Photochemical *cis*−*trans* Isomerization of *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ and the Molecular Structure of *trans*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$

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Visible irradiation of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ results in an efficient conversion to the *trans* isomer as confirmed by NMR, room-temperature UV−vis spectroscopy, and low-temperature matrix isolation studies. Laser flash photolysis of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ at 355 nm forms a solvated dicarbonyl species, (η^6-1,2-diphenylethene)Cr(CO)$_2$. Matrix isolation studies confirm that *cis* to *trans* isomerization occurs under low-energy irradiation ($\lambda_{exc} > 400$ nm), while photolysis with $\lambda_{exc} = 313$ nm is required to induce CO loss. Time-dependent density functional theory (TDDFT) calculations predict wavelength-dependent photochemical *cis* to *trans* isomerization for low-energy ($\lambda_{exc} > 400$ nm) irradiation, while high-energy irradiation ($\lambda_{exc} > 300$ nm) populates excited states that are labile to CO loss.

Introduction

The primary step in visual perception involves the *cis* to *trans* photoisomerization of unsaturated centers in the retinal chromophore.[1] Consequently, photoisomerization of alkenes has been extensively studied as model compounds in such systems. In addition photoisomerization processes such as these have applications in molecular switches, unidirectional molecular motors, and optical information storage devices.[2] In the studies of photochemically induced isomerizations, 1,2-diphenylethene has acquired the status of a prototypical system, with over 150 papers describing its photochemical properties.

The proposed pathway for photoisomerization in 1,2-diphenylethene proceeds via population of the $^1\pi-\pi^*$ state, or alternatively the more reactive $^3\pi-\pi^*$ state can be populated using triplet sensitizers.[3,4] In addition, the photochemistry of 1,2-diphenylethene exhibits wavelength dependency. Irradiation of *trans*-1,2-diphenylethene at 313 nm results in the generation of a photostationary state dominated (90%) by the *cis* isomer.[5] This isomerization occurs via a nonplanar transition state. The formation of the *cis* isomer is explained by nonbonding interactions between the two phenyl rings in this nonplanar transition state. The efficiency of intersystem crossing from the $^1\pi-\pi^*$ to the $^3\pi-\pi^*$ can be increased by the presence of a transition metal or alternatively by substitution of the 1,2-diphenylethene with a halogen. Transition metal chromophores can efficiently sensitize the 1,2-diphenylethene $^3\pi-\pi^*$ state following population of a ^{3}MLCT state in metal 1,2-diphenylethene systems.[6] Lees and co-workers have shown that rhenium(I)tricarbonyl complexes containing a 1,2-diphenylethene-like link undergo triplet−triplet energy transfer from the ^{3}MLCT state. This results in *trans* to *cis* isomerization of the linking 1,2-diphenylethene-type unit.[7] Room-temperature solutions of a *trans* trinuclear diimine rhenium(I)tricarbonyl-containing 4-ethynylpyridylbenzene as a bridging ligand are only weakly luminescent. An efficient intermolecular quenching explains the low emission quantum yields ($\Phi_{em} \approx 10^{-3}$) and short lifetime of the excited state (in the range 4.9−20.5 ns). Moore and co-workers demonstrated that *trans to cis* photoisomerization in a bridging styrylpyridine ligand linking a rhenium tricarbonyl center to either an amine or an azacrown ether occurs only following protonation of the amine group.[8] It was proposed that the MLCT state decays by intramolecular energy transfer to form a triplet state, localized on styrylpyridine, from which the isomerization occurs. More recently, Vlček and co-workers have studied the ultrafast excited-state dynamics of *fac*-[Re(Cl)(CO)$_3$-(*t*-4-styrylpyridine)$_2$] and *fac*-[Re(*t*-4-styrylpyridine)(CO)$_3$(2,2′-bipyridine)]$^+$ compounds.[9] The styrylpyridine-localized ^{3}IL state is efficiently populated following excitation of either the ^{1}IL state or Re to the bipyridine ^{1}MLCT state. Structural reorganization in the styrylpyridine ^{3}IL state was ascribed to a *trans* to *cis* perpendicular twist around the C═C bond.

In this paper we describe the photochemical properties of both *cis*- and *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$. This study was undertaken to examine the effect the presence of an electron-rich metal carbonyl moiety has on the photoisomerization of *cis*-1,2-diphenylethene. The crystal and molecular

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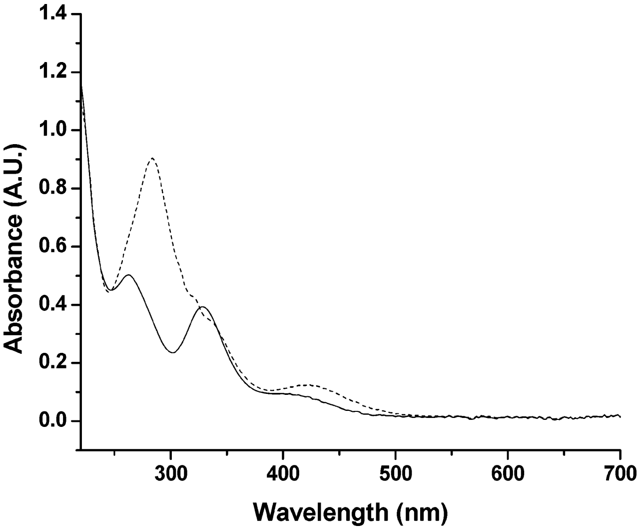

Figure 1. Electronic absorption spectra of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ (—) (2.99×10^{-5} M) and *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ (- - -) (3.55×10^{-5} M) in cyclohexane solution at room temperature.

Table 1. Spectroscopic Data for *cis*- and *trans*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ in Cyclohexane Solution

arene	ν_{CO} (cm^{-1})	λ_{max} (nm), ϵ (M^{-1} cm^{-1})	emission, λ_{max} (nm)
cis-(η^6-1,2-diphenylethene)Cr(CO)$_3$	1981 1916	263 (16 700) 330 (13 000) 406 (3200)	370
trans-(η^6-1,2-diphenylethene)Cr(CO)$_3$	1981 1916	285 (25 300) 422 (3660)	350

structures of the *trans* isomer are presented along with DFT calculations on the electronic structure of both the ground and low-lying excited states of these compounds.

Results and Discussion

Photophysical Characterization. Summarized in Table 1 are the absorption and emission data for the compounds in this investigation. The UV−vis spectra for both *cis*- and *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in cyclohexane are presented in Figure 1. The spectrum of the *trans* isomer contains a feature centered at 285 (ϵ = 25 300 M^{-1} cm^{-1}), while the equivalent feature in the *cis* isomer occurs at 263 nm (ϵ = 16 700 M^{-1} cm^{-1}) along with a weaker feature at 328 nm (ϵ = 13 000 M^{-1} cm^{-1}). Both compounds exhibit weak and broad absorptions in the visible region at approximately 420 nm. It should be noted that the absorption spectra of both compounds are considerably different from that of (η^6-benzene)Cr(CO)$_3$.[10] The λ_{max} at 285 nm in the spectrum of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ is assigned to a Cr to arene CT transition with some Cr to π^* CO CT character based on the corresponding benzene analogue.[11] The corresponding absorption for the *cis* isomer occurs at 330 nm. Two further absorption features are present at 408 and 430 nm for both the *cis* and *trans* compounds, respectively, and these are assigned to MLCT transitions.

The emission spectra of both compounds were recorded in cyclohexane solution at room temperature. The emissive characteristics of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ and *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ were compared to those of the free ligand following excitation with λ_{exc} = 332 nm. The general shape of the luminescence spectrum (Figure 2) is unaffected by complexation to the Cr(CO)$_3$ unit, suggesting that the nature of the emissive state is similar for both free and complexed 1,2-diphenylethenes. The luminescence intensity, however, is significantly reduced for the chromium compounds.

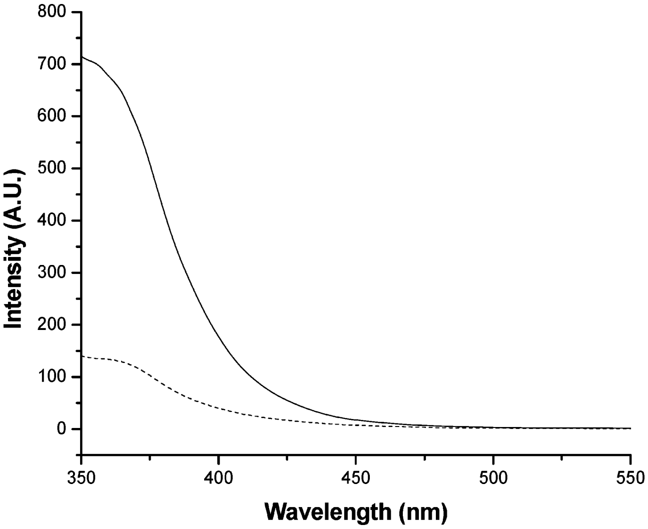

Figure 2. Emission spectra of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ (—) and *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ (- - -) in cyclohexane at room temperature, following excitation at 332 nm (both samples had an absorbance value of 0.2 AU at 332 nm).

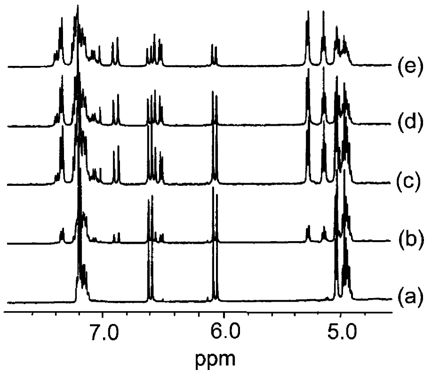

Figure 3. ^{1}H NMR spectra, obtained following broad-band irradiation of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ at λ > 400 nm, in degassed cyclohexane (d_{12}) solution at 10 min intervals.

^{1}H NMR Studies. Irradiation of a degassed solution of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ with λ_{exc} > 400 nm in cyclohexane-d_{12} under 1 atm of CO formed three photoproducts. Figure 3 displays the proton ^{1}H NMR spectra obtained following broad-band irradiation with λ_{exc} > 400 nm at 10 min intervals. The doublets at 6.5 and 6.9 ppm, together with the multiplets between 5.0−5.3 ppm and 7.1−7.4 ppm, are assigned to *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ (see Supporting Information or refs 12 and 13 for chemical shift and coupling data). The resonances compare well with those of an authentic sample of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in cyclohexane-d_{12}.[12] In addition to formation of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$, uncomplexed *cis*- and *trans*-1,2-diphenylethene were also

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[12] ^{1}H NMR (400 MHz, C$_6$D$_{12}$) for *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$: 7.399−7.098 ppm (m, 5H), 6.898 ppm (d, 1H, ^2J = 16 Hz), 6.549 ppm (d, 1H, ^2J = 16 Hz), 5.289−4.990 ppm (m, 5H); for *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$: 7.165−7.059 ppm (m, 5H), 6.695 ppm (d, 1H, ^2J = 12 Hz), 6.069 ppm (d, 1H, ^2J = 12 Hz), 5.043−4.920 ppm (m, 5H).

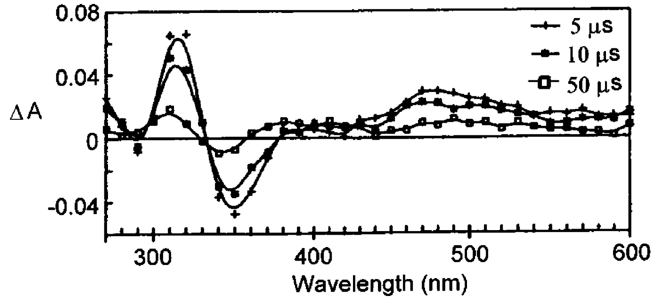
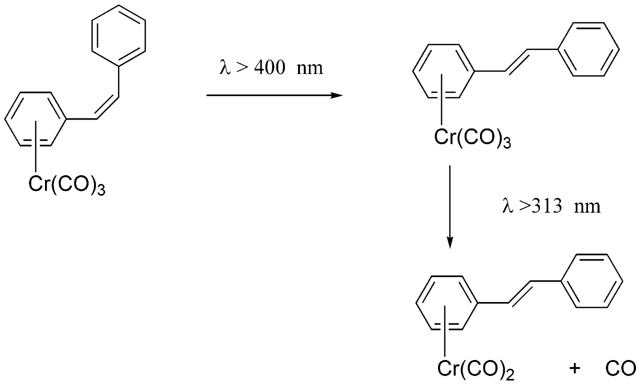


Figure 4. UV−vis transient absorption difference spectra, recorded at various time delays (5, 10, and 50 μs), following excitation (λ_{exc} = 355 nm) of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in CO-saturated cyclohexane solution at room temperature.

Scheme 1. Photoinduced *cis*−*trans* Isomerization of *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ Followed by CO Loss



produced in low yield (Scheme 1). The singlet at 7.0 ppm indicates formation of *trans*-1,2-diphenylethene, while the singlet at 6.5 ppm is assigned to the vinyl protons in *cis*-1,2-diphenylethene.[13] For both of these isomers the aromatic resonances fall in the range 7.0−7.4 ppm. Integrating the vinyl resonances confirms that *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ is the major product. Subsequent examination of the irradiated solution by infrared spectroscopy confirmed the presence of Cr(CO)$_6$ (ν_{CO} = 1988 cm^{-1}).

A degassed solution of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ was photolyzed under the same conditions as those above. Features of uncoordinated *trans*-1,2-diphenylethene were produced; however these features were very weak, indicating a low yield of the uncoordinated ligand.

Laser Flash Photolysis Studies. Pulsed photolysis (10 ns) of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in CO-saturated cyclohexane with λ_{exc} = 355 nm produced one transient signal assigned to the solvated *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_2$ intermediate. The transient absorption spectra recorded at various time intervals following the laser pulse are given in Figure 4. A λ_{max} is evident at 310 nm together with a broad absorption centered at ~ 480 nm. The depletion at ~350 nm corresponds to an absorption maximum of the parent compound. In the presence of 1 atm of CO the transient signal at 310 nm returns to the preirradiation value with a rate that is dependent on CO concentration. Plotting the observed rate constant versus CO concentration gave k_2 as a slope with a value of 7.0×10^6 M^{-1} s^{-1} at 300 K. The second-order rate constant obtained in this study is similar to that obtained for the reaction of (η^6-benzene)Cr(CO)$_2$(cyclohexane) with CO ($k_2 = 9.8 \times 10^6$ M^{-1} s^{-1} at 300 K).[10] Therefore we have assigned the transient signal to the coordinatively unsaturated *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_2$(cyclohexane) intermediate (reaction 1).

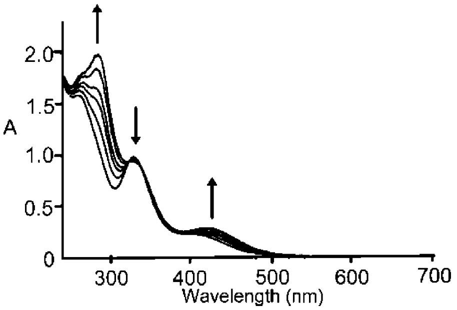
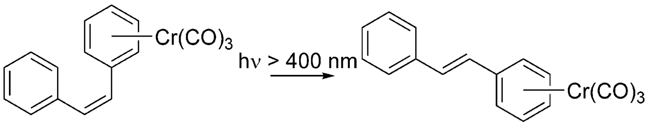


Figure 5. Steady-state UV−vis spectra recorded periodically during a laser flash photolysis (λ_{exc} = 355 nm) of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in CO-saturated cyclohexane at room temperature, showing the clean formation of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$.



(1)

Laser flash photolysis experiments on *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in CO-saturated cyclohexane (λ_{exc} = 355 nm) produced a persistent signal in the 280−300 nm region following pulsed excitation. Because the *trans* complex exhibits an absorption in this region while the *cis* complex does not (Figure 1), this would suggest that *cis* to *trans* isomerization occurs on a time scale shorter than the laser pulse (10 ns). As is usual during laser flash photolysis experiments, the steady-state UV−vis spectrum of the solution was monitored at various intervals, and the spectral changes observed are shown in Figure 5. An isobestic point at 312 nm is evidence of a reaction uncomplicated by side or subsequent reactions. An increase in absorbance was observed at ~280 nm and also in the region between 400 and 480 nm. These changes are consistent with the clean formation of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$. It should be noted, however, that because of the persistent nature of the absorbances produced in these experiments and the presence of CO in solution, it would not be possible to observe directly the formation of the CO-loss product from the *cis* isomer. However, given the efficiency of the *cis* to *trans* isomerization process, it is likely that CO loss occurs substantially from the photoproduced *trans* isomer.

Matrix Isolation Studies. Owing to the low volatility of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$, it was not possible to deposit this material in a low-temperature matrix. However, initial deposition of the more volatile *cis* isomer followed by photoinduced *cis* to *trans* isomerization allows the photochemistry of the *trans* isomer to be investigated albeit in the presence of residual *cis* isomer.

Photochemistry of *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ in a Methane Matrix at 20 K. Because the ν_{CO} absorption bands for both the *cis* and the *trans* complexes occur at similar wavenumbers, *cis* to *trans* isomerization is best monitored by UV−vis spectroscopy. Following irradiation of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in a methane matrix for 80 min at 20 K (λ_{exc} = 405 nm), absorption bands were observed at 295 and 445 nm. These spectroscopic changes, presented in Figure 6, suggest formation of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$.

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[13] ^{1}H NMR (400 MHz, C$_6$D$_{12}$) for *trans*-1,2-diphenylethene: 7.394−7.091 ppm (m, 10H), 7.009 ppm (s, 2H); for *cis*-1,2-diphenylethene in cyclohexane-d_{12}: 7.160−6.980 ppm (m, 10H), 6.474 ppm (2H).

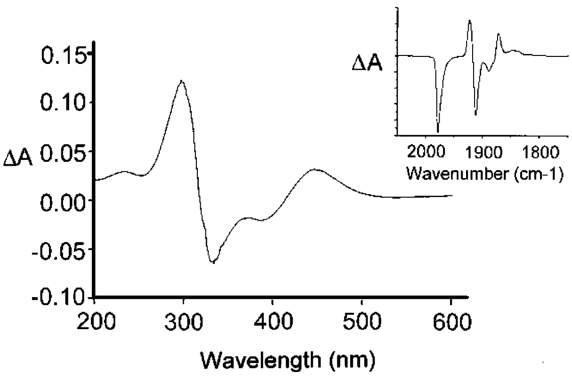

Figure 6. UV−vis difference spectrum of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in a methane matrix following irradiation at 405 nm for 80 min. The inset shows the IR difference spectrum of the same matrix following irradiation with $\lambda_{exc} = 313$ nm for 60 min.

Under these conditions the only changes observed in the IR spectrum were a slight reduction in intensity of the ν_{CO} bands. No evidence for the CO-loss product of either the *cis* or *trans* isomer was obtained from these experiments.

The two ν_{CO} (1978 and 1911 cm^{-1}) bands of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ decreased in intensity following irradiation with $\lambda_{exc} = 313$ nm for 60 min in a methane matrix at 20 K. Three new ν_{CO} bands at 2139, 1924, and 1873 cm^{-1} were formed. The weak feature at 2139 cm^{-1} was assigned to free CO in the matrix, and the remaining bands at 1924 and 1873 cm^{-1} to (η^6-1,2-diphenylethene)Cr(CO)$_2$. This latter assignment was based on the similarity of these band positions to those of analogous (η^6-arene)Cr(CO)$_2$S species (S = solvent or matrix material) presented in the literature.[14,15]

These results are consistent with *cis* to *trans* isomerization following irradiation of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ with $\lambda_{exc} = 405$ nm. The CO-loss species, (η^6-1,2-diphenylethene)Cr(CO)$_2$, is observed only following irradiation with $\lambda_{exc} = 313$ nm.

Photochemistry of *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ in a Dinitrogen Matrix. Spectroscopic changes observed in the UV−vis spectrum following photolysis ($\lambda_{exc} = 405$ nm) of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in a dinitrogen matrix confirmed formation of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$. No evidence of CO loss was obtained in these experiments. However, photolysis of the matrix at 313 nm produced (η^6-1,2-diphenylethene)Cr(CO)$_2$(N$_2$), with new bands in the matrix at 2151, 1940, and 1899 cm^{-1}. The UV−vis spectrum of this matrix would suggest the production of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_2$(N$_2$). The high-frequency band at 2151 cm^{-1} is assigned to a ν_{NN} vibration, confirming the generation of a single coordinated site on the metal following excitation.

Crystallographic Characterization. The molecular structure for *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ was determined by single-crystal X-ray crystallography. Orange crystals suitable for data collection were obtained from a benzene/pentane solution. Details of the data collection and other crystallographic parameters are presented in Table 2.

The six carbon atoms of the complexed benzene ring are essentially coplanar (Figure 7), and the three oxygen atoms lie in parallel, as reported for (η^6-benzene)Cr(CO)$_3$.[16] The C−C distances on the complexed ring vary from 1.38 to 1.42 Å. The average distance between the chromium atom and the carbon atoms of the complexed ring is 2.21 Å, with the C4−Cr bond at 2.243(2) Å being the longest, as expected due to the electron-withdrawing nature of the vinyl substituent. The perpendicular distance of the chromium atom from the plane of the coordinated aromatic ring is marginally greater than that in (η^6-benzene)Cr(CO)$_3$ (1.72 Å), (η^6-mesitylene)Cr(CO)$_3$ (1.72 Å), or (η^6-benzene)$_2$Cr$_2$ (1.60 Å).[17,18] The length of the acyclic C═C bond is 1.298(4) Å. One noticeable feature of this compound is that the *trans*-1,2-diphenylethene ligand is not planar. In contrast, the solid-state molecular structure of *trans*-1,2-diphenylethene has been shown to be almost planar.[19]

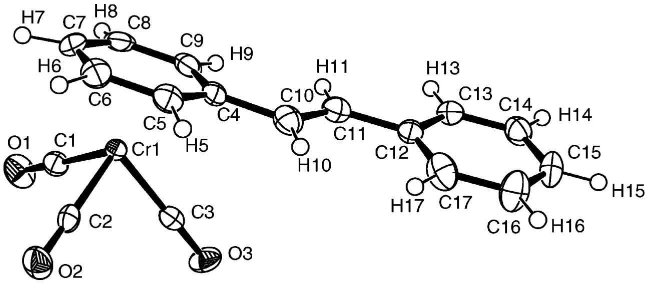

Figure 7. ORTEP[33] drawing of the molecular structure of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$, with thermal ellipsoids at the 50% probability level.

Table 2. X-ray Data Collection Parameters for *trans*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$

molecular formula	C$_{17}$H$_{12}$CrO$_3$
cryst dimens (mm)	0.2 × 0.12 × 0.05
color	orange
habit	prism
cryst syst	orthorombic
a (Å)	11.2450(14)
b (Å)	15.5538(19)
c (Å)	16.1900(2)
space group	*Pbca*
Z	8
D_{calc} (g cm^{-3})	1.440
F_{000}	1296
λ(Mo Kα) (cm^{-1})	0.71073
total no. of reflns	2501
independent reflns	1965
R_1	0.0512
wR_2	0.0924

Quantum Chemical Calculations. The ground-state electronic structures of *cis*- and *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ were calculated with the Gaussian 03 program suite using B3LYP/LANL2DZ model chemistry.[20] The molecular geometries were optimized without structural constraints, and the

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Table 3. Comparison of the Optimized Bond Lengths (Å) for *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ and *trans*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ with X-ray Crystallography Results for *trans*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$

	trans-(η^6-1,2-diphenylethene)Cr(CO)$_3$		*cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$
parameter	X-ray	calculated B3LYP/LANL2DZ	calculated B3LYP/LANL2DZ
C4−C10	1.479(4)	1.467	1.477
C10−C11	1.298(4)	1.359	1.360
C11−C12	1.481(4)	1.471	1.481
C4−Cr1	2.243(2)	2.367	2.358
C5−Cr1	2.219(3)	2.320	2.307
C6−Cr1	2.201(3)	2.316	2.313
C7−Cr1	2.207(19)	2.313	2.314
C8−Cr1	2.196(3)	2.310	2.308
C9−Cr1	2.216(19)	2.306	2.301
Cr1−C1	1.843(3)	1.832	1.832
Cr1−C2	1.838(3)	1.829	1.830
Cr1−C3	1.852(3)	1.832	1.832
C1−O1	1.153(3)	1.187	1.187
C2−O2	1.151(3)	1.188	1.188
C3−O3	1.145(3)	1.188	1.188

Table 4. Experimental (in cyclohexane solution at room temperature) and Calculated ν_{CO} Values for *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ and *trans*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ Based on an Optimized Geometry at B3LYP/LANL2DZ Model Chemistry

experimental		calculated		
ν_{CO} (cm^{-1})		ν_{CO} (cm^{-1})^a		
cis	*trans*	*cis*	*trans*	
1981	1981	1974	1972	sym
1916	1916	1914	1913	asym
		1912	1911	asym

[a] The calculated values have been corrected using an empirical factor of 1.02 derived from preliminary studies on Cr(CO)$_6$ at identical model chemistries.

resulting geometries were used in time-dependent density functional calculations to estimate the nature and energies of low-lying singlet excited states.

In general the predicted ground-state geometries are consistent with those derived from the single-crystal X-ray diffraction study with the exception of the acyclic double bond, where the calculated value is closer to the values obtained in other studies both theoretical and experimental.[21] As frequently observed, the bonding distances near the metal atom are longer in the calculated structure than those measured by X-ray diffraction (see Table 3 for a comparison of the calculated and experimental structural parameters).

The normal vibrational modes of both *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ and *trans*-(η^6-1,2 diphenylethene)Cr(CO)$_3$ were calculated, and the ν_{CO} are compared with experimental values in Table 4. As can be seen, the calculated values are close to the experimental values using a correction factor of 1.02 derived from calculations on Cr(CO)$_6$ at the same model chemistry.

The time-dependent density functional theory (TDDFT) method was used to estimate the nature and energies of the spectroscopically assessable excited states. The lowest 20 singlet states for each compound were probed using this method. A full list of electronic transitions, transition energies, and oscillator strengths is presented in the Supporting Information.

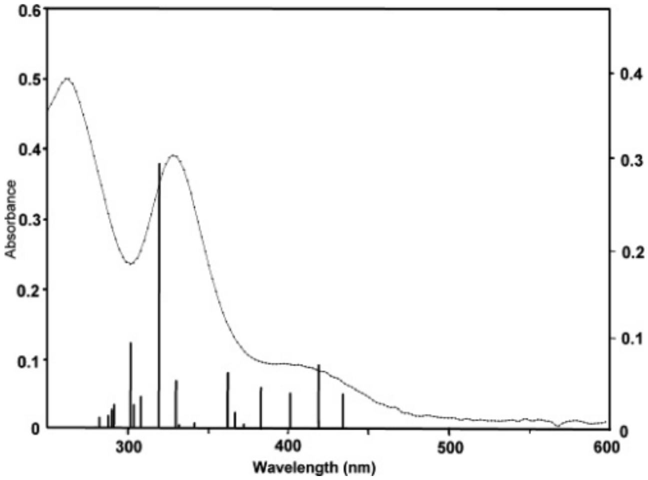

Figure 8. Superimposition of calculated individual electronic transitions (vertical lines) over the experimental UV−vis spectrum of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$.

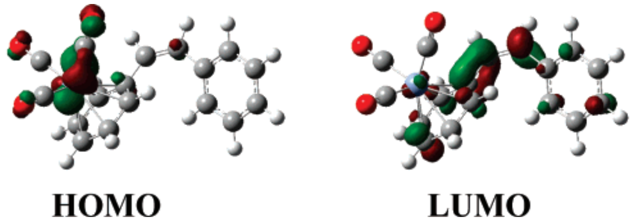

Figure 9. Molecular orbitals contributing to the most intense transition (HOMO to LUMO) at 418 nm.

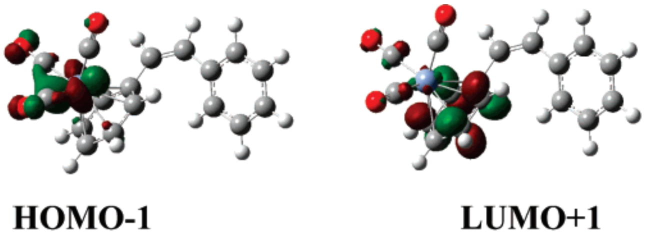

Figure 10. Molecular orbitals contributing to the most intense transition (HOMO−1 to LUMO+1) at 320 nm.

The calculated transitions for *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ are superimposed on the UV−vis spectrum of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ in Figure 8.

Three allowed electronic transitions (f = oscillator strength) contribute to the lowest absorption band at 422 nm: 418 nm, f = 0.0045; 418 nm, f = 0.0802; and 403 nm, f = 0.0032. The transitions involved are predominantly Cr to 1,2-diphenylethene CT in character, although some minor ligand−ligand charge transfer also contributes. The molecular orbitals involved are shown in Figure 9. Four electronic transitions contribute to the higher absorption band at 328 nm: 320 nm, f = 0.2846; 311 nm, f = 0.0271; 307 nm, f = 0.0233; and 304 nm, f = 0.0882 (Figure 10). These four transitions are predominantly MLCT in character, involving charge transfer from orbitals that are strongly bonding with respect to the Cr−CO interaction to the phenyl ring bearing the Cr(CO)$_3$ unit. Such a transition would be expected to labilize the Cr to CO interaction.

The TDDFT calculations predict isomerization of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ about the double bond following irradiation into the predominantly MLCT band at 422 nm. This occurs as a result of charge transfer from Cr to the ethyleneic

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double bond. Correspondingly it has been shown that irradiation of the MLCT band centered at 330 nm will result in CO labilization.

Concluding Comments

This work demonstrates that *cis*-1,2-diphenylethene coordinated to a Cr(CO)$_3$ moiety undergoes photoisomerization to the *trans* isomer following the absorption of low-energy photons ($\lambda_{exc} > 400$). The NMR experiments clearly identify *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ as the main photoproduct, and under these conditions CO loss was not observed. The CO-loss photoproduct was observed following high-energy photolysis of *cis*-(η^6-1,2-diphenylethene)Cr(CO)$_3$. Whether this CO loss occurs directly from the *cis* isomer or by way of secondary photolysis of the initially produced *trans*-(η^6-1,2-diphenylethene)-Cr(CO)$_3$ remains uncertain. However the UV−vis data obtained from matrix isolation experiments would suggest that the CO loss occurs via the *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$.

Experimental Section

Reagents. Spectroscopic-grade cyclohexane was used as obtained (Aldrich spectroscopic grade). Gases used for the matrix experiments and for the flash photolysis experiments (Ar, N$_2$, and CO) were BOC research grade (99.999% purity). Both the *cis*- and *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ were synthesized by the method reported by Hudeck et al.[22] Product purity was verified from standard spectroscopic techniques and microanalysis. All sample preparations were conducted under inert atmospheres.

Apparatus. Spectra were recorded on the following instruments: IR, Perkin-Elmer 2000 FT-IR (2 cm^{-1} resolution); UV−vis, Hewlett-Packard 8452A; NMR, Bruker AC 400. Emission spectra (accuracy ± 5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red-sensitive Hamamatsu R928 PMT detector.

The laser flash photolysis apparatus has been described previously.[23] For this work, the 355 nm line of a pulsed Nd:YAG laser was used (energy approximately 35 mJ per pulse; system response 10 ns). Solutions for analysis were placed in a fluorescence cuvette ($d = 1$ cm) attached to a degassing bulb and were degassed by three cycles of freeze−pump−thaw to 10^{-2} Torr, followed by liquid pumping to remove traces of water (this typically removed half the original volume of solvent). The absorbance of the solution at the excitation wavelength was adjusted to lie in the range 0.5−1.0 AU. The UV−vis spectrum of the sample solution was monitored throughout the experiments to monitor changes in absorbance. The concentration of CO was determined by the pressure of CO admitted to the cell. The solubility of CO in cyclohexane is 9.0×10^{-3} M, under 1 atm of CO at 298 K.[24] The laser flash photolysis data were obtained by the averaging of three shots.

NMR samples were prepared in a degasable NMR tube and were degassed by three cycles of freeze−pump−thaw to 10^{-2} Torr, followed by liquid pumping to remove traces of water. For all NMR experiments 1 atm of CO was admitted to the NMR tube.

The matrix isolation apparatus consists of a closed-cycle helium refrigerator, sample window, shroud, deposition tube, gas-mixing chamber, gas inlet, backing pump, diffusion pump, and temperature-control unit. Matrixes were deposited onto a CaF$_2$ window cooled to 20 K, with matching outer windows on the vacuum shroud. A thermocouple embedded into a cavity beside the window and connected to the temperature-control unit maintains the temperature. The window is cooled by a closed-cycle helium refrigerator (APD Cryogenics Inc.), mounted via a double O-ring seal in a stainless steel vacuum shroud. The system pumps to 8×10^{-4} Torr prior to cooling and achieves 10^{-7} Torr upon cooling to 20 K. Host gases (Cryo Service) are deposited onto a window via a needle valve. For mixed-gas matrixes, the gases are mixed in the correct ratio in the stainless steel mixing chamber prior to deposition. A ratio of sample molecule to host matrix in the region 1:2000 is desirable. Typically a rate of gas deposition of 0.6 Torr/min achieves sufficient dilution on the matrix window. Both the sample and gas are deposited simultaneously. *cis*-(η^6-1,2-Diphenylethene)Cr(CO)$_3$ was sublimed from a right-angled tube at 338 K as the gas stream entered the vacuum shroud. Deposition of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ using a variety of techniques proved to be unsuccessful. Deposition of the *cis* isomer was monitored by infrared spectroscopy. Deposition was stopped when the ν_{CO} absorbance was approximately 1 AU. Once the required absorbance was achieved, the sample was photolyzed and monitored on a Spectrum One FTIR spectrophotometer fitted with a KBr beam splitter. Spectra were recorded at 1 cm^{-1} resolution. UV−vis spectra were recorded on a Perkin-Elmer Lambda EZ201 spectrophotometer. Matrixes were photolyzed through a CaF$_2$ window with a 300 W−Xe arc or 200 W Hg−Ar lamp in combination with a water filter. Photolysis wavelengths were selected with cutoff or interference filters: $\lambda_{exc} = 405$, 313, >300, or >400 nm.

Crystals of *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$ suitable for collection of crystallographic data were grown from a benzene/pentane solution. Single-crystal analysis was made with a Bruker SMART APEX CCD area detector using graphite-monochromized Mo Kα ($\lambda = 0.71073$ Å) radiation at 296(2) K. The data reduction was performed using SAINT.[25] Lorentz, polarization, and a multiscan absorption correction were applied. The space group was determined from systematic absences and checked for higher symmetry. A full sphere of data was obtained using the ω-scan method. The structure was solved by direct methods using SHELXS[26] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons. Final Fourier syntheses showed no significant residual electron density in chemically sensible positions.

Density functional calculations were carried out using the Gaussian 03 package.[20] Initially geometry optimizations were at the Hartree−Fock (HF) level and subsequently Becke's three-parameter hybrid functional with the LYP correctional functional (B3LYP).[28,29] The size of the basis set used was increased incrementally from STO-3G to LanL2DZ. The final geometry optimization was carried out using the LanL2DZ basis set, which uses the Dunning−Huzinaga double-ζ basis functions (DZ) for carbon and hydrogen atoms.[30] The energies of the 20 lowest lying singlet−singlet energy transitions were calculated at the optimized geometry using the time-dependent density functional method. The orbital population of the 20 lowest lying excited states was visualized using Gaussview,[31] and extraction of the percentage

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contributions of the metal orbitals, CO, and the ligands in the excited-state structures was performed by locally created GaussSum software.[32]

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Supporting Information Available: Crystallographic data for *trans*-(η^6-1,2-diphenylethene)Cr(CO)$_3$, pseudo-first-order plots of k_{obs} versus [CO] for the reaction of (η^6-1,2-diphenylethene)Cr(CO)$_2$S with CO (S = cyclohexane), and ^{1}H NMR data and geometrical parameters for the quantum chemical calculations for both compounds are available free of charge via the Internet at http://pubs.acs.org.

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