

Mechanism of the photochemical carbon-carbon coupling reaction of tricarbonyl(η -6-1,3,5-cycloheptatriene)chromium with conjugated dienes. IR study in liquid noble gases and low-temperature matrices

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nyldimethylchlorosilane (4.23 g, 30 mmol) and 2 (8 g, 100 mmol) in 500 mL of *n*-pentane at $-78\text{ }^{\circ}\text{C}$. Isolation as before yields a colorless liquid (3.0 g; bp $55\text{ }^{\circ}\text{C}/10^{-2}$ mbar) which could be identified as a mixture of (*E/Z*)-12, 13, and 7. The cycloadducts were separated from 12 by distillation.

(*E*)-12: ^{13}C NMR δ 39.8 (CH_2), 12.1 (CH), 31.5 ($\text{C}(\text{CH}_3)_3$), 29.3 ($\text{C}(\text{CH}_3)_3$), 0.7 ($\text{Si}(\text{CH}_3)_2$); ^{29}Si NMR δ 8.6.

(*Z*)-12: ^{13}C NMR δ 39.9 (CH_2), 12.7 (CH), 31.3 ($\text{C}(\text{CH}_3)_3$), 29.4 ($\text{C}(\text{CH}_3)_3$), 2.6 and -4.8 ($\text{Si}(\text{CH}_3)_2$); ^{29}Si NMR δ 10.3. For ^1H NMR and MS of 12 see ref 30.

13: ^{13}C NMR δ 134.0, 133.5, 133.1, and 131.6 (CH olefinic), 40.5,

40.1, 27.3, 23.6, 22.9, and 22.4 (CH), 43.6, 42.9, 24.4, 21.8, 21.5, and 20.9 (CH_2), 30.5 ($\text{C}(\text{CH}_3)_3$), 29.6 ($\text{C}(\text{CH}_3)_3$), -1.5 -2.7 , -4.1 , and -4.2 ($\text{Si}(\text{CH}_3)_2$); MS *m/e* 222 (M^+ , 18), 85 ($\text{Me}_2\text{SiC}_2\text{H}_3$, 100), 59 (C_4H_{11} , 65), 135 ($\text{M}^+ - \text{Me}_2\text{SiC}_2\text{H}_3$, 20), 165 ($\text{M}^+ - \text{C}_4\text{H}_9$, 18), 137 ($\text{M}^+ - \text{Me}_2\text{SiC}_2\text{H}_3$, 10); MS *m/e* 222 (M^+ , 20), 85 ($\text{Me}_2\text{SiC}_2\text{H}_3$, 100), 59 (C_4H_{11} , 95), 135 ($\text{M}^+ - \text{Me}_2\text{SiC}_2\text{H}_3$, 30), 137 ($\text{M}^+ - \text{Me}_2\text{SiC}_2\text{H}_3$, 18), 163 ($\text{M}^+ - \text{C}_4\text{H}_{11}$, 15).

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Mechanism of the Photochemical C–C Coupling Reaction of Tricarbonyl(η^6 -1,3,5-cycloheptatriene)chromium with Conjugated Dienes. IR Study in Liquid Noble Gases and Low-Temperature Matrices

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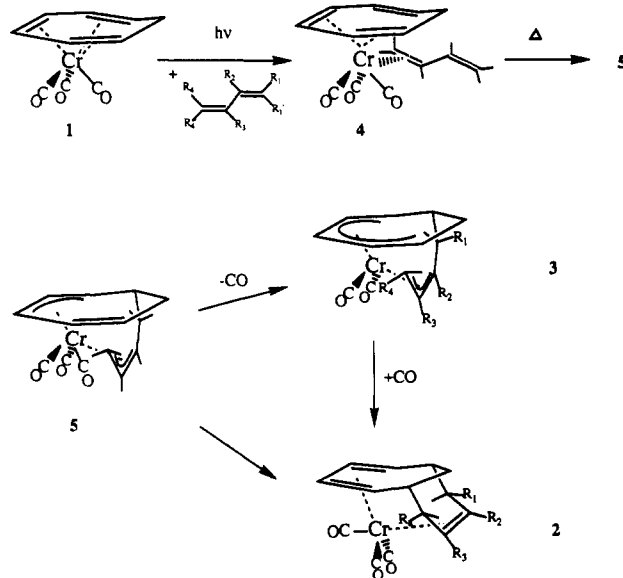
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The mechanism of the photochemical C–C coupling reaction of $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)$ ($\text{C}_7\text{H}_8 = 1,3,5$ -cycloheptatriene) with conjugated dienes, producing a ($\eta^{4,2}$ -bicyclo[4.4.1]undeca-2,4,8-triene)tricarbonyl- and/or a 1-butene-1,2-diyloctocyclohepta-2,4-dien-5-ylidicarbonylchromium complex, has been investigated. The primary photoprocesses were studied in low-temperature matrices, and the secondary thermal reactions, in liquefied noble gases and organic solvents. The reactions were followed by infrared spectroscopy. Two primary photoprocesses have been observed: CO loss and $\eta^6 \rightarrow \eta^4$ hapticity change of the triene ligand. In solution only the CO loss reactions gave rise to the coupling reaction under study, which is independent of the wavelength of irradiation ($\lambda > 350$ nm). The new C–C bonds were formed stepwise. In the last step of the reaction the dissociated CO reacted back to form the final tricarbonyl product. Methyl substituents on the dienes destabilized the observed intermediates and hindered the formation of the C–C bonds and the back-reaction with CO.

Introduction

Kreiter and co-workers investigated the photochemical reactions of the cycloheptatrienechromium complex $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)$ (1) and its heptafulvene derivative $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_{10}\text{H}_{12})$ (1') with conjugated dienes at reduced temperatures.¹ They observed the formation of (bicycloundecatriene)tricarbonylchromium complexes 2 (out of 1) and 2' (out of 1') with two new C–C bonds² and/or, if sterically more hindered dienes were used, a dicarbonyl complex 3' (out of 1') with one new bond³ (compare with Scheme I). 3' reacted with excess CO, forming 2', which process was favored by lowering the temperature.⁴ The formation of 3' indicated that the cycloaddition is not a concerted [6 + 4] cycloaddition but a stepwise process. A tentative mechanism for these reactions was proposed, which is depicted in Scheme I for the cycloheptatriene case. The first step of the reaction is a light-induced $\eta^6 \rightarrow \eta^4$ hapticity change of the triene ligand, leaving an open site for the diene, which binds to the metal in a η^2 -coordination. This η^4 - η^2 -complex 4 (or 4') reacts further by a C–C coupling between the diene and the 1- or 6-carbon atom of the heptatriene ligand, resulting in the formation of an $\eta^{3,3}$ -dienyl complex 5 (or 5'); see Scheme I. 5 (or 5') can react in two ways: either by formation of 2 (or 2') or by loss of CO, producing 3 (or 3').^{1,3}

Scheme I. Mechanism Proposed by Kreiter et al.¹ for the C–C Coupling Reaction between Tricarbonyl(η^6 -1,3,5-cycloheptatriene)chromium Complexes and Conjugated Dienes



Complex 1 shows also a C–C coupling reaction with alkynes.⁵ This reaction and the reaction with hydrogen,

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which exclusively results in 1,6-hydrogenation of the triene ligand, may proceed via a $\text{Cr}(\text{CO})_3(\eta^4\text{-C}_7\text{H}_8)$ or a dicarbonyl intermediate.⁵ The creation of an open site on the metal by a hapticity change of the triene ligand is one of the mechanisms proposed for the photochemical $\text{C}_7\text{H}_8 \rightarrow 1^4\text{-C}_7\text{H}_8$ exchange in 1.⁶ It has been proven to occur upon irradiation ($\lambda > 320$ nm) of 1⁷ and of $\text{Mo}(\text{CO})_3(\text{C}_7\text{H}_8)$ in CO matrices,⁸ which resulted in the formation of $\text{M}(\text{CO})_4(\eta^4\text{-C}_7\text{H}_8)$ complexes ($\text{M} = \text{Cr}, \text{Mo}$). In a 5% ^{13}C -doped CH_4 matrix the $\text{Mo}(\text{CO})_4(\eta^4\text{-C}_7\text{H}_8)$ could, however, not be detected. In that case only CO loss was observed. These results show that both CO loss and hapticity change can occur but that the product of the latter reaction can only be detected under exceptional conditions, viz. in the presence of excess CO.

Because of our interest in the photochemical C-C and C-H activation of olefins by transition-metal compounds, these reactions of 1 were investigated at low temperatures in order to establish their mechanism. The primary photoprocesses were studied by matrix isolation spectroscopy. Most experiments were performed by irradiation into the long-wavelength band of 1, around 500 nm. Due to the coordination of most polar solvents to the primary photoproduct of 1 at the desired temperatures, LXe was mainly used as a solvent.⁹ The great advantages of liquid noble gases as solvents have been demonstrated for an increasing number of spectroscopic techniques.^{9,10} Their complete transparency in the IR and UV-vis region allows the use of long optical pathlengths. This often compensates for the low solubility of many organometallic compounds, also of 1 (dipole moment 4.52 D^{11}), in these solvents.

Experimental Section

The organic solvents 2-chlorobutane and 2-methylbutane (Janssen Chimica) were dry and oxygen free. All samples and solvents were kept in an inert atmosphere. 1 was purchased from Strem Chemicals or synthesized from tris(acetonitrile)tricarboxylchromium¹² according to the literature¹³ and purified by column chromatography (Silicagel 60, 0.063–0.200 mm (Merck); eluent *n*-pentane). Both samples were finally recrystallized from *n*-hexane and stored under nitrogen at 277 K. Xenon and krypton were purchased in 99.995% purity from Air Products Nederland BV, the dienes and 1-pentene from Fluka Chemie AG, and the gaseous alkenes from Union Carbide, J. T. Baker Chemicals BV, and Hoek Loos Nederland BV; these were used as received.

All IR spectra were recorded on a Nicolet 7199B FTIR spectrometer, with a liquid nitrogen cooled MCT detector (resolution 1.0 cm^{-1} ; 32 (alkanes), 64 (LKr and LXe), or 128 (matrix experiments) scans), and the UV-vis spectra, on a Perkin-Elmer Lambda 5 UV-vis spectrophotometer (average of 10 scans). The Raman spectra were measured on a Dilor Raman spectrometer, type XY, using a Spectra Physics 2016 argon ion laser. A coherent CR-590 dye laser with Rhodamine 6G as a dye was used for excitation at longer wavelengths.

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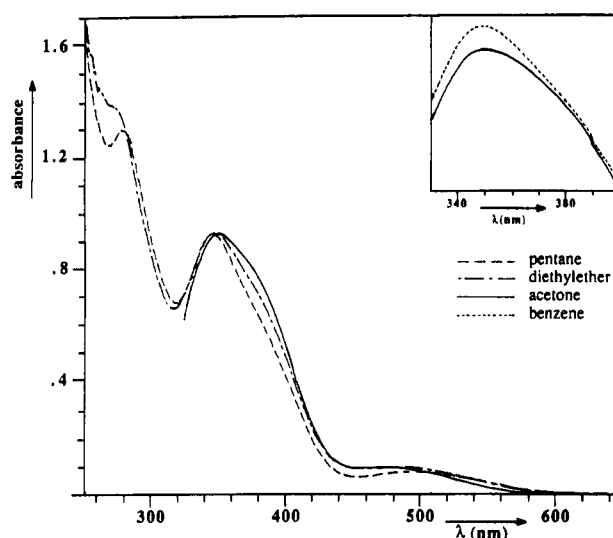


Figure 1. UV-vis spectra of 1, measured in *n*-pentane, diethyl ether, and acetone. Insert: Comparison of the spectra of 1 in acetone and benzene.

A Spectra Physics 2020 argon ion laser was used as irradiation source in the photochemical reactions ($\lambda = 351/364$ (1:4), 488, 514.5 nm). The power of the laser light varied from 30 to 60 mW; the beam was expanded by a lens to cover the whole IR window of the cells. Irradiation with other wavelengths was performed with an Oriol Corp. Model 6137 high-pressure mercury lamp, equipped with a 5-cm quartz water filter and an interference filter ($\lambda = 313, 365$ and 405 nm; FS10, Andover Corp.). The subsequent steps of the reactions were followed with IR spectroscopy.

The high-pressure-low-temperature cell, used for the liquid noble gas experiments, has been described before.⁹ The pressure above the solution was 10^5 Pa. The cell was filled under a helium flow to avoid the formation of the dinitrogen complex $\text{Cr}(\text{CO})_2(\eta^6\text{-C}_7\text{H}_8)(\text{N}_2)$ ($\bar{\nu}_{\text{N}_2}$ 2156 cm^{-1} , $\bar{\nu}_{\text{CO}}$ 1947 and 1896 cm^{-1} in LXe at 165 K; see also the section on the matrix isolation experiments). The liquid olefins were introduced with a syringe. The gaseous olefins were introduced by filling the cell with 10^5 Pa of the gas, followed by a 2000-fold dilution with helium before cooling.

The solution experiments have been performed in 2-methylbutane, 2-chlorobutane, liquid xenon (LXe), and liquid krypton (LKr), usually with *trans*-1,3-pentadiene as the added reactant. In a typical experiment a solution of 1 and a ca. 200-fold excess of the olefin were irradiated just above the freezing point, followed by slowly raising the temperature.

The matrices were made by slowly condensing 1 after sublimation at 265 K with excess matrix gas on a cold window (12 K, $P < 10^{-4}$ Pa), cooled by an Air Products Displex Model CSW-202 B closed-cycle helium refrigerator. The matrix gases methane and carbon monoxide were obtained in research quality from Aga Gas BV.

Results and Discussion

Electronic Transitions. The UV-vis spectra of 1 in *n*-pentane, diethyl ether, and acetone are depicted in Figure 1. UV-photoelectron spectra had shown that the three highest occupied orbitals of 1, of which two have almost the same energy, have metal d-character, while there is a close lying π_{ring} orbital.¹⁴ Extended Hückel calculations on a polyene complex with a triene intermediate between cycloheptatriene and norcaradiene showed that the lowest unoccupied molecular orbital has mainly d-character.¹⁵

In agreement with this the weak ($\epsilon = 450 \text{ mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$ in *n*-pentane) and solvent-independent 500-nm transition

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Table I. CO-Stretching Frequencies (cm⁻¹) of 1, 6–9, and Analogous Complexes in CH₄ and CO Matrices at 12 K

complex	matrix	$\bar{\nu}_{\text{CO}}$, cm ⁻¹			λ , nm	ref
Cr(CO) ₃ (η^6 -C ₇ H ₈) (1)	CH ₄	1987	1924	1902		7a
	CH ₄	1986	1923	1902		a
	CO	1985	1921	1898		7a
	CO	1992	1925	1901		a
	N ₂	1993	1929	1902		7a
	Ar	1991	1928	1900		7a
Cr(CO) ₂ (η^6 -C ₇ H ₈) (6)	CH ₄		1944	1864	$\lambda > 300$	7a
	CH ₄ ^b		1947	1860	365/405/488	a
	CO		1947 ^c	1861	365	a
	Ar		1945	1868	$\lambda > 300$	7a
	N ₂		1951	1864	$300 < \lambda < 400$	7b
Cr(CO) ₂ (η^6 -C ₇ H ₈) (7)	CH ₄		1932	1865	$280 < \lambda < 320$	7b
	CH ₄ ^b		1932	1865	313	a
Cr(CO) ₂ (η^6 -C ₇ H ₈)(N ₂)	N ₂	2153 ($\bar{\nu}_{\text{N}_2}$)	1958	1886	$\lambda > 300$	7a
Cr(CO) ₄ (η^4 -C ₇ H ₈) (8)	CO	2038	1952	1933	$\lambda > 300$	7a
Cr(CO) ₄ (η^4 -C ₇ H ₈)	CO	2033	1960 br	1930 ^d	365, 488	a
8 + 9		2041	1951 ^c			
Cr(CO) ₆	CO		1984		$\lambda > 320$	7
	CO		1987		$313 < \lambda < 488$	a
Cr(CO) ₄ (η^4 -norbornadiene)	CO	2031	1955	1941	1907	32
Cr(CO) ₄ (η^4 -butadiene)	CO	2043	1981	1949	1934	25
Cr(CO) ₄ (η^4 - <i>trans</i> -2,3-dimethylbutadiene)	CO	2033	1962	1941	1923	25

^aThis work. ^bFree CO at 2138 cm⁻¹. ^cCoinciding bands. ^dHidden by parent band.

is assigned to a ligand field (LF) transition. Although the band around 350 nm is hardly solvatochromic, it is too intense to belong to a single LF transition ($\epsilon_{346} = 4800 \text{ mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$ in *n*-pentane). In more polar solvents a shoulder emerged on the low-energy side of the band. Solvents of higher polarity than acetone, especially nitrogen donors, could not be used to get a better separation of the bands, since the complex partially decomposed by thermal loss of the triene ligand.¹⁶ The second derivative of the spectrum of 1 in *n*-pentane displayed the presence of two maxima, at 345 and 395 nm, respectively. The small negative solvatochromism of the low-energy shoulder points to a transition which has some triene to metal charge-transfer character.

The closely related complex Cr(CO)₃(η^6 -acenaphthene) has an intense, solvent-independent band at 440 nm. The resonance Raman spectra of this complex in benzene, excited with laser lines ranging from 612 to 458 nm, contained four weak bands, at 294, 800, 1404, and 1697 cm⁻¹. From these only the 294-cm⁻¹ band, belonging to the symmetrical metal-arene stretching vibration, increased in intensity upon approaching the maximum of the 440-nm absorption band. This result implies that the electronic transition involved is slightly metal-arene bonding to antibonding in character.¹⁷

Unfortunately, complex 1 was too photolabile to obtain reliable Raman spectra in solution.¹⁸ These spectra were therefore recorded in a KNO₃ disk at 110 K. Two weak bands with equal intensities were observed at 306 and 260 cm⁻¹, which showed an increasing resonance effect upon variation of the exciting wavelength from 578.5 to 458 nm. In accordance with previous assignments for the molybdenum and tungsten analogues of 1¹⁸ these bands are assigned to a ring-tilt and a metal-ring vibration, respectively. Again, just as for the acenaphthene complex, the resonant electronic transition has metal-ligand bonding to antibonding character. In this case, however, the exciting laser lines are only in preresonance with the composite band at 350 nm. The observed resonance Raman effects may therefore be connected with either of the two transitions

probably comprised by this band.

Free cycloheptatriene has a boat conformation,¹⁹ which upon coordination changes into an almost planar triene unit with the methylene group ca. 50° out of the plane.²⁰ Although this structural change may cause a shift to lower energy of the electronic transition of this ligand (at 261 nm in isooctane²¹), this transition is not expected to contribute to the 350-nm band of 1. In that case the preresonance Raman spectra would certainly have shown bands belonging to ligand stretching modes.

Of special interest is the spectrum of 1 in benzene (Figure 1, insert). The use of an aromatic solvent causes a solvatochromic shift of the 350-nm band—with regard to the spectrum in *n*-pentane—which is comparable with the shift in the much more polar solvent acetone. Recently this remarkable behavior has also been observed for some transition-metal complexes of tetracyanoethylene (TCNE) in which the olefin is π -coordinated to the metal.^{22a} Whereas the solvatochromism of the charge-transfer transition to TCNE of σ -bonded TCNE complexes is linearly dependent on the solvent parameter E^*_{MLCT} , derived by Manuta and Lees,²³ the interaction of the π -orbitals of the solvent with those of the π -bonded olefin results in a deviation from this correlation. Therefore a solvent parameter $E_{\text{CT}}(\pi)$ has been derived for complexes with π -bonded ligands.^{22b} The solvatochromic effects are too small, however, to make a valid comparison between these two solvent parameters for complex 1.

Primary Photoprocess: Matrix Isolation Spectroscopy. Hooker and Rest studied the primary photoprocesses of 1 in CH₄, Ar, N₂, and CO matrices upon irradiation with wavelengths below 400 nm⁷ (see Table I). In CH₄ matrices two Cr(CO)₂(η^6 -C₇H₈) products were

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Table II. Notations for the Olefins Used in the Solution Experiments

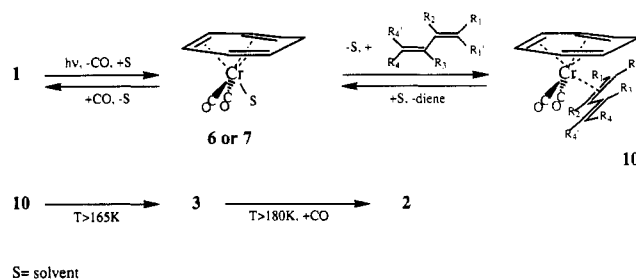
olefin	a, d, f, h-k:		b, c, e, g:				
	R ₁	R _{1'}	R ₂	R _{2'}	R ₃	R ₄	R _{4'}
a (<i>trans</i> -1,3-pentadiene)	H	H	H		H	CH ₃	H
b (propene)	H	H	H	CH ₃			
c (1-pentene)	H	H	H	C ₃ H ₇			
d (1,3-butadiene)	H	H	H		H	H	H
e (<i>trans</i> -2-butene)	CH ₃	H	H	CH ₃			
f (<i>trans,trans</i> -2,4-hexadiene)	CH ₃	H	H		H	CH ₃	H
g (isobutylene or 2-methylpropene)	H	H	CH ₃	CH ₃			
h (2-methyl-1,3-butadiene)	H	H	CH ₃		H	H	H
i (2,3-dimethyl-1,3-butadiene)	H	H	CH ₃		CH ₃	H	H
j (<i>trans</i> -2-methyl-1,3-pentadiene)	H	H	CH ₃		H	CH ₃	H
k (<i>cis</i> -1,3-pentadiene)	H	H	H		H	H	CH ₃

formed, depending on the wavelength of irradiation: **6** ($300 < \lambda < 400$ nm) and **7** ($280 < \lambda < 320$ nm). In an Ar matrix only **6** was formed ($280 < \lambda < 320$ nm). This complex was also produced in a nitrogen matrix, in addition to $\text{Cr}(\text{CO})_2(\eta^6\text{-C}_7\text{H}_8)(\text{N}_2)$. In a CO matrix $\text{Cr}(\text{CO})_4(\eta^6\text{-C}_7\text{H}_8)$ (**8**) and $\text{Cr}(\text{CO})_6$ were obtained, just as for the molybdenum complex. We have focused our attention on reactions induced by visible light.

Upon irradiation of **1** with $\lambda = 488$ nm (60 mW) in a CH₄ matrix only one (CO)₂ product, **6**, and free CO were formed in an extremely slow reaction (5% conversion in 2.5 h). The low conversion rate may be due to the weak absorption at this wavelength and/or be caused by a back-reaction of CO with the primary photoproduct, a process known to occur upon long-wavelength irradiation of coordinatively unsaturated transition-metal complexes in matrices.^{24,25} These include the dicarbonyl photoproducts of **17** and its molybdenum analogue.⁸ The presence of **6** must then be explained by partial diffusion of the free CO into the matrix (see also next paragraph). The same photoproduct **6** was formed upon irradiation with 405 nm, although with a higher conversion rate of the starting material.

Also in a CO matrix the primary photoprocess was irradiation wavelength dependent. After irradiation with $\lambda = 488$ nm (30 mW, 15% conversion in 4 h) a tetracarbonyl complex **9** was obtained ($\tilde{\nu}_{\text{CO}}$ at 2041 cm⁻¹) together with a small amount of the tetracarbonyl **8** with $\tilde{\nu}_{\text{CO}}$ at 2033 cm⁻¹. The latter photoproduct had also been observed by Hooker and Rest (see Table I). Upon irradiation with $\lambda = 365$ nm the situation was reversed, since the formation of **8** was then preferred. Complex **9** also showed a band at 1951 cm⁻¹, and complex **8** a band at 1960 cm⁻¹. Other bands appeared at 1987, 1930, and 1904 cm⁻¹. After prolonged irradiation the 1987-cm⁻¹ band increased in intensity with a concomitant decrease of the other bands, showing that $\text{Cr}(\text{CO})_6$ was formed as a secondary photoproduct.⁷ The 1930- and 1904-cm⁻¹ bands could not be assigned unambiguously, since they overlapped with parent bands. They belonged to complex **8** or **9** however. In the 365-nm irradiation experiments not only complex **8** was obtained but also a small amount of **6**. This resembles the behavior in a nitrogen matrix.

Hooker and Rest assigned **6** to a dicarbonyl complex in which the carbonyl under the methylene group (staggered conformation) had been released from complex **1**.^{7b} The

Scheme II. Reaction Scheme of the Photochemical C-C Coupling Reaction between **1** and Conjugated Dienes

stability of **6** in CO and N₂ matrices may then be due to a shielding of the open site on the metal by the methylene group of the triene ligand, which bends to the metal after the CO dissociation. This also explains the stability of **6** upon long-wavelength irradiation. Inversion of the methylene group was also proposed in the metal-assisted 1,5-H shift in **12^b** and might give rise to an agostic interaction. The occurrence of agostic interactions has now widely been established in organometallic chemistry. A recent review showed, however, that such interactions have mainly been studied by NMR spectroscopy. Only a few stretching vibrations of C-H bonds involved in such an agostic interaction have been reported so far, mainly for complexes of positively charged metals, but none of these studies concerned complexes of zerovalent chromium.²⁷ The frequencies found range from 2350 to 2800 cm⁻¹. No IR band could, however, be observed in this region for the photoproducts formed in our CO matrices. They might have escaped detection because of their low intensity.

From these results it is concluded that the primary photoprocesses after irradiation with all wavelengths are loss of CO and change of hapticity of the triene ligand. Which metal-CO or metal-triene bond is broken is determined by the wavelength of irradiation. A change of hapticity leads only to the formation of stable products under the exceptional conditions of a large excess of CO.

First Step of the Thermal Reaction: Formation of $\text{Cr}(\text{CO})_2(\eta^6\text{-C}_7\text{H}_8)(\eta^2\text{-diene})$ (10**).** After irradiation (351/364 nm, 514.5 nm) of 1/*trans*-1,3-pentadiene (**a**) mixtures in 2-methylbutane, 2-chlorobutane, or LXe at temperatures below 165 K the formation of a dicarbonyl complex **10a** was observed (see Figure 2 and Scheme II).

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Table III. CO-Stretching Frequencies (cm^{-1}) and Force Constants k (N m^{-1}) of 10 and 3 in LXe at 167 K

olefin	complexes 10				complexes 3			
	A'	A''	k	k_c	A'	A''	k	k_c
a	1936	1878	1467	45	1943	1869	1468	57
b	1933	1873	1463	46				
c	1933	1873	1463	46				
d	1938	1881	1473	44	1948	1874	1475	57
e	1927	1867	1454	46				
f	1929 ^a	1872	1459	44	1943	1869	1468	57
g	1920	1865	1446	43				
h	1943	1865	1465	60	1945	1869	1469	59
i	1942	1858	1459	64	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
j	1939	1863	1460	58	1945	1868	1468	59

^a Band hidden by parent band. ^b Not observed; see text.

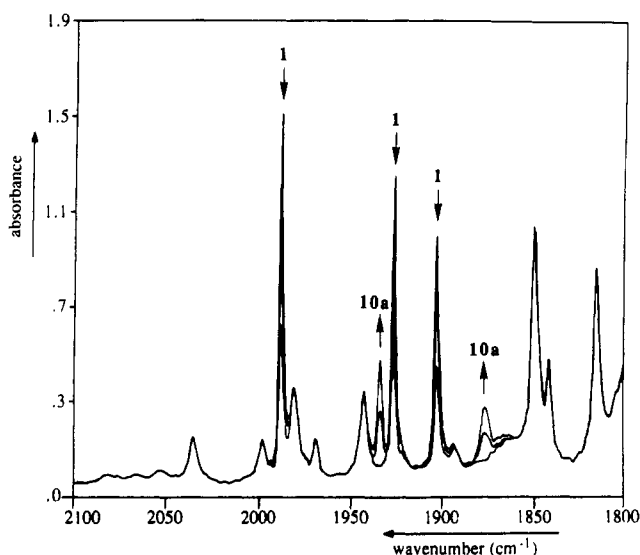


Figure 2. IR spectrum displaying the formation of 10a after irradiation of 1 with *trans*-1,3-pentadiene (a) at 167 K with $\lambda = 514.5$ nm in LXe.

This complex is proposed to be $\text{Cr}(\text{CO})_2(\eta^6\text{-C}_7\text{H}_8)(\eta^2\text{-C}_5\text{H}_8)$ by comparison of its CO-stretching frequencies in LXe at 167 K with those of the analogous complexes 10b–j of the olefins propene (b), 1-pentene (c), 1,3-butadiene (d), *trans*-2-butene (e), *trans,trans*-2,4-hexadiene (f), isobutylene or 2-methylpropene (g), 2-methyl-1,3-butadiene (h), 2,3-dimethyl-1,3-butadiene (i), and *trans*-2-methyl-1,3-pentadiene (j) (see for the notation also Table II). The only other $\text{Cr}(\text{CO})_2(\eta^6\text{-C}_7\text{H}_8)\text{L}$ complexes described in the literature are pyridine-, arsine-, phosphite-, and phosphine-substituted complexes,²⁸ e.g. (PPh_2) at 1902 and 1818 cm^{-1} (Nujol mull, room temperature).^{28a} An attempt to obtain $\text{Cr}(\text{CO})_2(\eta^6\text{-C}_7\text{H}_8)(\eta^2\text{-cyclooctene})$ in THF at ca. 200 K by $\lambda = 366$ nm irradiation was unsuccessful.^{28a} The IR data of the LXe experiments are presented in Table III, together with the force constants k and k_c ,²⁹ assuming (a) a pseudooctahedral structure for the complexes and (b) approximate equivalence of the two CO groups. Since the results will only be used to compare a series of molecules (vide infra), these assumptions are acceptable. LKr measurements gave the same results (1, 1989, 1928, and 1905 cm^{-1} , and 10j, 1939 and 1863 cm^{-1} , in LXe at 173 K; 1, 1994, 1934, and 1911 cm^{-1} , and 10j, 1950 and 1874 cm^{-1} , in LKr at 163 K).

The values in Table III, which will be discussed hereafter in more detail, give information about the bonding of the

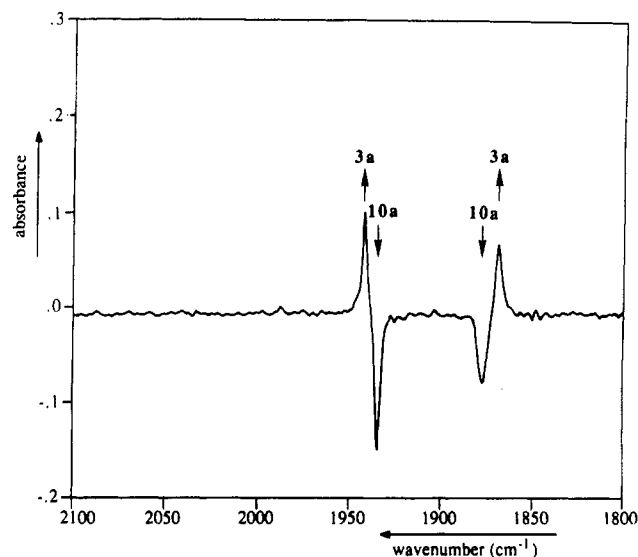


Figure 3. Thermal reaction at 173 K, forming 3a. Shown is the 1:1 difference of the spectra before and after the reaction.

olefin in the complexes. The large resemblance between the data of the mono- and diolefin complexes, together with the fact that the formation of a C–C bond with propene is highly improbable, justifies the conclusion that all olefins are η^2 -coordinated to the metal without formation of a C–C bond, while the triene ligand maintains its η^6 -coordination. No trace of a tricarbonyl complex 4 was observed in accordance with the previous observations that the formation of the tetracarbonyl complexes 8 and 9 is very difficult in matrices.

First C–C Coupling Step: Formation of 3. If the temperature of a 2-methylbutane solution of 10a, formed upon irradiation of 1 in the presence of *trans*-1,3-pentadiene, was raised to 165 K, a dicarbonyl complex was formed with CO-stretching vibrations at 1942 and 1870 cm^{-1} , respectively. The same reaction was observed in LXe: after irradiation of 1 and *trans*-1,3-pentadiene at $T = 167$ K a mixture of (mainly) 10a and this complex was formed, from which 10a slowly disappeared, forming the new complex in a thermal reaction, as shown by the IR spectral changes after the exclusion of all light (see Figure 3). A small part of 10a reacted back with CO to form 1. This back-reaction was the only process—apart from decomposition—taking place if the diene was sterically hindered, like *trans*-2,3-dimethylbutadiene (i). In 2-chlorobutane solutions the IR absorption bands were too broad to distinguish between those of complex 10 and this new complex.

Michels and Kreiter reported the formation at reduced temperatures of a product 3'i, with vibrations at 1944 and 1871 cm^{-1} in *n*-hexane at room temperature (in this case

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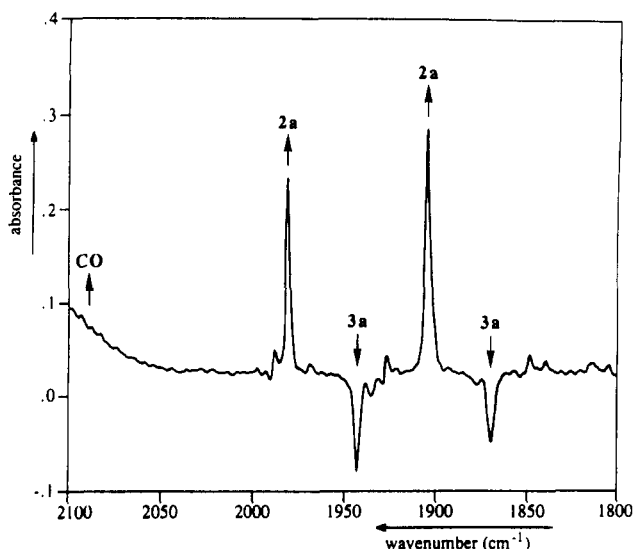


Figure 4. Thermal reaction at 190 K after addition of 10^5 Pa CO at 150 K, forming the final product **2a**, shown as a 1:1 difference.

the cycloalkatriene is heptafulvene).^{3,4} Considering their results (see Scheme I) we conclude that the product of the reaction with *trans*-1,3-pentadiene is **3a** (see Scheme II). This assignment is certainly justified because the differences between alkanes and LXe and between **1** and **1'** are only minor if the frequencies of the CO vibrations and their temperature dependence are considered (in cm^{-1} : **3a**, 1943 and 1869 in LXe and 1941 and 1869 in 2-methylbutane at 183 K; **1**, 1987, 1925, and 1901 in *n*-heptane, 1989, 1928, and 1905 in LXe at 173 K, and 1985, 1924, and 1900 in *n*-hexane at room temperature;³⁰ **1'**, 1985, 1931, and 1905 in cyclohexane at room temperature³¹). The CO-stretching frequencies of these new products of the dienes are presented in Table III (complexes **3**). Contrary to the values for the complexes **10**, these frequencies hardly depend on the substituents of the dienes. The CO_{free} absorption around 2135 cm^{-1} was very weak as expected at this high temperature.

Second C-C Coupling Step: Formation of 2. After the temperature of the **3a** solutions mentioned in the previous section was raised to 173 K, the formation of a new product was observed (see Figure 4), which was thermally stable (in 2-methylbutane) up to room temperature. Following the same reasoning as in the previous section, we conclude that this tricarbonyl species is the final product **2a**,⁴ formed by the reaction of **3a** with CO and a second C-C bond formation between the ends of the enyl systems. A similar formation of the final product **2'** out of **3'** and CO has been observed by Kreiter; see the Introduction.

Contrary to the experiments performed in standard thin-layer IR cells, hardly any product formation was observed in the much larger LXe cell, probably because the free CO had escaped to the gaseous xenon above the solution.⁹ This was proven by freezing the solution after the formation of **3a**, followed by adding 10^5 Pa CO. Already at 173 K the formation of some **2a** was then observed, but this reaction proceeded much faster after raising the temperature to 183 K (Figure 4).

Reaction with *cis*-1,3-Pentadiene (k**).** Kreiter already reported that the above mentioned reactions did not occur

Table IV. CO-Stretching Frequencies of the Products Formed in the Photochemical Reactions of $\text{Cr}(\text{CO})_6$ and **1** with *trans*- (**a**) and *cis*-1,3-Pentadiene (**k**) in 2-Chlorobutane and in the Subsequent Thermal Reactions

T (K)	CO-stretching vibrations of the products (cm^{-1})	
reaction: $\text{Cr}(\text{CO})_6 + \mathbf{a}$	$\text{Cr}(\text{CO})_5(\eta^2\text{-diene})$	$\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$
253	2072, 1955, 1937	2033, 1959 ^a , 1938 ^a , 1919
reaction: $\text{Cr}(\text{CO})_6 + \mathbf{k}$	$\text{Cr}(\text{CO})_5(\eta^2\text{-diene})$	$\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$
253	2073, 1957, 1939	2033, 1956 ^a , 1939 ^a , 1920
reaction: 1 + a	10a	2a
143	1914, 1854 ^b	
173	1918, 1855 ^b	1968, 1891 ^c
193	1918, 1855 ^b	1969, 1890
213		1970, 1892
reaction: 1 + k	10k	2a
143	1914, 1852 ^b	
173	1918, 1855 ^b	
193	1920, 1857 ^b	(1972) ^{d, e}
203	1921, 1859	1972, ^e
213	1921, 1860	1972, ^e
233		1972, 1889

^a Overlap with pentacarbonyl bands. ^b CO_{free} vibration at $2130\text{--}2135 \text{ cm}^{-1}$ (very weak at 193 K). ^c Only traces present. ^d Very weak; see text. ^e Weak; hidden by parent band.

if 1,3-pentadiene had a *cis* configuration, since **2k** and **3k** are sterically too crowded to be formed.³⁰ In order to determine at which stage of the reaction the configurational effect is largest, we irradiated ($\lambda = 514.5 \text{ nm}$) a 143 K solution of **1** in 2-chlorobutane in the presence of *cis*- (**k**) and *trans*-1,3-pentadiene (**a**), respectively, and gradually raised the temperature. Whereas in the case of *trans*-1,3-pentadiene the reaction followed the course described above, *cis*-1,3-pentadiene only gave rise to the formation of a single dicarbonyl complex, which was even stable at 213 K (see Table IV). Although it is impossible to distinguish unambiguously between complexes **10** and **3** in 2-chlorobutane (vide supra), the dicarbonyl complex, present in the *cis*-pentadiene solution is assumed to be **10k**. **3k** is—like **2k**—sterically too crowded to be formed, and **3a**, which can be formed by a *cis*-*trans* isomerization of the diene unit, would have reacted with CO at this temperature to form **2a**. At 193 K a very weak band at 1971 cm^{-1} showed up, indicating that at this temperature such a *cis*-*trans* isomerization can occur, resulting in the formation of complex **2a**. Its yield was, however, negligible when compared with that of the back-reaction with CO to form **1**. The same weak band also showed up after irradiation at 193 K, in addition to the bands of the main products, **10k** and free CO. Irradiation at 213 K and higher temperatures resulted in the formation of a mixture of **2a** and a small amount of $\text{Cr}(\text{CO})_5(\eta^2\text{-olefin})$, without a trace of $\text{Cr}(\text{CO})_4(\eta^4\text{-1,3-pentadiene})$, the main decomposition product in the case of *trans*-1,3-pentadiene at temperatures above 213 K. An analogous decomposition has been observed in the reaction of $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)$ with dienes, which resulted in the formation of $\text{Mo}(\text{CO})_4(\eta^4\text{-diene})$ and $\text{Mo}(\text{CO})_2(\eta^4\text{-diene})_2$.³⁰

The pentacarbonyl complex mentioned in the previous paragraph is assigned to $\text{Cr}(\text{CO})_5(\eta^2\text{-cis-1,3-pentadiene})$. Products with the same CO vibrations were obtained after irradiation ($\lambda = 313 \text{ nm}$) of a solution of $\text{Cr}(\text{CO})_6$ in 2-chlorobutane in the presence of *cis*- or *trans*-1,3-pentadiene at 253 K (Table IV). In a CO matrix it was impossible to identify a $\text{Cr}(\text{CO})_5(\eta^2\text{-C}_7\text{H}_8)$ complex because of its fast loss of the triene ligand to produce $\text{Cr}(\text{CO})_6$.⁷ Whereas in an early stage of the reaction of $\text{Cr}(\text{CO})_6$ with *trans*-1,3-pen-

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tadiene the formation of $\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$ was observed, hardly any tetracarbonyl complex was produced in the case of *cis*-1,3-pentadiene, due to a steric hindrance by the methyl group (see also next section).

At temperatures higher than 213 K the loss of the triene ligand in **10k** started to be of importance, which was reflected in the composition of the product mixture after irradiation of the *cis*-1,3-pentadiene solution at different temperatures. At 253 K hardly any **2a** was formed, while at 213 and 233 K a significantly higher percentage could be observed. The temperature dependence of the loss of the triene ligand is also visible in the *trans*-1,3-pentadiene case: irradiation of **1** at 213 K hardly produced any tetracarbonyl dissociation product, while the amount increased at higher temperatures (233 and 253 K). A photochemical step in the mechanism of this decomposition process can, however, not be excluded, considering the photochemical change of hapticity of the triene ligand in a CO matrix and the $\text{C}_7\text{H}_8 \rightarrow {}^{14}\text{C}_7\text{H}_8$ exchange, mentioned in the Introduction.

Olefin Bonding and Temperature Effects. $\text{Cr}(\text{CO})_4(\eta^4\text{-C}_7\text{H}_8)$ Complexes. From the CO-stretching vibrations of $\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$ complexes it can be derived whether the two olefinic groups bonded to the metal are conjugated or not. In the former case the $\text{Cr}(\text{CO})_4$ unit is more distorted than in the latter, which is reflected in a lowering of the CO force constants k_1 and k_2 .³² From the highest CO-stretching frequencies of **8** and **9** alone it cannot unambiguously be concluded by comparison with the data of other CO matrix-isolated $\text{Cr}(\text{CO})_4(\eta^4\text{-diene})$ complexes (diene = norbornadiene,³³ 1,3-butadiene, and 2,3-dimethyl-1,3-butadiene;²⁵ Table I) which double bond is released upon irradiation of **1** in CO matrices.

Complexes 3 and 10: Olefin Bonding. In the complexes **10b–d,g** the olefin has only terminal double bonds available for coordination; in the complexes **10e,f** the double bonds are only internal. If the CO-stretching frequencies of **10a** are compared with those of **10d,f**, there is a better agreement with those of **10d** than of **10f**. This is also reflected in the values of the stretching force constants k . We therefore propose that *trans*-1,3-pentadiene (**a**) is bonded via the terminal bond. It has been demonstrated that in complex **10h** the diene binds to the triene ligand with the sterically least hindered bond.⁴ This implies that the double bond coordinated to the metal in complex **10** forms the new C–C bond.

A recent investigation showed that after irradiation at 275 K complex **2** and some derivatives could be isolated for a variety of dienes, with yields which were independent of the electronic nature of the substituents.³⁴ The electronic effect of the methyl substituents of the diene on the carbonyl spectrum of the complexes **3** is small (see Table III). Since the olefins in **10** are much less constrained in their coordination than the π -allyl systems in **3**, electronic effects of the substituents might have more influence on the bonding properties and CO-stretching frequencies of the former complexes. However, no such effects are observed for the monoolefin complexes **10b,c**. Both complexes have the same CO stretching frequencies although the propyl group of **c** is more electron donating than the methyl group of **b**, while the steric effects exerted by these olefins are nearly the same. On the other hand, introduction of a second methyl group causes a larger decrease

of the CO-stretching frequencies in **10g** than in **10e**. Most probably steric effects induced by the second methyl group are responsible for these shifts, since the olefins **e** and **g** are expected to exert similar electronic effects. On the basis of these observations it is therefore tentatively concluded that also in the case of the dienes frequency shifts taking place by the introduction of an extra methyl group are mainly caused by steric effects. An increase of steric interaction between the diene and the metal fragment will prevent the favored coordination of the olefin, viz. perpendicular to the double bond of the triene ligand at the other side of the metal.³⁵ As a result the overlap between the metal d and olefin orbitals will decrease. This will cause a weakening of the metal to olefin back-bonding³⁶ and a shift of the CO-stretching vibrations to lower frequencies.

These steric influences are directly reflected in the force constants (Table III) although it has to be recalled that the k values have been derived by assuming approximate equivalence of the two carbonyls and a pseudooctahedral structure for the complexes. Of the diene complexes, **10a,d,h** have no substituents at the coordinated double bond and $k \approx 1470 \text{ N m}^{-1}$. For the complexes **10f,i**, having one methyl substituent at this bond, $k \approx 1460 \text{ N m}^{-1}$. An electronic reason for the lowering of k is the increased σ -donation and decreased π -back-donation upon introduction of a methyl group. The decrease of the vibrational energy, which is a result of this increase of the steric hindrance by the olefin in the complexes **10**, can be explained with the Dewar–Chatt–Duncanson³⁶ model for the binding of π -bonds to a metal. In these chromium complexes the empty d-orbital responsible for the σ -bonding must then have a larger space distribution than the smaller, occupied orbital involved in π -back-donation. In this way an increased metal–ligand bond length results in a higher electron density on the metal, which is reflected in the observed shift to lower energy of the CO-stretching vibrations.

Another steric effect is a distortion from the octahedral geometry to achieve a better overlap of the metal and olefin orbitals. This can be illustrated by the effect of the substituents at the noncoordinated double bond. The large values of k_c for the complexes **10h,i** are due to the influence of the R_2 or R_3 substituent on the noncoordinated double bond. An R_1 or R_4 substituent on this bond does not influence the carbonyl frequencies that much: upon going from butadiene (**d**) to *trans*-1,3-pentadiene (**a**) or from the latter diene to *trans,trans*-2,4-hexadiene (**f**), the k_c value hardly changes, whereas on going from butadiene (**d**) to 2-methyl-1,3-butadiene (**h**) the change is significant. The large k_c 's of the complexes **10h,i**, **3**, and **3'** are in between normal k_c and k_t ($t = \text{trans}$) values for dicarbonylchromium complexes. In the Cotton–Kraihanzel approach $k_t = 2k_c$, due to the interaction of the two CO ligands with the same d-orbital in the *trans* case and with different d-orbitals in the *cis* case.²⁹ The k_c 's of the complexes **10h,i**, **3**, and **3'** indicate a significant deviation of the ideal octahedral geometry: the OC–Cr–CO angle is enlarged to achieve a better overlap between metal and olefin orbitals and thus a stronger metal–olefin bond.³⁷

A special case is the bonding of *trans*-2-methyl-1,3-pentadiene in complex **10j**. The CO-stretching vibrations resemble those of **10h** and **10i**. According to the above

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reasoning this implies coordination by the internal double bond, with steric hindrance by the R_2 methyl group at the noncoordinated double bond. It is known, however, that in complex **3j** the terminal double bond has formed the first new C-C bond.⁴ It is therefore concluded that in complex **10j** the olefin coordinates by the terminal double bond. Coordination by this bond, with steric hindrance by the R_4 methyl group at the noncoordinated double bond and by the R_2 methyl group at the coordinated bond, is preferred in this complex over the reverse situation. The combined effect of the steric hindrance by the two methyl substituents (Table II) is then responsible for the large k_c value.

Complexes 3 and 10: Configuration and Temperature Effects. Another steric effect is the influence of the configuration of the diene. Since in the reaction with *cis*-1,3-pentadiene (**k**) **10k** is very easily formed, the rate-determining step for the reaction with this diene must be the formation of the first C-C bond. In complex **3k** the methyl group of the diene is sterically hindered by the triene ligand. A *cis*-*trans* isomerization around C_4 is necessary to form **a** or **3a**, which apparently occurs at temperatures above 193 K but which is in competition with the loss of the triene ligand to form $\text{Cr}(\text{CO})_5(\eta^2\text{-cis-1,3-pentadiene})$. This isomerization is also the retarding factor in the described reaction between $\text{Cr}(\text{CO})_6$ and *cis*-1,3-pentadiene.

The formation of complex **3** also involves a *trans*-*cis* isomerization: the diene unit itself usually has a *s*-*trans* configuration. In complex **3** this unit has a *s*-*cis* form. The energy of the *trans*-*cis* isomerization of free butadiene is ca. 6 kcal/mol; that of 2,3-dimethylbutadiene (**i**) is lower, due to a destabilization of the ground state by methyl-methylene interactions.³⁸ The slow formation of the complexes **3a,d,f,h,j** and the absence of complex **3i** in the LXe experiments imply that the isomerization takes place while the diene is coordinated to the metal: in that case the steric hindrance by the substituents on the diene in **10i** is so large that **3i** can only be formed at a higher temperature. However, before this temperature is reached the competitive back-reaction with CO or decomposition has resulted in the total disappearance of complex **10i**. A comparable steric effect was observed by Michels et al.⁴ after irradiation of **1'** in the presence of the sterically hindered olefins **h**, **i**, or **j** the dicarbonyls **3'h**, **3'i**, and **3'j** and the corresponding tricarbonyls could be isolated, whereas in the case of the dienes **a**, **d**, and **f** only the tricarbonyls were formed. A temperature effect on the isomerization was probably also observed by Kotzian et

al.:³² the photochemical preparation of $\text{Cr}(\text{CO})_4(\text{diene})$ complexes out of $\text{Cr}(\text{CO})_6$ and the desired diene in *n*-hexane proceeded faster and with higher yield if the temperature of the reaction mixture was raised from 233 to 253 K.

The temperature of the reaction mixture also plays a role in the relative amounts of **2'** and **3'**, obtained by Kreiter et al. upon irradiation at temperatures between 220 and 260 K. It turned out that lowering the temperature favored the formation of the final product **2'**.⁴ This may be explained in two ways: according to Scheme I—mentioned in the Introduction—complex **5'** will be sufficiently stabilized at lower temperatures to enable the second C-C bond formation before dissociation of CO; in Scheme II the higher viscosity of the solution will keep the CO, formed in the first step of the reaction, in the vicinity of the complex, favoring the formation of **2'**.

Concluding Remarks

In view of the previous results we conclude that the reaction follows the course presented in Scheme II. An unresolved question is the mechanism of the final reaction step. That no trace of complex **5** has been observed so far does not necessarily mean that the back-reaction of CO and the formation of the second C-C bond proceed according to a concerted mechanism. It is still possible that complex **5** is formed first, followed by the formation of **2**: a higher activation barrier for the reaction of **3** with CO than for the C-C bond formation in **5** or a negligible difference in the influence of the bonding of the olefin ligand on the energies of the CO-stretching vibrations of **2** and **5** might as well explain why complex **5** was not observed.

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Registry No. **1**, 12125-72-3; **2a**, 86039-46-5; **3a**, 138630-41-8; **3d**, 138630-42-9; **3f**, 138630-43-0; **3h**, 138630-44-1; **3j**, 138630-45-2; **6**, 138630-29-2; **8**, 138630-30-5; **10a**, 138630-31-6; **10b**, 138630-32-7; **10c**, 138630-33-8; **10d**, 138630-34-9; **10e**, 138630-35-0; **10f**, 138630-36-1; **10g**, 138630-37-2; **10h**, 138630-38-3; **10i**, 138630-39-4; **10j**, 138630-40-7; **10k**, 138666-08-7; **a**, 2004-70-8; **b**, 115-07-1; **c**, 109-67-1; **d**, 106-99-0; **e**, 624-64-6; **f**, 5194-51-4; **g**, 115-11-7; **h**, 78-79-5; **i**, 513-81-5; **j**, 926-54-5; **k**, 1574-41-0; $\text{Cr}(\text{CO})_3(\eta^6\text{-acenaphthalene})$, 81434-75-5; $\text{Cr}(\text{CO})_5(\eta^2\text{-1,3-pentadiene})$, 138630-46-3.

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