studies indicated that room-temperature photolysis of *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ led to the production of *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ and (η^5-C_5Me_5)Re$(CO)_3$. At lower temperatures, the cis–trans isomerism is the sole detectable reaction. This result prompted us to study the cis–trans isomerism in more detail for the following reason.

In an earlier synthetic study[8] the molecules (η^5-C_5Me_5)Re$(CO)_2X_2$ (X = Cl, Br, I) were prepared and shown to undergo photochemical cis–trans isomerism according to eq 1. Interestingly it was noted that when

$$cis\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2 \xrightarrow{h\nu} trans\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2 \quad (1)$$

cis-(η^5-C_5Me_5)Re$(CO)_2I_2$ was irradiated in a chlorinated solvent, the product was primarily *trans*-(η^5-C_5Me_5)Re$(CO)_2Cl_2$. This seemed to indicate that the mechanism of the isomerism involved photochemistry resulting in halogen loss. There is some precedent for halogen loss being responsible for the reactivity of transition-metal halides.[9] For example, the trans–cis isomerism of Pt$(PEt_3)_2$PhCl is reported to occur via photochemical chloride loss.[10] Although this seemed reasonable for the dihalides, such a mechanism did not seem likely for the dimethyl complex where an analogous sequence would result in methyl radicals.

The following work was undertaken to determine the primary photoprocess for the isomerism and to investigate the origin of its unidirectional nature. We have studied both the dimethyl complex and the series of halides in order to determine if the mechanism for the isomerism in these complexes is similar or if they react through different pathways.

Results

Irradiation of methylcyclohexene solutions of *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ at room temperature leads to loss of FTIR absorptions due to the starting complex and the production of (η^5-C_5Me_5)Re$(CO)_3$, as evidenced by FTIR absorptions at 2011 and 1919 cm^{-1}, and *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ as indicated by its FTIR absorptions at 1994 and 1919 cm^{-1}. At longer photolysis times an absorption due to a new dicarbonyl appears at 1948 and 1876 cm^{-1}. The new dicarbonyl is complexed to the olefin solvent and is formulated as (η^5-C_5Me_5)Re$(CO)_2$(η^2-4-methyl-1-cyclohexene).[11] This product, which only appears after (η^5-C_5Me_5)Re$(CO)_3$ is produced, is probably a result of photolysis of the tricarbonyl. Evidence for this interpretation is obtained by photolysis of 4-methyl-1-cyclohexene solutions containing (η^5-C_5Me_5)Re$(CO)_3$. The only observed photoreaction is the conversion of (η^5-C_5Me_5)Re$(CO)_3$ to (η^5-C_5Me_5)Re$(CO)_2$(η^2-4-methyl-1-cyclohexene). At lower temperatures the photoreaction of *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ proceeds without the production of the tricarbonyl: at 100 K in a 4-methyl-1-cyclohexene glass the cis–trans isomerism is clean, by FTIR, the only observable product being *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$.

The product *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ is assigned a trans stereochemistry on the basis of the relative intensity of the symmetric and antisymmetric IR bands. The ratio I_{asymm}/I_{symm} is given by $\tan^2 \theta$.[12] For trans isomers the higher energy symmetric band is less intense and the angle C–Re–C is calculated from this as 113°. For the cis isomer the angle is calculated as 86°. For *trans*-(η^5-C_5Me_5)Re$(CO)_2Br_2$, where a similar calculation resulted in a predicted angle of 115°, the X-ray crystal structure yielded a value of 104°.[8]

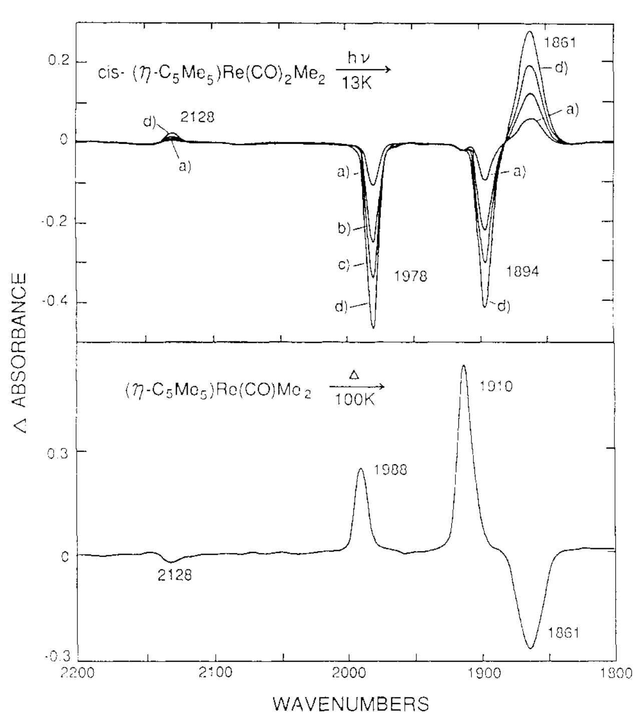

Figure 1. Top: infrared spectral changes accompanying UV photolysis of *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ at 13 K in a 4-methyl-1-cyclohexene glass. The negative peaks at 1978 and 1894 cm^{-1} are due to loss of *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$: the positive peak at 2128 cm^{-1} is associated with the production of free CO and the positive peak at 1861 cm^{-1} is due to (η^5-C_5Me_5)Re(CO)Me_2. Photolysis times are (a) 5 s, (b) 10 s, (c) 25 s, and (d) 85 s. Bottom: FTIR spectral changes associated with warming photoproduced (η^5-C_5Me_5)Re(CO)Me_2 from 13 to 100 K in 4-methyl-1-cyclohexene glass. The positive peaks at 1988 and 1910 cm^{-1} are due to production of *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$; the negative peaks are assigned as above.

Although no intermediate was observed upon monitoring the FTIR spectral changes following photolysis at 100 K an intermediate can be generated in sufficient concentration to observe at lower temperatures. Photolysis of cis-(η^5-C_5Me_5)Re$(CO)_2Me_2$ at 13 K leads to the changes in the FTIR spectra as shown in Figure 1. Loss of FTIR absorptions due to the starting complex at 1978 and 1894 cm^{-1} occurs upon photolysis. The production of two new absorptions at 2128 and 1861 cm^{-1} is observed and found to occur proportionately to the loss of intensity associated with *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$. The absorption at 2128 cm^{-1} is due to the production of free CO in the glass. The other absorption is logically due to the CO loss product (η^5-C_5Me_5)Re(CO)Me_2. This assignment is consistent with the observed single absorption band, as expected for a monocarbonyl, and also with the subsequent chemistry of this photoproduct.

Upon warming the glass containing (η^5-C_5Me_5)Re(CO)Me_2 to 100 K, absorptions due to CO and the unsaturated complex are lost and new absorptions appear at 1988 and 1910 cm^{-1} as shown in Figure 1. These are the IR bands of *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$. Although some

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Table I. FTIR and UV-Vis Spectral Data for Relevant Complexes

complex	$\nu(CO)$,[a] cm^{-1} (rel intensity)	UV-vis,[d] nm (ϵ, M^{-1} cm^{-1})
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$	1978 (1.1), 1894 (1.0)[b]	340 (500)[e]
$(\eta^5\text{-}C_5Me_5)Re(CO)Me_2$	1861[b]	
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$	1988 (1.0), 1910 (2.2)[b]	320 (400 sh)
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$	1968 (1.2), 1879 (1.0)	
$(\eta^5\text{-}C_5Me_5)Re(CO)Me_2$	1840	
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$	1976 (1.0), 1892 (2.3)	
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$	1982 (1.2), 1900 (1.0)[c]	
$(\eta^5\text{-}C_5Me_5)Re(CO)Me_2$	1864[c]	
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$	1992 (1.0), 1918 (2.2)[c]	
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Cl_2$	2032 (1.3, 1953 (1.0)	344 (380), 403 (360), 470 (170 sh)
$(\eta^5\text{-}C_5Me_5)Re(CO)Cl_2$	1912	
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Cl_2$	2048 (1.0), 1966 (2.2)	386 (390), 460 (130 sh)
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Br_2$	2028 (1.5), 1953 (1.0)	340 sh (1200), 426 (710)
$(\eta^5\text{-}C_5Me_5)Re(CO)Br_2$	1910	
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Br_2$	2039 (1.0), 1963 (2.5)	401 (770)
cis-$(\eta^5\text{-}C_5Me_5)Re(CO)_2I_2$	2017 (1.6), 1947 (1.0)	368 (1040), 486 (550)
$(\eta^5\text{-}C_5Me_5)Re(CO)I_2$	1905	
trans-$(\eta^5\text{-}C_5Me_5)Re(CO)_2I_2$	2020 (1.0), 1951 (2.7)	365 (1290), 484 (360)

[a] All data recorded of glasses at 13 K. The solvent is (1.2-epoxyethyl)benzene unless otherwise noted. [b] Solvent 4-methyl-1-cyclohexene. [c] Solvent methylcyclohexane. [d] Data are all from room-temperature solutions in benzene unless noted otherwise. In addition to the bands listed all complexes exhibit higher energy charge-transfer bands at ~280 nm. [e] Toluene solution.

decomposition occurs at room temperature making the measurement of extinction coefficients difficult, the reaction does appear to be quantitative at low temperature since all the CO produced in the photolysis is subsequently consumed upon warming, without the production of any tricarbonyl species.

It is this reaction, to produce the *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$, which confirms the assignment of the intermediate as a simple CO loss product. If, upon photolysis, in addition to CO loss the methyl groups were lost, the result of this intermediate reacting with CO would not produce the trans isomer. The intermediate generated must retain the other portions of its coordination sphere and is hence $(\eta^5\text{-}C_5Me_5)Re(CO)Me_2$.

The above procedure was repeated by using methylcyclohexane as the solvent. The results were essentially the same; FTIR absorptions are given in Table I. Unfortunately, due to low solubility of *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ in this solvent and poor optical characteristics, we were unable to affirm, on the basis of our data, that no *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ was formed upon warming. In addition we cannot affirm with any accuracy that all the CO is consumed in the back-reaction at 100 K. We can however confirm that all the $(\eta^5\text{-}C_5Me_5)Re(CO)Me_2$ is consumed and that tricarbonyl is not produced. This is most consistent with an efficient back reaction process occurring.

Unfortunately, *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ (X = Cl, Br, I) are only sparingly soluble in either methylcyclohexane or 4-methyl-1-cyclohexene making their study in these solvents not feasible. The most soluble derivative was the iodine complex, but upon cooling 4-methyl-1-cyclohexene solutions containing *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2I_2$ the FTIR indicated that it had precipitated before reaching temperatures sufficiently low to observe an intermediate. The experiments were hence conducted in (1,2-epoxyethyl)benzene for the halogen complexes *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ (X = Cl, Br, I). This solvent forms a glass, optically transparent at temperatures as low as 13 K, and appears to be inert toward many unsaturated organometallic complexes.[13] In order to facilitate a comparison of the reaction of the dihalides with that of the dimethyl complex, a more complete study of the photochemistry of $(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ was conducted in this solvent.

A (1,2-epoxyethyl)benzene solution of *cis*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$ was prepared and cooled to 13 K. Photolysis at 13 K led to the production of a monocarbonyl species and free CO. Relevant FTIR absorptions are given in Table I. Warming to 100 K caused reaction of the photogenerated intermediate with the CO producing *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2$. As in the experiment conducted in 4-methyl-1-cyclohexene all of the CO produced by photolysis at 13 K was consumed in the reaction at 100 K. The sample was also photolyzed with the wavelength region 320–400 nm. In this region only d–d absorption occurs (see Table I for electronic spectral data). No difference in behavior was noted (the photolysis times required were longer using this filter).

A similar photolysis of the trans isomer was conducted. Once again CO was lost to produce the unsaturated species. This was confirmed to be the same as that produced by the cis on the basis of both its identical IR absorption and its reactivity upon warming. Only the trans isomer was produced in the back-reaction with CO. Using unfiltered output of the lamp this reaction was not observable on the same time scale as CO loss from the cis isomer. However, if we use the wavelength range 320–400 nm, the efficiency of the reaction is comparable to CO loss from the cis.[14]

The d–d transitions at room temperature show maxima at 340 nm in the cis complex. At ~290 nm the absorption edge of the charge-transfer bands obscures higher energy d–d transitions. In the trans complex the d–d absorption is observed only as a shoulder to the more intense charge-transfer transitions. This qualitative ordering is expected to be followed at low temperature in (1,2-epoxyethyl)benzene. Using the 320–400 nm wavelength range allows us to irradiate in a region where both isomers display d–d absorbance, and under these conditions the sensitivity is approximately the same. If we utilize the unfiltered light, the trans isomer is less sensitive since its d–d absorption band overlaps to a much greater extent with the higher energy charge-transfer absorptions.

The above sequence of experiments were repeated for the other complexes *cis*- and *trans*-$(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2$ (X = Cl, Br, I). The results were qualitatively the same; FTIR absorption bands for these complexes are given in Table I, and Figure 2 shows the spectral changes for the

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(13) We have found photolysis of a number of complexes in this solvent lead to the production of a simple CO loss species. In each case no reaction of the epoxide ring was apparent.

(14) We are indebted to a referee for suggesting that we use wavelength selective photolysis.

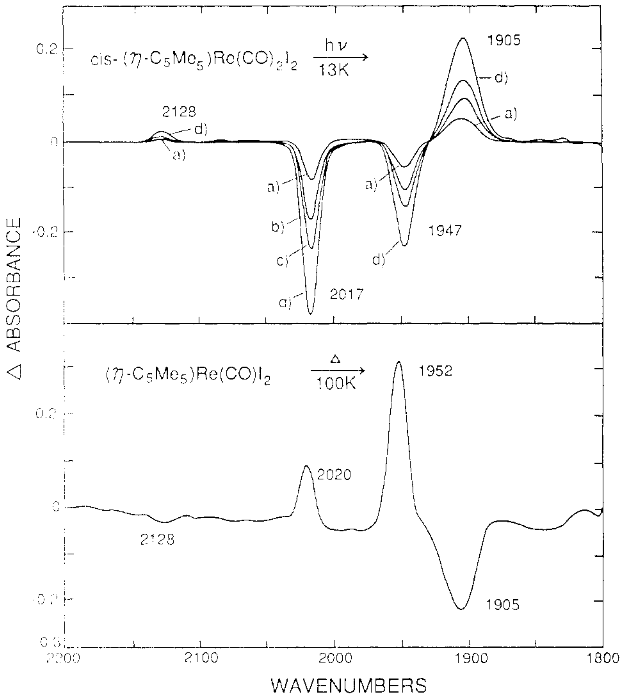

Figure 2. Top: infrared spectral changes accompanying UV photolysis of *cis*-(η^5-C_5Me_5)Re$(CO)_2I_2$ at 13 K in a (1,2-epoxyethyl)benzene glass. The negative peaks at 2017 and 1947 cm^{-1} are due to loss of *cis*-(η^5-C_5Me_5)Re$(CO)_2I_2$: the positive peak at 2128 cm^{-1} is associated with the production of free CO and the positive peak at 1905 cm^{-1} is due to (η^5-C_5Me_5)Re(CO)I_2. Photolysis times are (a) 5 s, (b) 15 s, (c) 25 s, and (d) 145 s. Bottom: FTIR spectral changes associated with warming photoproduced (η^5-C_5Me_5)Re(CO)I_2 from 13 to 100 K. The positive peaks at 2020 and 1952 cm^{-1} are due to production of *trans*-(η^5-C_5Me_5)Re$(CO)_2I_2$; the negative peaks are assigned as above.

cis diiodide derivative. Irradiation at 13 K resulted in loss of CO from the coordination sphere and the production of (η^5-C_5Me_5)Re(CO)X_2 (X = Cl, Br, I) and free CO in the matrix. When the resultant glass was warmed to 100 K, bands due to the unsaturated species and free CO were lost and those due to *trans*-(η^5-C_5Me_5)Re$(CO)_2X_2$ (X = Cl, Br) were produced. Once again use of different irradiation wavelengths (in this case pass λ = 320–400 nm, pass $\lambda >$ 380 nm, and pass $\lambda >$ 310 nm) to irradiate only the d–d transitions did not affect the course of the reaction. For these complexes both the cis and trans isomers exhibit well-resolved d–d absorptions at lower energy than the charge-transfer bands.

Discussion

Previous studies of the photochemistry of *cis*-(η^5-C_5Me_5)Re$(CO)_2X_2$ (X = Cl, Br, I) indicated that they underwent cis–trans isomerism. Here we find that the related complex *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ also undergoes photochemical cis–trans isomerism according to eq 2. At low temperature the reaction is near quantitative. The reaction is unidirectional as the *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ does not produce the cis isomer, at least not at temperatures at or below 100 K.

$$cis\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2 \xrightarrow{h\nu} trans\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2Me_2 \quad (2)$$

At low temperatures the reaction is quantitative; however, at ambient temperatures some production of (η^5-C_5Me_5)Re$(CO)_3$, and its photoproducts, occurs. The tricarbonyl complex is presumably produced via a reaction of the photogenerated unsaturated species with starting complex leading eventually to (η^5-C_5Me_5)Re$(CO)_3$.

The primary photoprocess for the complexes *cis*- and *trans*-(η^5-C_5Me_5)Re$(CO)_2X_2$ is CO loss to generate the unsaturated complexes (η^5-C_5Me_5)Re(CO)X_2 (X = Me, Cl, Br, I) according to eq 3. In each case the observed reaction

$$(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2 \xrightarrow{h\nu} CO + (\eta^5\text{-}C_5Me_5)Re(CO)X_2 \quad (3)$$

$$X = Me, Cl, Br, I$$

is independent of irradiation wavelength. No differences in reactivity were observed if only the ligand field transitions (Table I) were irradiated compared with irradiation of both ligand field and charge-transfer states, although the apparent photosensitivity increased in all cases except *trans*-(η^5-C_5Me_5)Re$(CO)_2Me_2$. This is consistent with efficient relaxation to ligand field excited states occurring in these molecules. The unsaturated photoproducts do not appear to be coordinated by the glass. One way in which the extent of coordination may be assessed is to observe the changes in absorption band position upon changing solvents. If we look at the absorption frequency of (η^5-C_5Me_5)Re(CO)Me_2, it shifts from 1861 to 1840 cm^{-1} upon changing the solvent from 4-methyl-1-cyclohexene to 1,2-epoxyethylbenzene. The absorption position in the noncoordinating solvent methylcyclohexene is 1864 cm^{-1}. The similarity between absorption frequency in methylcyclohexane and 4-methyl-1-cyclohexene indicates that the olefin does not coordinate to the CO loss product. The shift observed upon using the epoxide as solvent compared with methylcyclohexane, 24 cm^{-1}, is, however, quite substantial. It should be noted that the absorption bands of *cis*-(η^5-C_5Me_5)Re$(CO)_2Me_2$ are 1982 and 1900 cm^{-1} in methylcyclohexane and 1968 and 1879 cm^{-1} in (1,2-epoxyethyl)benzene, a shift of 14 cm^{-1} for the symmetric and 21 cm^{-1} for the antisymmetric vibrations. The shift of absorption frequency of the CO loss product is only marginally larger than the shift observed for the coordinatively saturated starting complex. We conclude that any interaction between the unsaturated complex and solvent is very weak and that (η^5-C_5Me_5)Re(CO)Me_2 is best considered a coordinatively unsaturated molecule in all of the three solvents utilized in this study.

The dihalides *cis*-(η^5-C_5Me_5)Re$(CO)_2X_2$ (X = Cl, Br, I) are less soluble in hydrocarbon solvent, and we have been unable to prepare their CO loss product in either methylcyclohexane or 4-methyl-1-hexene. This precludes an analysis similar to above; however, we can compare the difference in frequency between the saturated complexes and their CO loss product in (1,2-epoxyethyl)benzene. It is notable that the CO loss product of each of the halides (η^5-C_5Me_5)Re(CO)X_2 (X = Cl, Br, I) absorbs 80 cm^{-1} lower than average band positions of the starting complex. This shift is similar to the frequency difference of 83 cm^{-1} between the average band position of *cis*-(η^5-C_5Me_5)$(CO)_2Me_2$ and the absorption band of (η^5-C_5Me_5)Re(CO)Me_2 in (1,2-epoxyethyl)benzene. On the basis of this similarity, we belive that the CO loss products of the dihalide complexes are also best considered as unsaturated species.

On warming the glass containing (η^5-C_5Me_5)Re(CO)X_2 and free CO, reaction occurs to produce the trans isomer according to eq 4. In each case only the trans isomer and

$$(\eta^5\text{-}C_5Me_5)Re(CO)X_2 + CO \rightarrow trans\text{-}(\eta^5\text{-}C_5Me_5)Re(CO)_2X_2 \quad (4)$$

none of the cis isomer is formed in the thermal back-reaction. The reason for the specific attack trans to the coordinated CO is not obvious.

In each case all the photoproduced carbon monoxide formed in the photolysis at 13 K is consumed in reaction

4. Since no detectable amounts of other products are formed, the reactions must be essentially quantitative.

It should be noted that the occurrence of back-reaction at 100 K is probably not indicative of the energetics of CO interacting with the unsaturated fragments. Since all the complexes (η^5-C_5Me_5)Re(CO)X_2 react with CO at ~100 K, it is probably a reflection of the rate of CO diffusion through the glass. A careful examination of the warmup of (η^5-C_5Me_5)Re(CO)Me_2 in 4-methyl-1-cyclohexene indicated that although the bulk of recombination with CO occurred at 100 K, the back-reaction with CO is observable, to a small extent, at temperatures as low as 20 K. This probably is due to reaction of molecules which have free CO occupying the same solvation sphere. In this case the rate of reaction would be affected by either the rate of rotational motion in the glass or possibly the true energetics of the back-reaction. At these lower temperatures the CO cannot diffuse; hence molecules with no CO in the primary coordination sphere will not react. At 100 K the glass is less rigid allowing the CO to diffuse and hence react with (η^5-C_5Me_5)Re(CO)X_2. The fact that some reactivity is observed at 20 K does support our supposition that the CO loss product (η^5-C_5Me_5)Re(CO)Me_2 is truly a coordinatively unsaturated molecule.

The photochemistry of the trans isomers is the same, CO loss to generate the unsaturated species. Since this reacts with CO upon warming to generate only the trans isomer, no net photochemistry is observed. The trans isomers appear to be less photosensitive. This is at least in part a result of the higher energy of the d–d absorption bands of the trans isomers. In the case of the dimethyl complex this d–d transition is largely hidden by the charge-transfer absorptions.

The overall cis–trans isomerism for all the complexes studied here occurs by the same process: Initial CO loss to generate the unsaturated intermediate followed by reaction of this intermediate to produce only the trans product. The trans isomer when photolyzed leads to the same intermediate and hence does not undergo a trans to cis isomerism. The observation noted earlier that *cis*-(η^5-C_5Me_5)Re(CO)$_2I_2$ when photolyzed in chlorinated solvents produces *trans*-(η^5-C_5Me_5)Re(CO)$_2Cl_2$ must not be a result of the simple isomerism. This product must arise from either a concurrent exchange process or subsequent reactivity of the trans isomer at room temperature. It must be remembered that the experiments conducted here, at low temperature, in a glass, may tend to suppress radical processes (due to the extremely low activation energy for back-reaction of the photoproduced radicals). We therefore cannot rule out the possibility that homolytic cleavage may be an important process at room temperature in fluid solution.

Experimental Section

The complexes *cis*-(η^5-C_5Me_5)Re(CO)$_2Me_2$ and (η^5-C_5Me_5)Re(CO)$_2X_2$ were obtained from the laboratories of D. Sutton and A. H. Klahn-Oliva but may be prepared by known procedures.[8,15,16] FTIR spectra were obtained with a Bruker IFS 85 spectrophotometer. The samples were cooled in CaF_2 IR cells using a CTI-Cryogenics Model 22 cryocooler and a 350R compressor system equipped with a Lake Shore Cryotronics DRC 80C temperature controller. The temperature was monitored with a Lake Shore Cryotronics silicon diode sensor (DT500 DRC). The solvents methylcyclohexane, 4-methyl-1-cyclohexene, and (1,2-epoxyethyl)benzene were obtained from Aldrich and used without further purification.

The light source used was a 100-W Hg lamp filtered in each case with H_2O (1-cm path length) contained in quartz. In addition other filters used were Corning 7-51 (pass λ = 320–400 nm), 3-75 (pass $\lambda > 380$ nm), and 0-54 (pass $\lambda > 310$ nm).

Low-Temperature Photolysis. Several experiments were done by the following procedure. A solution of *cis*-(η^5-C_5Me_5)-Re(CO)$_2Me_2$ was prepared such that the optical density of the most intense absorption due to the CO ligands was between 0.3 and 1. This solution was loaded into CaF_2-faced FTIR cells and cooled with the cryocooler to a temperature of 13 K and allowed to equilibrate. The FTIR spectra were then obtained in the region from 2200 to 1700 cm^{-1}. The sample was removed from the optical bench and irradiated with the water-filtered output of a 100-W high-pressure Hg lamp for 5 s. The cold head and sample were subsequently reinserted into the optical bench and the FTIR spectra obtained. This was repeated until no appreciable change in the FTIR spectrum was observed upon further irradiation. The sample was then heated and FTIR spectra obtained at 10 K intervals until 100 K where a change in the spectrum had occurred. The sample was thermostated at 100 K and FTIR spectra obtained until no further change occurred (Figure 2). The temperature of the sample was raised to 298 K and its FTIR spectra obtained. This sample, which now contained predominately trans-(η^5-C_5Me_5)Re(CO)$_2Me_2$, was again cooled to 13 K and its FTIR spectrum obtained.

Similar experiments were conducted in the other solvents and with the halides in (1,2-epoxyethyl)benzene. In (1,2-epoxyethyl)benzene the experiments were done by using different optical filters to determine the effect of wavelength on the reaction.

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(15) Diaz, G.; Klahn-Oliva, A. H.; Manzur, C. *Polyhedron* **1988**, *7*, 2743.

(16) The complex *cis*-(η^5-C_5Me_5)Re(CO)$_2Me_2$ is prepared via methylation of the dihalide: Klahn-Oliva, A. H.; Manzur, C., manuscript in preparation.