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The photochemistry of $(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3$ in frozen gas matrices at *ca.* 12 K

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Received 10th October 2002, Accepted 29th October 2002
First published as an Advance Article on the web 7th March 2003

We have investigated the photochemistry of $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ in low temperature matrices. In an argon matrix we see CO loss from only the Mn end of the molecule and $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ is the only observed photoproduct. However, in a N_2 matrix photosubstitution is observed at both metal centres and we were able to identify $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_2(N_2)]$, $[(CO)_3(N_2)Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ and $[(CO)_2(N_2)_2Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$. In all these experiments, characterisation of photoproducts was aided by comparison with experiments using the mononuclear fragments $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ and $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_4]$ where we were able to characterise $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2]$, $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_2(N_2)]$, $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_3(N_2)]$ and $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$.

Introduction

There is continuing interest in the reaction mechanism of photochemical substitution reactions of bimetallic or higher nuclearity metal carbonyl compounds.[1] The photochemistry of homonuclear complexes, such as $[CpM(CO)_3]_2$ (M = Cr, Mo and W)[2–19] and $[CpFe(CO)_2]_2$,[20–35] has been extensively studied.[36] However, there have been comparatively few studies on the photochemistry of heterodinuclear complexes. Wrighton and co-workers found that irradiation of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2\text{-}Mn(CO)_5]$ (R = H, Me) produced both homolytic cleavage of the Fe–Mn bond[37,38] and CO loss.[39] Irradiation of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2Mn(CO)_5]$ in the presence of PR_3 (R = Ph, OPh) resulted in formation of $[(\eta^5\text{-}C_5R_5)Fe(CO)_2Mn(CO)_4(PR_3)]$.[39] Irradiation of $MnRe(CO)_{10}$ in the presence of PPh_3 led to the Mn-substituted species $[Mn(CO)_4(PPh_3)Re(CO)_5]$.[40] Firth *et al.* found that photolysis of $[MnRe(CO)_{10}]$ led to the formation of $[(CO)_4Mn(\mu\text{-}CO)Re(CO)_4]$ with CO being lost exclusively from the Mn centre.[41] By contrast, *thermal* substitution of CO in $[MnRe(CO)_{10}]$ also occurs at the Re.[42,43] More recently, Stufkens and co-workers[44] showed that photochemical substitution of PPh_3 into $[(CO)_5ReMn(CO)_3(\alpha\text{-diimine})]$ led exclusively to $[(CO)_5ReMn(CO)_2(PPh_3)(\alpha\text{-diimine})]$ through photo-dissociation of CO from Mn.

In this paper, we investigate the photochemistry of the compound $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**1**). The synthesis of **1** was recently reported by Lyons and Wright and is documented in this paper for completeness.[45a] Unlike the compounds listed above, this complex does not contain a metal–metal bond. In the solid state the Mn and Cr carbonyl moieties lie above and below the phenyl–allyl plane of the ligand, Fig. 1.[45b]

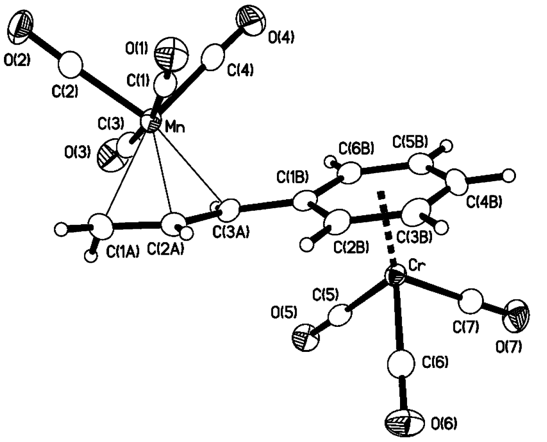

Fig. 1 Ellipsoid plot drawing of **1** with 50% probability displacement ellipsoids.

Although the photochemistry of this dinuclear compound is largely unexplored, the photochemistry of the constituent mononuclear fragments is known. For instance, the photochemistry of $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$ has been examined in low temperature matrices as part of elegant experiments by Rest and co-workers[46] on the precursor $[(\eta^1\text{-}C_3H_5)Mn(CO)_5]$ species. Photolysis of $[(\eta^1\text{-}C_3H_5)Mn(CO)_5]$ isolated at high dilution in Ar and CH_4 matrices at 12 K resulted in ejection of a CO ligand together with a σ–π rearrangement of the η^1-allyl ligand to generate the complex $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$. Subsequent UV photolysis led to loss of a second carbonyl ligand and formation of the sixteen-electron species $[(\eta^3\text{-}C_3H_5)Mn(CO)_3]$. The same initial photodecarbonylation and allyl rearrangement was observed in a nitrogen matrix, with formation of the complex $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$. Extended photolysis led to new ν(CO) and ν(NN) bands, which were assigned to $[(\eta^3\text{-}C_3H_5)Mn(CO)_3(N_2)]$. The photochemistry of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in Ar matrices has also been investigated by Rest and co-workers.[47] The unsaturated species $[(\eta^6\text{-}C_6H_6)Cr(CO)_2]$ was formed as the primary photoproduct. In a nitrogen matrix, $[(\eta^6\text{-}C_6H_6)Cr(CO)_2]$ was not observed but instead new ν(CO) and ν(NN) bands were generated which were assigned to the nitrogen substituted complex $[(\eta^6\text{-}C_6H_6)Cr(CO)_2(N_2)]$, which was subsequently shown to be a stable isolable complex. More recently the photochemistry of $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ has been studied in alkane solution at room temperature by Creaven *et al.*[48] who observed $[(\eta^6\text{-}C_6H_6)Cr(CO)_2(n\text{-heptane})]$ in *n*-heptane solution at room temperature.

In this paper, our strategy has been to use these mononuclear compounds to investigate the photochemistry of the dinuclear complex. We begin by showing that the two metal carbonyl moieties are essentially vibrationally uncoupled. We then analyse the spectra of the primary photoproducts as the superposition of the spectra of two mononuclear fragments.

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DOI: 10.1039/b206697a

Results and discussion

Fig. 2 shows the infrared spectra of [(CO)$_4$Mn(μ-η^3:η^6-C$_3$H$_4$C$_6$H$_5$)Cr(CO)$_3$] (**1**), [Mn(η^3-C$_3$H$_4$C$_6$H$_5$)(CO)$_4$] (**2**) and [(η^6-C$_6$H$_5$C$_2$H$_5$)Cr(CO)$_3$] (**3**), all in *n*-heptane solution, at room temperature. In the absence of vibrational coupling between the metal centres, the coaddition of the carbonyl regions of the infrared spectra of the mononuclear compounds should be very similar to that of the dinuclear compound. It is clear from Fig. 2 this is indeed the case; the superimposed IR spectra of the mononuclear complexes gives a band pattern very similar to the spectrum of the dinuclear compound. It also clear from Fig. 2 that the superimposition of their individual spectra yielded a set of *ν*(CO) bands with relative intensities which match very closely the pattern of *ν*(CO) bands in the spectrum of **1**. We concluded therefore that there is no appreciable vibrational coupling between the two metal centres. Thus, the manganese and chromium mononuclear compounds can be used as a model of the dinuclear compound to aid interpretation of spectra. Therefore, each of the *ν*(CO) bands of the dinuclear complex can be assigned to the vibrations of the carbonyl ligands on the two metal centres.

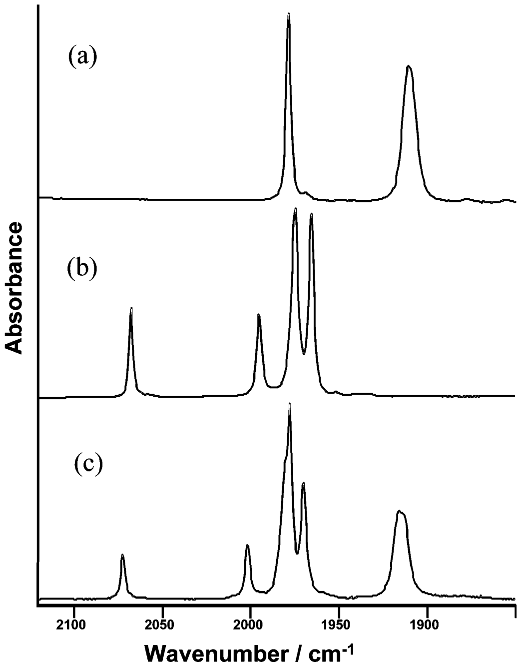

Fig. 2 FTIR spectra of (a) **3** (b) **2** and (c) **1** in *n*-heptane solution at room temperature.

As explained above, the photochemistry of [(η^3-C$_3$H$_5$)-Mn(CO)$_4$] and [(η^6-C$_6$H$_6$)Cr(CO)$_3$] have been examined in low temperature matrices by Rest and co-workers. We now extend this work to **2** and **3** which we then use as models to unravel the photochemistry of **1**.

(a) Photolysis of (η^3-C$_3$H$_4$C$_6$H$_5$)Mn(CO)$_4$ (2) isolated in an Ar matrix

Fig. 3(a) shows the IR spectrum of **2** in an Ar matrix at high dilution at 12 K. Four *ν*(C–O) bands are observed, 3a′ + a″, consistent with the complex having C_s symmetry. These bands were much narrower than those in solution spectra but they are split by matrix effects. UV irradiation (λ > 300 nm) resulted in depletion of the parent bands and growth of three new bands at 2032, 1956 and 1930 cm^{-1}, see Fig. 3(b). These changes can be seen more clearly in the subtraction spectrum, Fig. 3(c). Further UV irradiation caused more depletion of the parent together with large increases in the intensity of these new bands which all grew in at the same rate during the course of the experiment and indicate the formation of a single species. An additional band at 2138 cm^{-1} is readily assigned to the presence of free carbon monoxide. The three new *ν*(C–O) bands are shifted to lower wavenumbers than the parent molecule bands and are assigned to [(η^3-C$_3$H$_4$C$_6$H$_5$)Mn(CO)$_3$] (**4**) by comparison with Rest's data for [(η^3-C$_3$H$_5$)Mn(CO)$_3$], see Table 1. Irradiation of the matrix with visible light (λ > 450 nm) caused the intensity of the bands due to **4** to decrease and the parent bands to be regenerated. This reversal could also be initiated by annealing the matrix to *ca.* 38 K, for five minutes.

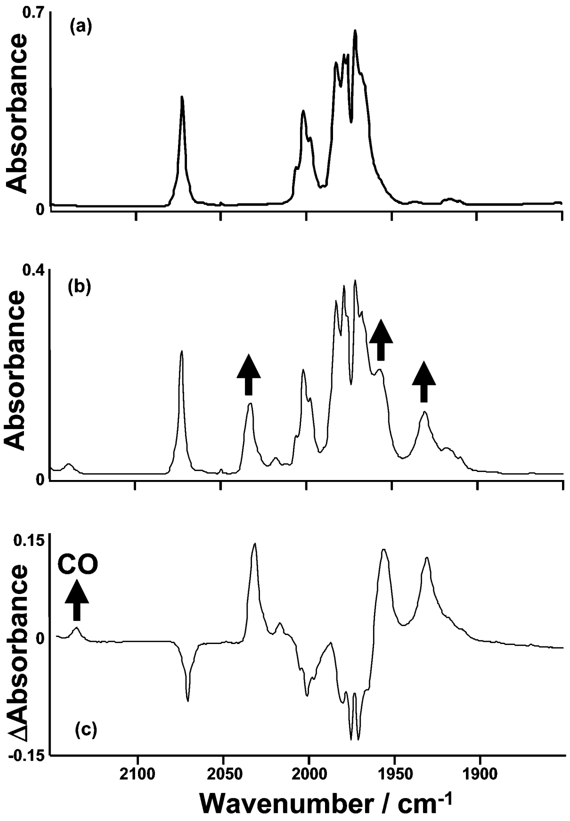

Fig. 3 FTIR spectra of **2** isolated in an argon matrix at 12 K (a) before photolysis and (b) 30 minutes after photolysis (λ > 300 nm). (c) This spectrum was generated by subtraction of (a) from (b). The negative *ν*(C–O) bands show depletion of parent and the positive absorptions show the growth of three new product bands assigned to [(η^3-C$_3$H$_4$C$_6$H$_5$)Mn(CO)$_3$] (**4**).

The bands for **4** are on average 4 cm^{-1} lower than those for [(η^3-C$_3$H$_5$)Mn(CO)$_3$], a shift which can be rationalised by the increase in electron donation onto the metal from the phenyl ring thus weakening the C–O bonding. There was no evidence for ejection of a second carbonyl ligand; **4** was the only photoproduct seen during the course of the experiment.

(b) Photolysis of [(η^3-C$_3$H$_4$C$_6$H$_5$)Mn(CO)$_4$] (2) in nitrogen matrices

The spectrum of **2**, isolated in a nitrogen matrix, was very similar to that observed in an argon matrix, Table 1. UV irradiation (λ > 300 nm) resulted in the formation of a photoproduct with two new *ν*(C–O) absorptions, at 2032 and 1960 cm^{-1} (broad), Fig. 4(a). At the same time, two bands grew in at higher wavenumbers, a band at 2138 cm^{-1} due to free CO, and a weak band at 2249 cm^{-1} which was assigned to a *ν*(N–N) vibration. The growth of these suggests that the photoproduct is most likely to be [(η^3-C$_3$H$_4$C$_6$H$_5$)Mn(CO)$_3$(N$_2$)] (**5**).

The exact structure of **5** is not known, since the N$_2$ group could be in either an axial or equatorial position. Both axially or equatorially substituted products would have C_s symmetry and should display three *ν*(CO) bands, 2a′ + a″. However, only two *ν*(CO) bands were observed but this is could due to failure

Table 1 IR frequencies (cm^{-1}) of Mn complexes observed in low-temperature matrices

Complex	Matrix Ar	Matrix N_2	Assignment
$[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_4]$ (**2**)	2072	2073	$\nu(CO)$
	2001	2003}[a] 1998}[a]	$\nu(CO)$
	1981	1982	$\nu(CO)$
	1971	1975	$\nu(CO)$
$[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$[b]	2083		$\nu(CO)$
	2004}[a] 2002}[a]		$\nu(CO)$
	1986		$\nu(CO)$
	1972		$\nu(CO)$
$[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_3]$ (**4**)	2032		$\nu(CO)$
	1956		$\nu(CO)$
	1930		$\nu(CO)$
$[(\eta^3\text{-}C_3H_5)Mn(CO)_3]$[b]	2041		$\nu(CO)$
	2060		$\nu(CO)$
	1933		$\nu(CO)$
$[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_3(N_2)]$ (**5**)		2251	$\nu(NN)$
		1960	$\nu(CO)$
$[(\eta^3\text{-}C_3H_5)Mn(CO)_3(N_2)]$[b]		2257	$\nu(NN)$
		2019	$\nu(CO)$
		1960	$\nu(CO)$
$[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$ (**6**)		2212	$\nu(NN)$
		2180	$\nu(NN)$
		1949	$\nu(CO)$

[a] Matrix split. [b] Ref. 7.

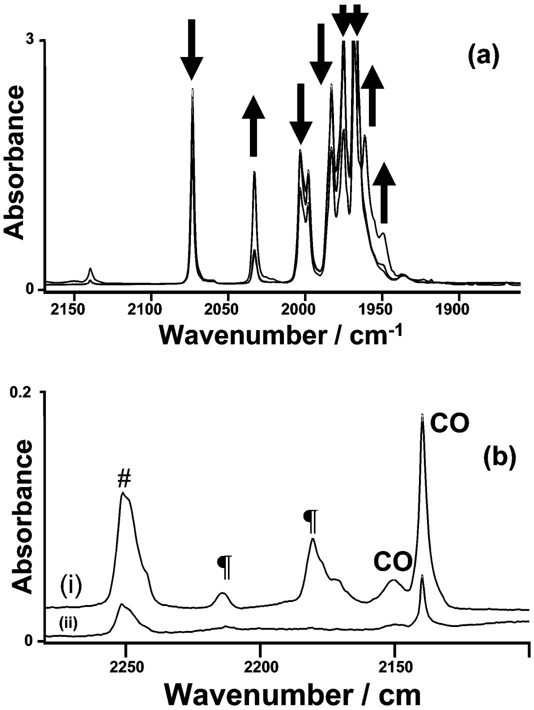

Fig. 4 (a) A series of FTIR spectra obtained following photolysis of $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_4]$ in a N_2 matrix at 12 K. The spectra were initially obtained after photolysis at $\lambda > 300$ nm and then after photolysis at $\lambda > 254$ nm. The bands marked # are due to the generation of $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_3(N_2)]$ (**5**) and those marked ¶ are assigned to $[(\eta^3 C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$ (**6**).

Table 2 IR frequencies (cm^{-1}) of Cr complexes observed in low-temperature matrices

Complex	Matrix Ar	Matrix N_2	Assignment
$[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$	1990	1984	$\nu(CO)$
	1923	1914	$\nu(CO)$
$[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ (**3**)	1983		$\nu(CO)$
	1915		$\nu(CO)$
$[(\eta^6\text{-}C_6H_6)Cr(CO)_2]$	1938		$\nu(CO)$
	1885		$\nu(CO)$
$[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ (**7**)	1930		$\nu(CO)$
	1876		$\nu(CO)$
$[(\eta^6\text{-}C_6H_6)Cr(CO)_3(N_2)]$		2148	$\nu(NN)$
		1940	$\nu(CO)$
		1896	$\nu(CO)$

to resolve the low a′ and a″ vibrations, as occurs[50] in $[(\eta^5\text{-}C_5H_5)V(CO)_3(N_2)]$. The ν(N–N) band at 2249 cm^{-1} has a shoulder at *ca.* 2242 cm^{-1}. Annealing of the matrix caused this shoulder to decrease as the main band increased in intensity. This shift could either be due to the product changing its site in the matrix or less probably to thermal interconversion of the two isomers of **5**.

Extended UV photolysis ($\lambda = 254$ nm) of **2** in the N_2 matrix caused an increase in the intensity of the bands of **5** and more depletion of the parent molecule. During this photolysis the production of free CO increased, indicating that further decarbonylation was occurring, see Fig. 3(a). The ν(N–N) band at 2250 cm^{-1} increased in intensity and ν(C–O) bands at 2212 and 2180 cm^{-1} grew in at an equal rate. This allows us to assign these bands to a single photoproduct $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$ (**6**) with two carbonyl ligands substituted for N_2 molecules. The ν(N–N) bands at 2212 and 2180 cm^{-1} grew in at the same rate and are assigned to a single photoproduct, see Fig. 4(b). From these results the new photoproduct bands were tentatively assigned to the disubstituted product $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$ (**6**). These results should be compared with an experiment carried out by Rest and co-workers on $[(\eta^3\text{-}C_3H_5)Mn(CO)_4]$ in a N_2 matrix. Their results were similar to those above; however, UV photolysis produced only the mono-N_2 substituted species, $[(\eta^3\text{-}C_3H_5)Mn(CO)_3(N_2)]$, whereas we have evidence for the formation of the disubstituted compound $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$ (**6**).

(c) Photolysis of $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ (3) isolated in an Ar matrix

The photolysis of **3** produced results very similar to those obtained by Rest and co-workers for $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$. The IR spectrum of **3** in an Ar matrix shows two strong bands consistent with a_1 (1983 cm^{-1}) and e (1914 cm^{-1}) vibrational modes of a $Cr(CO)_3$ fragment, having local C_{3v} symmetry. UV photolysis of **3** in an Ar matrix, ($\lambda > 300$ nm) resulted in depletion of the parent band, appearance of free CO and the production of a complex with two new ν(CO) bands at 1930 and 1876 cm^{-1} which were readily assigned to $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_2]$ (**7**) by analogy with $(\eta^6\text{-}C_6H_6)Cr(CO)_2$ formed in a similar matrix, see Table 2.

(d) Photolysis of $[(CO)_4Mn(\mu\text{-}\eta^3\text{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (1) in an Ar matrix

The IR spectrum of **1** in an Ar matrix showed five prominent bands in the carbonyl stretching region of the spectrum, see Fig. 5(a). As in solution, the pattern of these bands is very similar to that obtained by coaddition of the spectra of **2** and **3**. UV photolysis ($\lambda > 254$ nm) of the matrix resulted in the appearance of four new bands at 2037, 1963, 1934 and 2138 cm^{-1}, Fig. 5 (b). The first three bands all grew in at the same

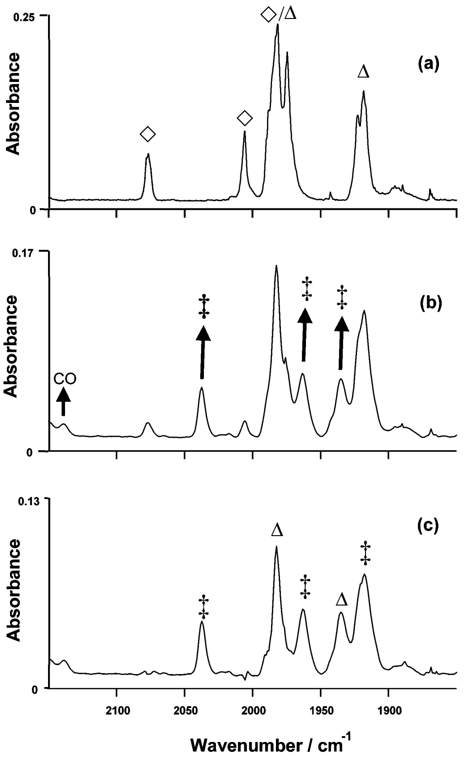

Fig. 5 FTIR spectrum of $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ isolated in an argon matrix (a) before photolysis, the bands marked ◇ and △ are due to the $Mn(CO)_4$ and $Cr(CO)_3$ groups respectively, (b) after 5.5 hours photolysis (λ > 254 nm). (c) This is (b) with the ν(C–O) bands of the parent subtracted from the spectrum to show only the product bands. The bands marked ‡ and △ are due to the $Mn(CO)_3$ and $Cr(CO)_3$ moieties in $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$.

rate as the band due to free carbon monoxide (2138 cm^{-1}). These bands were therefore attributed to the generation of a single photoproduct which occurs by loss of a CO ligand.

There are two possible structures for the product, either $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ or $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_2]$. In the case of $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$, three new bands, 2a′ + a″, due to vibrations of the $Mn(CO)_3$ group would be expected. If, however, CO was lost from the chromium centre, only two new ν(C–O) bands would be expected. The three bands that grew in were all approximately 40 cm^{-1} lower than the manganese parent bands; a shift characteristic of loss of one carbonyl ligand from a metal centre. The positions of the ν(CO) bands and their relative intensities were similar to those observed during the photolysis of **4** in an argon matrix. Fig. 6 compares the subtraction spectrum for the photoproduct of $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$, with the respective spectra of the photoproducts of **4** and **7** in argon matrices. The close resemblance of the spectra in Fig. 6(a) to Fig. 6(b) strongly suggests that the product was $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**9**). No new ν(CO) bands were observed which could be assigned to a $Cr(CO)_2$ moiety in the dinuclear complex, suggesting that there was no loss of CO from the Cr centre. Furthermore, the parent absorptions of the $Cr(CO)_3$ moiety decreased only slightly during photolysis, whereas those due to $Mn(CO)_4$ were greatly reduced in intensity. The absence of a $Cr(CO)_2$ species could have been either due to the lowest energy excited state not being labile with respect to CO loss from the Cr centre or to the $Cr(CO)_2$ undergoing photoreversible CO loss.

(e) Photoreactions of $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (1) in a N_2 matrix

The IR spectrum of **1** in a N_2 matrix at 12 K, is similar to that recorded in an Ar matrix, with only small shifts in band positions, and a slightly different matrix splitting pattern. Photolysis with visible radiation (λ > 400 nm) generated a small ν(CO) band at 1937 cm^{-1}, together with weaker bands at 2037 and 1895 cm^{-1}, Fig. 7. In the ν(NN) region of the spectrum, a new band grew in at 2147 cm^{-1} alongside the band due to free CO (2138 cm^{-1}). This new photoproduct was assigned to $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_2(N_2)]$ (**10**) by comparison with the bands of **8** and $[(\eta^6\text{-}C_6H_6)Cr(CO)_2(N_2)]$, Tables 1 and 2. The formation of **10** means that the CO loss from the Cr centre does occur. The results obtained in an Ar matrix indicate that in a weakly coordinating matrix CO loss is reversible, maybe due to a photoinduced back reaction.

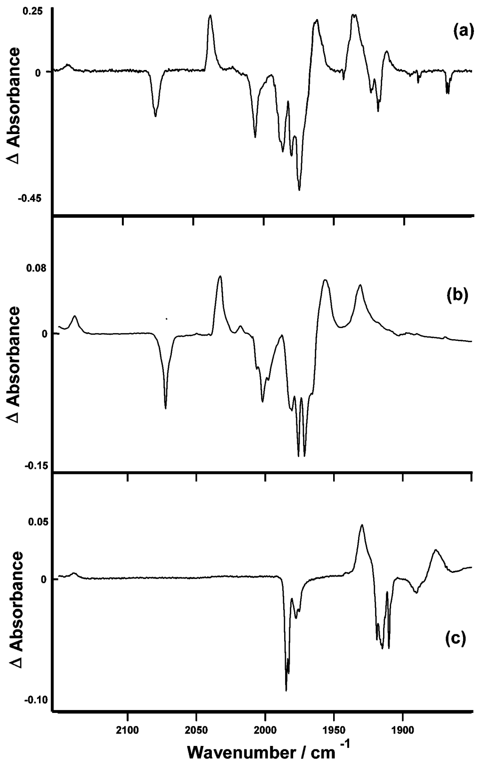

Fig. 6 Subtraction spectra showing the photoproducts generated by photolysis of (a) $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (b) $[(\eta^3\text{-}C_3H_4\text{-}C_6H_5)Mn(CO)_4]$ and (c) $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ in argon matrices at 12 K.

UV photolysis (λ > 300 nm), of the matrix caused the bands assigned to **10** and free CO to grow in further. New ν(CO) bands grew in at 2036 and 1964 cm^{-1} (Table 3); they were generated at the same rate as a new ν(NN) band at 2255 cm^{-1}. The appearance of these new bands indicated that a second nitrogen substituted product had been generated; the similarity in positions and relative intensities, compared with the spectrum of **5**, suggested that the photoproduct was $[(CO)_3(N_2)Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**11**). Only after extensive UV photolysis (λ > 254 nm), did the bands due to **11** become more intense than those of **10**. This prolonged photolysis also caused the production of more new ν(CO) and ν(NN) bands, Fig. 6. A new ν(NN) band grew in at 2181 cm^{-1} with a weaker band at 2218 cm^{-1}. In the carbonyl stretching region of the spectrum, the broad band at *ca.* 1964 cm^{-1} split into two, as a new band at 1954 cm^{-1} increased in intensity. These new ν(CO) and ν(NN) bands were assigned to the bis-substituted nitrogen product $[(CO)_2(N_2)_2Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**12**) by comparison with the results obtained from photolysis of **2** in a N_2 matrix (see above).

Overall, these results bear a close resemblance to those for the photolysis of the mononuclear manganese and chromium compounds in nitrogen matrices. CO was photoejected from either end of the parent molecule and nitrogen substituted products were formed; these were identified by their ν(CO) and

Table 3 IR frequencies (cm^{-1}) of Mn/Cr complexes observed in low-temperature matrices

	Matrix	
Complex	Ar	N_2
$[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**1**)	2076 2005 1981 1975 1918	2076 2006 1978 1970 1916}[a] 1914}[a] 1910}[a]
$[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**9**)	2037 1963 1934	
$[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_2(N_2)]$ (**10**)		2149 1937 1895
$[(CO)_3(N_2)Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (**11**)		2036 1964

[a] Matrix splitting.

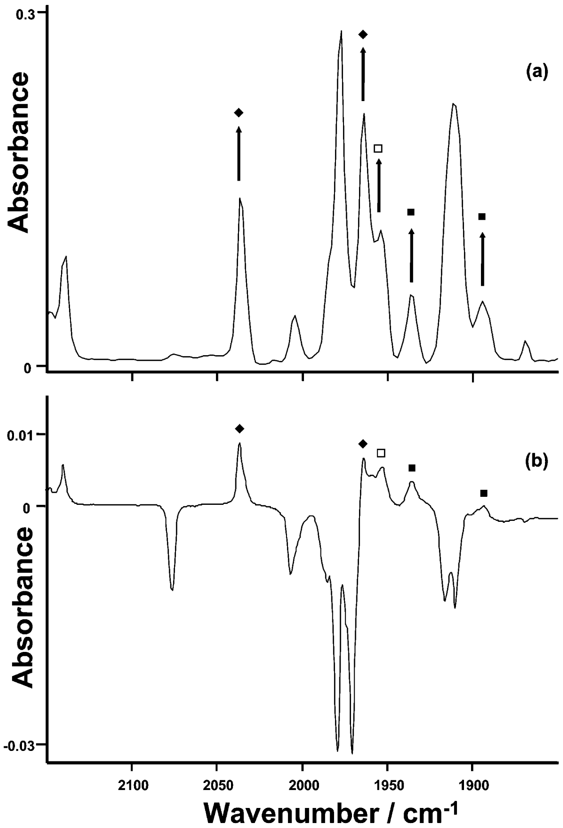

Fig. 7 FTIR spectra recorded after 60 minutes photolysis (λ > 240 nm) of $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ in a N_2matrix at 12 K and (b) subtraction spectrum showing the ν(C–O) bands of (◆) $[(CO)_3(N_2)Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$, (□) $[(CO)_2(N_2)_2Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ and (■) $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_2(N_2)]$.

ν(NN) bands, which were very similar to the bands of the photoproducts of the mononuclear complexes.

Conclusions

Photolysis of $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ in N_2 matrices at 12 K resulted in photosubstitution at both the Mn and Cr centres. We have identified $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_2(N_2)]$, $[(CO)_3(N_2)Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ and $[(CO)_2(N_2)_2Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ by comparison with the mononuclear complexes $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_2(N_2)]$, $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_3(N_2)]$ and $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_2(N_2)_2]$ formed following photolysis of either $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ or $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_4]$ in a N_2 matrix at 12 K. Irradiation of $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ in an Ar matrix produced only $[(CO)_3Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$. However, $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_2]$ could be generated from $[(\eta^6\text{-}C_6H_5C_2H_5)Cr(CO)_3]$ in an Ar matrix.

Experimental

Matrix isolation

The matrix isolation apparatus (Air Products Displex CS202) used in these experiments has been described previously.[49] The principal photolysis source was a Philips HPK 125 W medium pressure Hg arc lamp, the output of which was controlled using a variety of filters with cut off wavelengths as outlined in the main text. All IR spectra were obtained using a Nicolet MX-3600 FTIR interferometer. Matrices were prepared using the "slow spray-on" technique in which a mixture of evaporating solid and matrix gas are co-condensed at low temperatures.

Synthesis

$[Mn(CO)_5(\eta^1\text{-}C_3H_4C_6H_5)]$. A solution of $Mn_2(CO)_{10}$ (2.0 g, 5.1 mmol) in THF (50 ml) was added to a sodium amalgam (0.5 cm^3 in 10 ml Hg) and stirred vigorously for 30 minutes. The resulting solution of $[Mn(CO)_5]^-Na^+$ was cannula-filtered into a solution of cinnamyl chloride (1.56 g, 10.2 mmol) in THF (10 ml). After 30 min stirring the suspension yielded an orange–yellow oil $[Mn(CO)_5(\eta^1\text{-}C_3H_4C_6H_5)]$ which was used directly in the preparation of $[Mn(CO)_4(\eta^3\text{-}C_3H_4C_6H_5)]$ (**2**).

$[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_4]$ (2). A solution of freshly sublimed trimethylamine oxide (1.4 g, 18.7 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a solution of $[Mn(CO)_5(\eta^1\text{-}C_3H_4C_6H_5)]$ in CH_2CH_2 (20 ml). Stiring for 30 minutes gave a dark yellow solution. Removal of the solvent (*in vacuo*), extraction with diethyl ether followed by filtering through Kieselguhr yielded a yellow oil. Sublimation (70 °C, 0.3 mmHg) gave $[Mn(CO)_4(\eta^3\text{-}C_3H_4C_6H_5)]$ (1.9 g, 65%) as a yellow solid. ^1H NMR ($CDCl_3$) δ 7.08–7.41 (m, 5H, C_6H_5), 5.43 (td, 1H, $CH_2CH\text{-}CHC_6H_5$, J = 14, 9 Hz), 3.60 (d, 1H, $CH_2CHCHC_6H_5$, J = 14 Hz), 2.63 (dd, 1H, *syn*-$CH_2CHCHC_6H_5$, J = 9, 1 Hz), 1.72 (dd, 1H, *anti*-$CH_2CHCHC_6H_5$, J = 14, 1 Hz). ^{13}C NMR (deuteroaceetone) δ 221.5, 219.8, 217.0, 216.0 (4CO), 141.2 (quaternary of –C_6H_5), 129.7, 125.8 (*ortho* and *meta* of –C_6H_5), 127.1 (*para* of –C_6H_5), 91.02, 67.0 ($CH_2CHCHC_6H_5$), 37.8 ($CH_2CHCHC_6H_5$). *m*/*z* 284 ($M^=$), 256 ($M^=$ − CO), 228 ($M^=$ − 2CO), 200 ($M^=$ − 3CO), 172 ($M^=$ − 4CO). Found: C, 55.2; H, 3.2. Calculated: C, 54.9; H, 3.2%.

$[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (1). $[(\eta^3\text{-}C_3H_4C_6H_5)Mn(CO)_4]$ (1.0 g, 3.5 mmol) and chromium hexacarbonyl (2.0 g, 9 mmol) were heated to relux in THF–n-butyl ether (v/v 1 : 8) for 16 hours under an inert atmosphere. The reaction mixture was cooled and the solvent and excess chromium hexacarbonyl were removed *in vacuo*. The green–yellow residue was extracted into diethyl ether and filtered through Kieselguhr followed by recrystallisation from diisopropyl yielding $[(CO)_4Mn(\mu\text{-}\eta^3{:}\eta^6\text{-}C_3H_4C_6H_5)Cr(CO)_3]$ (1.5 g, 25%) as a bright yellow solid. ^1H MNR (deuteroacetone) δ 5.68–5.92 (m, 5H, C_6H_5), 5.48 (m, 1H, $CH_2CHCHC_6H_5$), 3.48 (d, 1H, $CH_2CHCHC_6H_5$, J = 14 Hz), 2.97 (dd, 1H, *syn*-$CH_2CHCHC_6H_5$, J = 10, 2 Hz), 2.18 (dd, 1H, *anti*-$CH_2CHCHC_6H_5$, J = 12, 2 Hz). ^{13}C MNR (deuteroacetone) δ 235.1 ($Cr(CO_3)$), 113.1 (quaternary of –C_6H_5), 96.2, 96.0, 93.6, 92.1, 91.2, 87.7 (*ortho*, *meta* and *para* of C_6H_5 and $CH_2CHCHC_6H_5$ or $CH_2CHCHC_6H_5$), 60.7

($CH_2\mathit{C}HCHC_6H_5$ or $CH_2CH\mathit{C}HC_6H_5$), 40.9 ($\mathit{C}H_2CHCHC_6H_5$). *m*/*z* 420 ($M^{=} - CO$), 392 ($M^{=} - 2CO$), 363 ($M^{=} - 3CO$), 336 ($M^{=} - 4CO$), 284 ($M^{=} - Cr(CO)_3$). Found: C, 45.8; H, 2.2. Calculated: C, 45.7; H, 2.1%.

Acknowledgements

We thank the EPSRC, University of Notingham, BP (C. H.), for financial support. M. W. G. wishes to acknowledge the support of the Sir Edward Frankland Fellowship. We are also grateful to Mr J. Yang for helpful advice.

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45 (*a*) S. B. L. Lyons, Ph.D. Thesis, University of Nottingham, 1993; (*b*) Crystal data: $C_{16}H_9CrMnO_7$, $M = 420.17$, triclinic, $a = 7.0572(9)$, $b = 11.0698(14)$, $c = 11.1706(14)$ Å, $\alpha = 112.507(2)$, $\beta = 95.440(2)$, $\gamma = 93.583(2)^\circ$, $U = 797.9(3)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.749$ g cm^{-3}, μ(Mo-Kα) = 1.508 mm^{-1}, 3579 unique, absorption-corrected reflections ($R_{int} = 0.026$) used in all calculations. Final R_1 [$2610F > 4\sigma(F)$] = 0.0363 and wR(all F^2) was 0.0883. CCDC reference number 189753. See http://www.rsc.org/suppdata/dt/b2/b206697a/ for crystallographic data in CIF or other electronic format.
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