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Photolysis of Group VI metal carbonyls, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in Nujol at 77 K

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Abstract

Photolysis of $\text{M}(\text{CO})_6$, where $\text{M} = \text{Cr, Mo, and W}$, in Nujol mulls at 77 K resulted in the formation of "free" CO and C_4v $\text{M}(\text{CO})_5$ photoproducts. This reaction was found to be photochemically and thermally reversible. Similarly, the photolysis of the metal "half-sandwich" complexes $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in Nujol at 77 K was found to form the corresponding dicarbonyl photoproducts and "free" CO. These reactions were found to be photochemically reversible. $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ were also found to produce small amounts of dinuclear products directly upon photolysis, while $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ formed similar species upon annealing.

Introduction

Inert gas matrix isolation photochemistry is widely recognized as an important technique in the study of transient reaction intermediates in organometallic chemistry. Applications of this methodology to organometallic problems have been reviewed by several workers [1]. In general, there are two limitations to the application of this technique, i.e. the compounds to be studied must be volatile which severely limits the fraction of compounds that can be examined, and the substantial cost of the apparatus for these studies limits their availability to a few groups.

Recently, two of us (AJR and JM) reported a preliminary study of the use of a simple, inexpensive glass cryostat using Nujol mulls at 77 K to study the intermediates generated in the photochemistry of $\text{W}(\text{CO})_6$, $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Ir}(\text{CO})_2$, and

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$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ [2]. In many respects, this Nujol technique parallels and complements the use of hydrocarbon glasses which have been described by Braterman and his coworkers [3], and Hill and Wrighton [4]. We have recently described the use of the Nujol technique to examine the photochemistry of tetrahydrofurfurylcymantrene, which was found to generate both an uncomplexed 16e^- species and an isomeric intramolecularly complexed 18e^- species upon photolysis [5]. We have now expanded upon our earlier, preliminary report to examine the Nujol matrix photochemistry of the Group VI metal carbonyls, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{-Mn}(\text{CO})_3$, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$. Our intent in this work was to adjudicate the applicability of this technique to a broad range of problems in organometallic chemistry. As such, we have selected for study complexes for which the photochemistry is well understood.

Results and discussion

Group VI metal carbonyls

Frozen mulls of the Group VI metal carbonyls, $\text{M}(\text{CO})_6$ where $\text{M} = \text{Cr}, \text{Mo},$ and W , were prepared. IR spectra of these samples at 77 K showed two bands corresponding to the symmetric E_g and asymmetric T_{1u} bands predicted by group theory for an O_h symmetry. Both IR band positions and electronic absorption maxima of these samples were fully consistent with those reported for these compounds in hydrocarbon glasses at 77 K [6] and frozen CH_4 at 12 K [7]. IR band positions and electronic absorption maxima for these compounds are summarized in Tables 1 and 2, respectively, along with data for other matrices for comparison. The IR spectrum of $\text{Mo}(\text{CO})_6$ in Nujol at 77 K is presented in Fig. 1a. The IR spectra of $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ are completely analogous to those of the molybdenum compound [2].

Table 1

Infrared data (in cm^{-1}) for $\text{M}(\text{CO})_6$ and $\text{M}(\text{CO})_5$ in various media

Species	Nujol ^a 77 K	CH_4 ^b 12 K	Hydrocarbon glass ^c 77 K	Symmetry assignment ^d
$\text{Cr}(\text{CO})_6$	not obs.	not obs.		E_g
	1984	1985		T_{1u}
$\text{Cr}(\text{CO})_5$	2085	2093	2087	A_1
	1956	1966	1953	E
	1931	1936	1925	A_1
$\text{Mo}(\text{CO})_6$	2018	not obs.		E_g
	1986	1987		T_{1u}
$\text{Mo}(\text{CO})_5$	2089	2093	2090	A_1
	1962	1967	1961	E
	1927	1926	1922	A_1
$\text{W}(\text{CO})_6$	2013	not obs.		E_g
	1980	1981		T_{1u}
$\text{W}(\text{CO})_5$	2088	2092	2082	A_1
	1953	1957	1951	E
	1926	1926	1921	A_1

^a This study. ^b Data from ref. 7a. ^c Data from ref. 6d. ^d Symmetry assignments based on O_h symmetry for the $\text{M}(\text{CO})_6$ molecules and on C_{4v} for the $\text{M}(\text{CO})_5$ species.

Table 2

Electronic spectral data (in nm) for $M(\text{CO})_6$ and $M(\text{CO})_5$ in various media

Species	Nujol ^a 77 K	Ar ^b 12 K	CH ₄ 12 K	Hydrocarbon glass ^c 77 K
Cr(CO) ₆	238 277	225 277		
Cr(CO) ₅	- ^e 490	237 542	- ^e 489	- ^e 501
Mo(CO) ₆	242 288	228 286		
Mo(CO) ₅	- ^e 412	245 435	- ^e 411	- ^e 413
W(CO) ₆	236 289	225 286		
W(CO) ₅	248 415	239 440	- ^e 413	- ^e 427

^a This study. ^b Data taken from ref. 7c. ^c Data taken from ref. 7d. ^d Data taken from ref. 6d. ^e Band obscured by band overlap or the scattering nature of the medium.

After 15 min of photolysis of the $\text{Mo}(\text{CO})_6$ mull ($250 \text{ nm} < \lambda < 390 \text{ nm}$) the infrared spectrum contained four new bands at 2131, 2089, 1962, and 1927 cm^{-1} , and the electronic spectrum contained a new absorption band at 412 nm. The IR spectra are presented as Figs. 1b and 1c. The weak band at 2131 cm^{-1} is assigned to the known stretching mode of "free" CO in hydrocarbons. The three remaining bands compare favorably in position and intensity with bands observed in CH_4 and hydrocarbon glasses which have been assigned to the A_1 , E , and A_1 modes, respectively, of the C_{4v} $\text{Mo}(\text{CO})_5$ fragment. Spectra observed for the photoproducts of $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ are also consistent with previously reported $M(\text{CO})_5$ fragments with C_{4v} symmetry {6,7}.

The photochemical and thermal behavior of the $M(\text{CO})_5$ fragments have also been examined. $M(\text{CO})_5$ fragments have been found to have electronic absorptions in the range of $400 < 500 \text{ nm}$. Irradiation into this band ($350 \text{ nm} < \lambda$) results in a decrease in intensity of those bands associated with $M(\text{CO})_5$ and "free" CO, and corresponding growth of bands associated with the parent $M(\text{CO})_6$ compounds. This is illustrated in Fig. 1d for $\text{Mo}(\text{CO})_6$. A suggestion as to the nature of this photochemical phenomenon will be discussed below.

Annealing, i.e. a controlled warm-up, of the mulls causes the matrix to soften slightly, allowing the photolysis fragments to migrate and react. Annealing is accomplished by removing the liquid nitrogen from the cold finger of the cryostat, allowing the apparatus to sit for a period of time, e.g. 15 min, and then refreezing the matrix to 77 K. Refreezing is necessary to obtain reliable subtraction spectra. The present apparatus is not equipped with a thermocouple at the cell, thus it is not possible to establish the temperature of the cell after warm-up.

Upon annealing photolyzed samples containing $M(\text{CO})_5$ and "free" CO, the bands of these photoproducts are found to decrease in intensity while the bands of the parent species increase in intensity. No new bands are observed in the annealed samples. A photolysis sequence followed by warm-up for $\text{Mo}(\text{CO})_6$ is illustrated in Fig. 2. The small band which appears at approximately 1974 cm^{-1} in the spectra presented in Fig. 2 appears to be due to an impurity, although we cannot fully rule

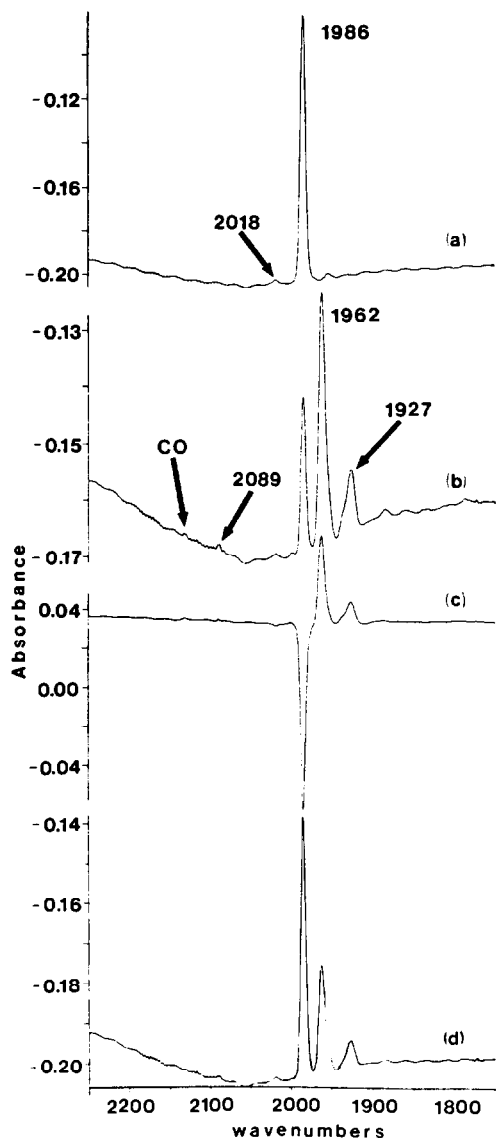


Fig. 1. Infrared spectra of $\text{Mo}(\text{CO})_6$ in a Nujol mull. (a) $\text{Mo}(\text{CO})_6$ in Nujol at 77 K, (b) after 15 min of irradiation ($250 < \lambda < 390 \text{ nm}$), (c) subtraction spectrum (b)–(a), (d) after 15 min of irradiation ($350 \text{ nm} < \lambda$).

out the formation of a small amount of $\text{Mo}(\text{CO})_4$ or dinuclear photoproduct in this case.

Photolysis of samples as Nujol mulls at 77 K yield photoproducts which have analogous IR and electronic bands to those previously reported for CH_4 at 12 K or hydrocarbon glasses at 77 K [7]. It is reasonable to assume that in all cases $\text{M}(\text{CO})_6$ is being photolyzed to give a C_{4v} $\text{M}(\text{CO})_5$ and “free” CO. It is important to emphasize that in the case of the mulls, we do not know how much of the sample has actually dissolved in the Nujol and how much is present as microcrystallites. As

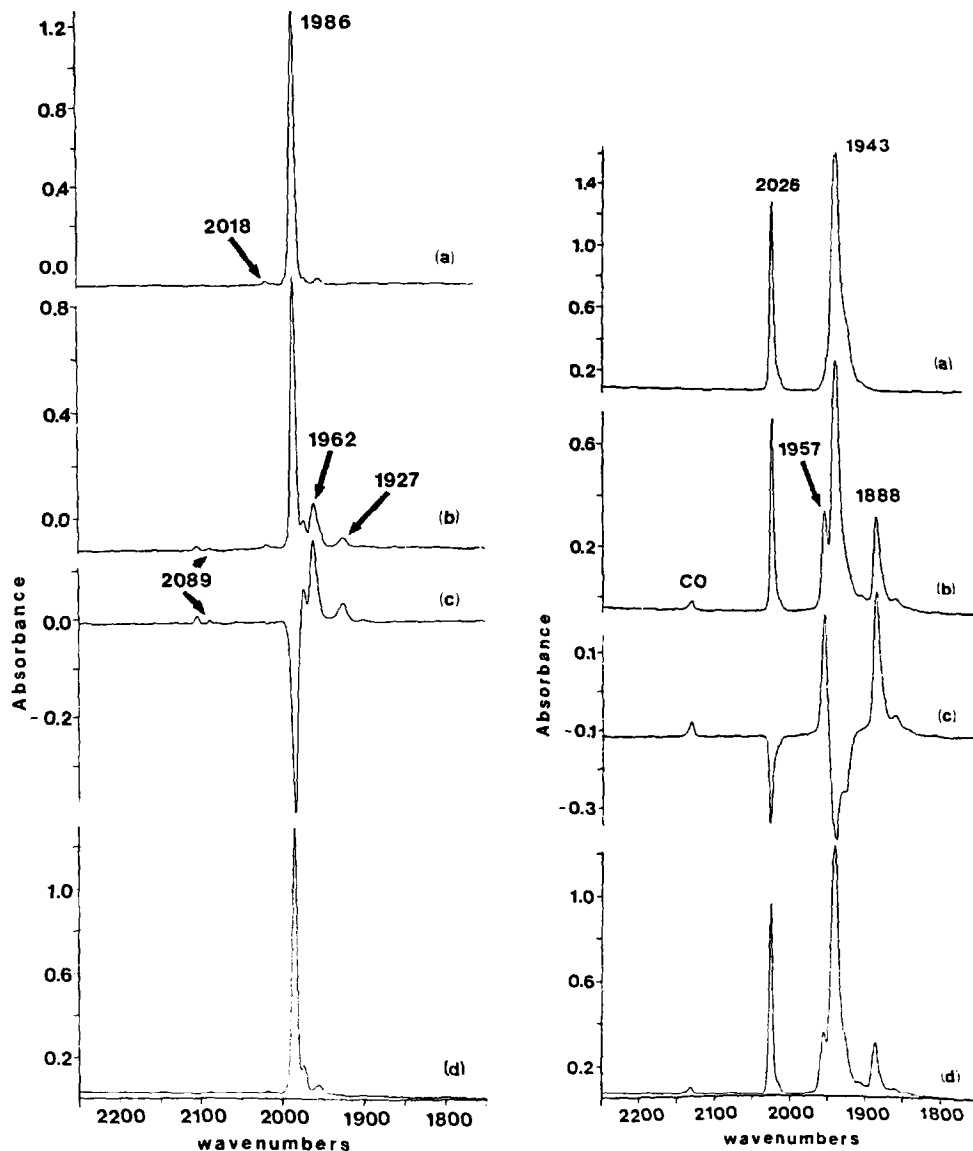


Fig. 2. Infrared spectra of $\text{Mo}(\text{CO})_6$ in a Nujol mull. (a) $\text{Mo}(\text{CO})_6$ in Nujol at 77 K, (b) after 15 min of irradiation ($250 < \lambda < 390 \text{ nm}$), (c) subtraction spectrum (b) - (a), (d) after annealing mull for 10 min.

Fig. 3. Infrared spectra of $(\eta^3\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ in a Nujol mull. (a) $(\eta^3\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ in Nujol at 77 K, (b) after 15 min of irradiation ($250 < \lambda < 390 \text{ nm}$), (c) subtraction spectrum (b) - (a), (d) after 15 min of irradiation ($350 \text{ nm} < \lambda$).

a consequence, it is not clear whether the observed photofragments are surrounded by a hydrocarbon cage, whether they are in their crystalline lattice sites, or both. The stretching frequencies of the carbonyl groups give no information on the environment of these species, however it has been suggested by a referee that the sharpness and number of observed bands argue for a solution environment.

The observed photoreversal and annealing reaction of the $M(CO)_5$ and “free” CO in Nujol mulls parallel reactions observed in frozen gases. In both of these reactions there is a question as to whether the vacant site in the $M(CO)_5$ fragment is occupied by a loosely bound solvent molecule. In the case of a microcrystallite in a mull, and adjacent molecule in the crystal might interact with the vacant site. In either case, photoreversal is reasonably described as the ejection of this weakly bound species and recapture of the CO. During annealing solvent bound and free $M(CO)_5$ fragments may be in equilibrium, making recapture of CO possible.

Arene and cyclopentadienyl metal tricarbonyl complexes

Four “half-sandwich” compounds have been examined in this series including $(\eta^6-C_6H_6)Cr(CO)_3$, $(\eta^5-C_5H_5)Mn(CO)_3$, $(\eta^5-CH_3C_5H_4)Mn(CO)_3$, and $(\eta^5-C_5H_5)Re(CO)_3$. Photolyses of Nujol solutions of tetrahydrofurfurylcymantrene have been reported separately [5]. $(\eta^5-C_5H_5)Mn(CO)_3$ and $(\eta^5-CH_3C_5H_4)Mn(CO)_3$ appear to form true solutions in Nujol, whereas the chromium and rhenium complexes appeared to form microcrystalline mulls. As in the case of $M(CO)_6$ it is not possible to estimate the relative amounts of compounds that may be present as microcrystalline particles and that dissolved. A summary of the IR bands of these compounds and all of their photochemical and thermal products are presented in Tables 3 and 4 along with results of analogous studies in frozen gases [8] and hydrocarbon glasses [4,9].

$(\eta^5-C_5H_5)Mn(CO)_3$ in Nujol solution at 77 K shows two bands, an A_1 band at 2027 cm^{-1} and a broader E band at 1943 cm^{-1} as shown in Fig. 3a. Electronic absorption bands of this compound were found at 327 nm and 243 nm. Upon irradiation of this solution for 15 min into the electronic absorption bands ($25\text{ nm } \lambda < 390\text{ nm}$) new IR bands appeared at 2132, 1957, and 1888 cm^{-1} as shown in Figs. 3b and 3c. As noted above, the band at 2132 cm^{-1} is identified as “free” CO. By comparison with results of a photolysis study of cymantrene in gas matrices and frozen glasses, the remaining two peaks were assigned to the carbonyl loss fragment, $(\eta^5-C_5H_5)Mn(CO)_2$. No additional bands were observed in the carbonyl stretching region after this photolysis.

Photoreversal of the solution for 15 min ($350\text{ nm} < \lambda$) caused a decrease in intensity of the photoproduct bands and corresponding increase in the intensities of the parent bands as shown in Fig. 3d.

In a separate experiment, a sample of $(\eta^5-C_5H_5)Mn(CO)_3$ which had been photolyzed as above, was annealed by allowing the solution to warm for 15 min followed by refreezing to 77 K. Similar annealing experiments by Hill and Wrighton [4] are reported to result in simple recombination of $(\eta^5-C_5H_5)Mn(CO)_2$ and “free” CO. As expected, in our experiment the intensities of the photoproduct bands are observed to decrease with a concurrent increase in the intensity of the parent bands. However, inspection of the spectrum after annealing revealed the presence of a new species with bands at 1991, 1955, 1908, and 1770 cm^{-1} . This spectrum is presented in Fig. 4. The band at 1770 cm^{-1} is in the bridging carbonyl region of the spectrum suggesting that the new species is dinuclear. Poliakoff and coworkers [10] have conducted flash photolysis studies of $(\eta^5-C_5H_5)Mn(CO)_3$ and have observed the formation of a species with carbonyl stretching bands at 1993, 1955, 1934, 1907, and 1777 cm^{-1} . This species is believed to be $(\eta^5-C_5H_5)_2Mn_2(CO)_5$ which is the manganese analogue of the isolable Re complex $(\eta^5-C_5H_5)_2Re_2(CO)_5$ [11]. The

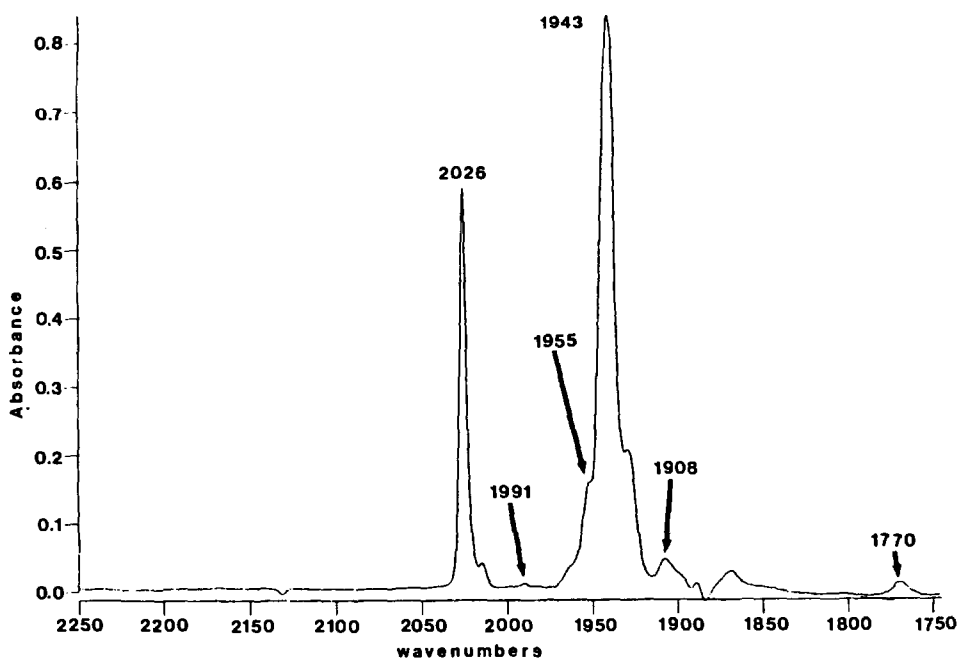


Fig. 4. Infrared spectrum of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ in a Nujol mull at 77 K after 15 min of irradiation ($250 < \lambda < 390$ nm) followed by 15 min of annealing. Bands attributed to $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ have been subtracted out.

strong correlation between the bands observed by Poliakoff and his coworkers and those observed in this work indicate that the dinuclear manganese species is formed upon annealing of the Nujol solution. In our case, the 1934 cm^{-1} region is obscured by a parent band at 1943 cm^{-1} .

A series of photochemical and annealing studies conducted with Nujol solutions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}(\text{CO})_3$ gave results which were fully consistent with those of the parent compound. The IR spectral band positions for $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_2$ and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_5$ are presented in Tables 3 and 4.

Hill and Wrighton [4] have reported that the poor solubility of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in low temperature methylcyclohexane precluded study of the photochemical behavior of the compound. $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in Nujol at 77 K was found to have an IR spectrum consisting of two bands at 1982 cm^{-1} and 1915 cm^{-1} (Table 3) as shown in Fig. 5a. The electronic spectrum of this compound had bands at 313 nm and 257 nm. Photolysis for 15 min ($250\text{ nm} < \lambda < 390\text{ nm}$) resulted in the appearance of four new bands at 2132, 1925, 1870, and 1778 cm^{-1} as shown in Fig. 5b. Subtraction of the parent bands (Fig. 5c) revealed two additional small bands at 1937 and 1885 cm^{-1} . The band at 2132 was assigned to "free" CO. Those at 1925 and 1870 cm^{-1} were assigned to the dicarbonyl photochemical fragment on the basis of previous studies in inert gas matrices [8]. The remaining bands were attributed to a previously unobserved dinuclear species, $(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}_2(\text{CO})_5$, which is the chromium analogue of the manganese dinuclear compounds described above (Table 4). Photolysis of the mull for 15 min at longer wavelength ($350\text{ nm} < \lambda$) resulted in a decrease in

Table 3

Infrared data (in cm^{-1}) for half-sandwich complexes in various media

Complex	Nujol ^a 77 K	CH ₄ ^b 12 K	Hydrocarbon glass 77 K ^c	Hydrocarbon glass 100 K ^d
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$	1980	1983	1956	
	1909	1913	1871	
$(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2$	1921	1925		
	1868	1870		
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$	2027	2029	2026	2027
	1943	1943	1938	1942
$(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$	1957	1961	1955	1950
	1888	1893	1886	1880
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$	2023		2022	
	1939		1936	
$(\eta^5\text{-CH}_3\text{CH}_2\text{C}_4\text{H}_4)\text{Mn}(\text{CO})_2$	1953		1950	
	1884		1881	
$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$	2029			2028
	1934			1934
$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2$	1947	1949		1946
	1879	1880		1879

^a This study. ^b Data taken from refs. 8b and 12. ^c Data taken from ref. 6c. ^d Data taken from ref. 4.

the bands associated with “free” CO and the dicarbonyl photochemical fragment and concurrent increase in the bands of the parent compound (Fig. 5d). The bands associated the dinuclear species were unaffected by long wavelength photolysis.

A photolyzed mull of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ was annealed for 15 min and then refrozen to 77 K. As expected, the “free” CO bands and dicarbonyl photoproduct bands decreased and the bands of the parent compound increased. In addition, those bands associated with the dinuclear compound increased somewhat during annealing.

In order to confirm the assignment of the bands which we have attributed to a dinuclear species, a sample of ¹³CO labeled $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ was prepared. The IR spectrum of the Nujol mull of this material at 77 K reveals a complex set of bands to be expected for a sample containing a mixture of ¹²CO and ¹³CO. IR spectrum of this mixture after photolysis for 15 min ($250 < \lambda < 390$ nm) clearly showed bands at 2132 cm^{-1} and 2085 cm^{-1} associated with “free” ¹²CO and ¹³CO,

Table 4

Infrared data (in cm^{-1}) for dinuclear species in various media

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_5$ ^a	1993	1955	1934	1907	1777
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_5$ ^b	1991	1955	– ^d	1908	1770
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Mn}_2(\text{CO})_5$ ^b	1973	1948	1920	1885	1762
$(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}_2(\text{CO})_5$ ^b	1989	1937	– ^d	1885	1778
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_5$ ^c	1992	1956	1923	1904	1745
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_5$ ^b	1992	– ^d	– ^d	– ^d	1773

^a Spectrum recorded in cyclohexane at 298 K. Data taken from ref. 11a. ^b This study. ^c Spectrum recorded in cyclohexane at 298 K. Data taken from ref. 10. ^d Band obscured by other bands.

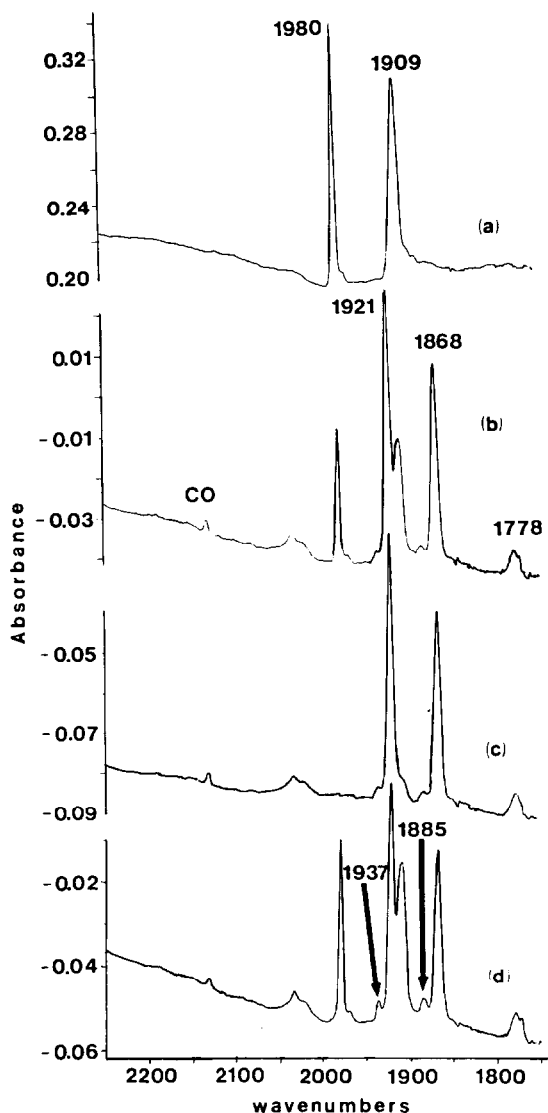


Fig. 5. Infrared spectra of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in a Nujol mull. (a) $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in Nujol at 77 K, (b) after 15 min of irradiation ($250 < \lambda < 390$ nm), (c) subtraction spectrum (b)–(a), (d) after 15 min of irradiation ($350 \text{ nm} < \lambda$).

respectively, and bands at 1778 cm^{-1} and 1735 cm^{-1} associated with bridging ^{12}CO and ^{13}CO , respectively. The appearance of only two bands in the bridging carbonyl regions of the isotopically mixed compound permits us to conclude that the dinuclear photoproduct has only one bridging carbonyl group. Two or more bridging carbonyls would require a complex set of coupled bands associated with isotopically mixed species. The complexity of the terminal carbonyl region precluded our extracting useful information from the subtraction of parent bands from photoproduct bands.

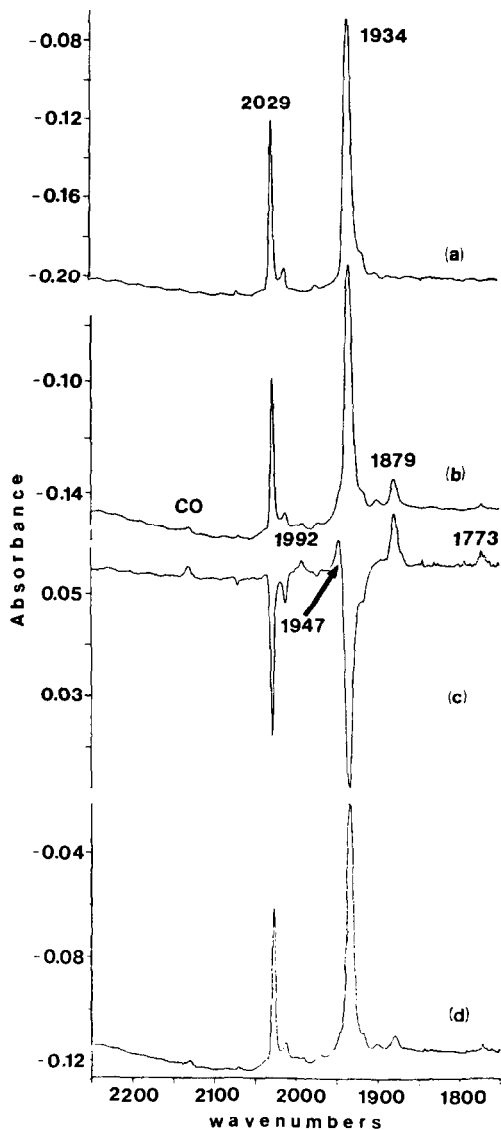


Fig. 6. Infrared spectra of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in a Nujol mull. (a) $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in Nujol at 77 K, (b) after 15 min of irradiation ($250 < \lambda < 390$ nm), (c) subtraction spectrum (b) - (a), (d) after annealing mull for 15 min.

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ dispersed in Nujol was found to have two strong IR bands at 2029 and 1934 cm^{-1} (Table 3) as shown in Fig. 6a and an electronic absorption band at 260 nm. Photolysis into this electronic absorption band for 15 min ($250 < \lambda < 390$ nm) resulted in the appearance of five new bands at 2132, 1992, 1947, 1879, and 1773 cm^{-1} (Figs. 6b and 6c). The band at 2132 cm^{-1} was assigned to "free" CO, while those at 1947 cm^{-1} and 1879 cm^{-1} were attributed to the dicarbonyl photolysis product. These bands are consistent with those reported by Hill and Wrighton [4] for $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2$ in methylcyclohexane glasses. The

bands at 1992 and 1773 cm^{-1} can probably be assigned the dinuclear species, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_5$ (Table 4), which has been isolated by Graham [11a], Caulton [11b] and their coworkers from the photolysis of solutions of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$. Bands attributed to a dinuclear species have also been observed upon long term photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ in N_2 matrices [12]. IR carbonyl stretching bands for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}_2(\text{CO})_5$ in cyclohexane have been reported to be at 1992, 1956, 1923, 1904, and 1745 cm^{-1} . We believe that the expected bands at 1956, 1923 and 1904 cm^{-1} are obscured in our sample. Annealing of the mull resulted in decreases in the intensities of all the photoproduct bands and increases in the bands of the parent compound (Fig. 6d).

Irradiation for 15 min ($250 < \lambda < 390$ nm) as before, followed by longer wavelength irradiation ($350 \text{ nm} < \lambda$) was found to decrease the intensity of bands associated with "free" CO and the dicarbonyl photoproduct and increase the intensity of the bands of the product materials. The band at 1992 cm^{-1} was found to decrease in intensity while that at 1773 cm^{-1} appears to decrease and shift to longer wavelengths. It is not clear whether long wavelength photolysis of the initially formed dinuclear product is driving a geometric change, i.e. *trans* to *cis*, or whether a second isomer is initially present which is only visible after partial loss of the first product.

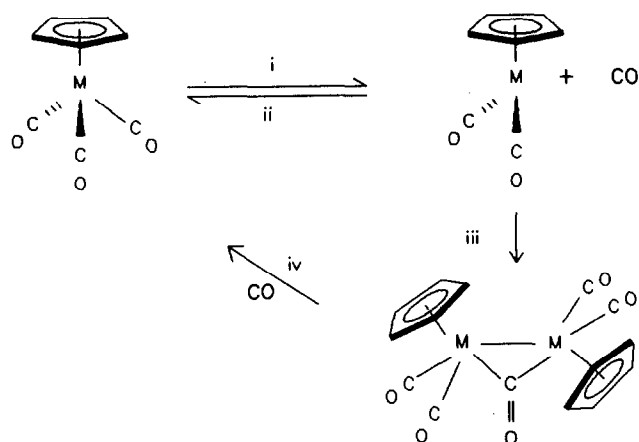
Conclusions

Photolysis of Group VI metal carbonyls, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$, and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ as solutions or mulls in Nujol at 77 K has been shown to yield products which closely parallel those observed when these materials are photolyzed in frozen gases at 12 K, or in hydrocarbon glasses at 77 K. In all cases, the expected carbon monoxide loss fragments are observed. Long wavelength photolysis and annealing behavior of the Group VI metal carbonyls results in simple reversal of the carbonyl ejection photolysis. For the arene and cyclopentadienyl metal tricarbonyl complexes, dinuclear products are formed in initial photolysis or annealing. These products probably result from reactions of dicarbonyl photoproducts with parent tricarbonyl complexes. These reactions are summarized in Scheme 1. It may be significant that no dinuclear compound is observed upon initial photolysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ which apparently form solutions in Nujol, while $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$, which are present as microcrystalline mulls, do give these products upon initial photolysis.

We believe that the use of Nujol mulls at 77 K provides a broadly applicable technique for the study of photochemical intermediates which bridges the gap between frozen gases and solution studies. The technique is applicable to nonvolatile organometallic and inorganic complexes, and can be used to study reactions of photoproducts and other species under controlled annealing conditions.

Experimental technique

Photochemistry was carried out in a glass cryostat as illustrated in Fig. 7 [13]. The copper sample cell screws into a Kovar (alloy)-to-glass graded seal at the bottom of the liquid nitrogen well. Good thermal contact is provided by indium



Scheme 1. (i) Photolysis with Filter ($250 \text{ nm} < \lambda < 390 \text{ nm}$). (ii) Photolysis with Filter ($350 \text{ nm} < \lambda$) or annealing. (iii) For $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3$ dimer is formed upon initial photolysis. For $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ annealing is required. (iv) On annealing.

seals between the cell and the graded seal, and between the cell and the windows. CaF_2 windows were used both in the cell and as the exterior windows of the cryostat because of their good optical transparency over the region 160 to 10,000 nm (62,500

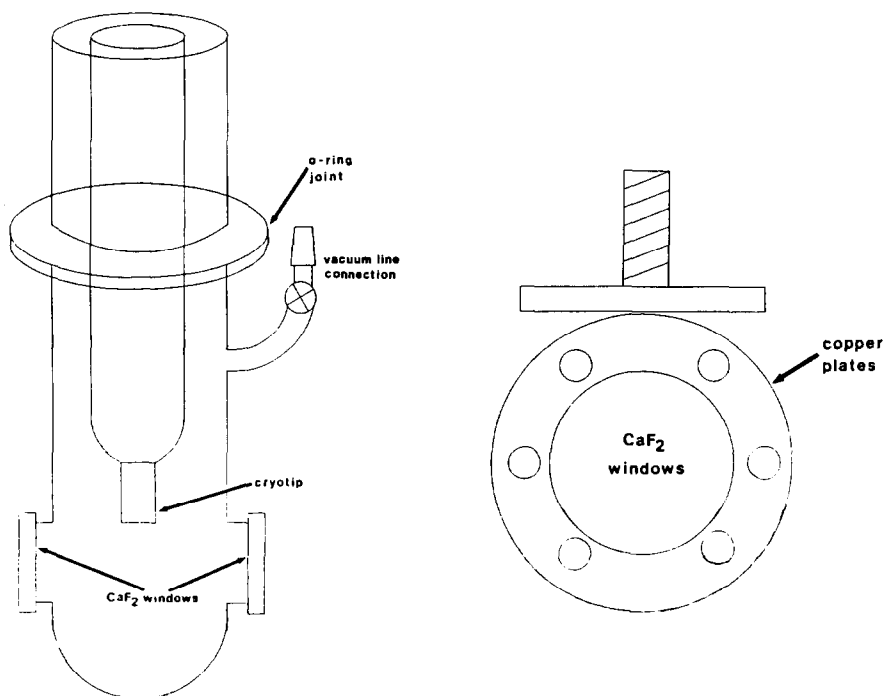


Fig. 7. Diagram of Cryostat and Cell Holder. 85 mm "o" ring is secured with clamps during evacuation. 38 mm \times 6 mm CaF_2 windows are secured with Halocarbon grease, Series 1500. IR cell windows are 24 \times 4 mm CaF_2 . The copper cell holder screws into the base of the cryotip. Indium gaskets are used between the cell holder and the cryotip and between the cell holder and the windows for good heat transfer.

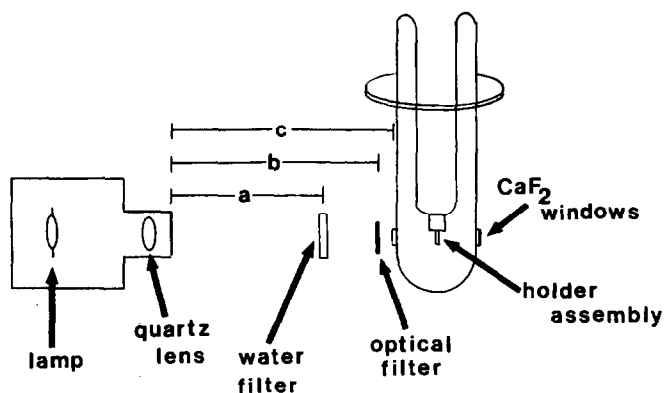


Fig. 8. Schematic of Photolysis Bench. Distances used in this study were: $a = 17.5$, $b = 25.4$, $c = 27.9$ cm. Note: Distances will vary with lamp power and age. In this work a 350 Watt high pressure Hg lamp was used.

to $1,000\text{ cm}^{-1}$), and also because of their resistance to fogging in moist air. The exterior windows were mounted onto the cryostat with a fluorocarbon wax (Halocarbon grease Series 1500, Halocarbon Products Corp.) which provided a good vacuum seal. The apparatus can be easily moved between the photolysis bench, FT-IR and UV-visible spectrometers. A Bio-Rad FTS-15/80 FT-IR spectrometer and a Cary 2200 UV-visible spectrometer were used in these studies.

Photochemistry was carried out using a UVP, Inc. 350 watt high pressure mercury lamp. The broad band output from this lamp was directed through a series of filters as shown in Fig. 8 which permitted selection of irradiation wavelengths consistent with the absorption bands in the electronic spectra of the molecules of interest. Filters employed were: ($250 < \lambda < 390\text{ nm}$) Hoya filter U330, and ($\lambda > 350\text{ nm}$) Corion filter LG-350. A 20 mm quartz circular cell filled with water was used in all experiments to remove heat and IR radiation from the incident light on the sample.

Sample preparation for photochemistry parallels normal mull methods with approximately 1 mg of sample being dispersed in 65–80 mg of Nujol. A wide variation of sample solubility was observed with some samples, such as cymantrene giving true solutions, while others, such as the Group VI metal carbonyls, gave microcrystalline mulls. We presume that in all cases some of the compound dissolves in the Nujol. The nature of the sample, solution or mull, does not appear to significantly influence either the photochemistry or the spectra of the observed intermediates.

Concentrations of solution samples were sufficiently high to allow the cell to be used without spacers. Low solubility materials or mulls with low intensity bands generally required the use of teflon spacers. When spacers were used, it became necessary to freeze the mull prior to evacuating the cryostat to avoid losing the mull from the cell during pump-down. In these cases, the cryostat was flushed with dry nitrogen for 15–20 min prior to freezing to purge water vapor from the cryostat.

$\text{M}(\text{CO})_6$, where $\text{M} = \text{Cr}, \text{Mo},$ and W , $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ and $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ were purchased from Strem and used as received. Nujol was purchased from Fisher and used as received.

[15] were prepared by standard literature routes. $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(^{13}\text{CO})$ was prepared by photolysis of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ in benzene under an atmosphere of ^{13}CO by analogy to a reported procedure [16].

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References

- 1 (a) A.J. Rest, *J. Mol. Struct.*, 222 (1990) 87; (b) A.E. Stiegman and D.R. Tyler, *Coord. Chem. Rev.*, 63 (1985) 217; (c) T.J. Meyer and J.V. Caspar, *Chem. Rev.*, 85 (1985) 187; (d) R.B. Hitam, K.A. Mahmoud and A.J. Rest, *Coord. Chem. Rev.*, 55 (1984) 1; (e) G.L. Geoffroy and M.S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979; (f) M.S. Wrighton, *Chem. Rev.*, 74 (1974) 401; (g) W.L. Waltz and R.G. Sutherland, *Chem. Soc. Rev.*, 2 (1972) 217.
- 2 J. Mascetti and A.J. Rest, *J. Chem. Soc., Chem. Commun.*, (1987) 221.
- 3 M.J. Boylan, J.D. Black and P.S. Braterman, *J. Chem. Soc., Dalton Trans.*, (1980) 1646; (b) M.J. Boylan, J.D. Black, P.S. Braterman and A. Fullarton, *ibid.*, (1980) 1651.
- 4 R.H. Hill and M.S. Wrighton, *Organometallics*, 6 (1987) 632.
- 5 T.E. Bitterwolf, K.A. Lott and A.J. Rest, *J. Organomet. Chem.*, 408 (1991) 137.
- 6 (a) I.W. Stolz, G.R. Dobson and R.K. Sheline, *J. Am. Chem. Soc.*, 84 (1962) 3589; (b) *idem*, *ibid.*, 85 (1963) 1013; (c) M.J. Boylan, P.S. Braterman and A. Fullarton, *J. Organomet. Chem.*, 31 (1971) C29; (d) M.J. Boylan, J.D. Black and P.S. Braterman, *J. Chem. Soc., Dalton Trans.*, (1980) 1646; (e) O.L. Chapman, J. Pacansky and P.W. Wojtkowski, *J. Chem. Soc., Chem. Commun.*, (1973) 681.
- 7 (a) R.N. Perutz and J.J. Turner, *Inorg. Chem.*, 14 (1975) 262; (b) J.K. Burdett, M.A. Graham, R.N. Perutz, M. Poliakoff, A.J. Rest, J.J. Turner and R.F. Turner, *J. Am. Chem. Soc.*, 97 (1975) 4805; (c) M.A. Graham, M. Poliakoff and J.J. Turner, *J. Chem. Soc. (A)*, (1971) 2939; R.M. Perutz and J.J. Turner, *J. Am. Chem. Soc.*, 92 (1975) 4971.
- 8 (a) N.J. Fitzpatrick, A.J. Rest and D.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1979) 351; (b) A.J. Rest, J.R. Sodeau and D.J. Taylor, *J. Chem. Soc., Dalton Trans.*, (1978) 651.
- 9 (a) J.D. Black, M.J. Boylan and P.S. Braterman, *J. Chem. Soc., Dalton Trans.*, (1981) 73; (b) P.S. Braterman and J.D. Black, *J. Organomet. Chem.*, 39 (1972) C3; (c) O. Crichton and A.J. Rest, *J. Chem. Soc., Dalton Trans.*, (1973) 536.
- 10 B.S. Creaven, A.J. Dixon, J.M. Kelly, C. Long and M. Poliakoff, *Organometallics*, 6 (1987) 2600.
- 11 (a) A.S. Foust, J.K. Hoyano and W.A.G. Graham, *J. Organomet. Chem.*, 32 (1971) C65; (b) L.N. Lewis and K.G. Caulton, *Inorg. Chem.*, 20 (1981) 1139.
- 12 J. Chetwynd-Talbot, P. Grebenik, R.N. Perutz and M.H.A. Powell, *Inorg. Chem.*, 22 (1983) 1675.
- 13 R.H. Hooker, Ph.D. Thesis, University of Southampton, Southampton, 1989.
- 14 R.B. King and R.H. Reimann, *Inorg. Chem.*, 14 (1976) 179.
- 15 M.D. Rausch, *J. Org. Chem.*, 39 (1974) 1787.
- 16 R.B. Hitam, R. Narayanaswamy and A.J. Rest, *J. Chem. Soc., Dalton Trans.*, (1983) 1351.