Solution and Matrix Photochemistry of the Isoelectronic Series of 'Half-sandwich' Carbonyl(η^5-cyclopentadienyl)nitrosyl Complexes of Manganese, Chromium, and Vanadium, $[M(\eta^5\text{-}C_5H_5)(CO)_{3-n}(NO)_n]$ ($n = 0$, M = Mn; $n = 1$, M = Cr; $n = 2$, M = V)

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Photolysis of the isoelectronic η^5-cyclopentadienyl (cp) half-sandwich compounds [Mn(cp)(CO)$_3$] (1), [Cr(cp)(CO)$_2$(NO)] (2), and [V(cp)(CO)(NO)$_2$] (3) in either low-temperature matrices (CH$_4$, Ar, CO, N$_2$) or ambient-temperature solutions [hexane, tetrahydrofuran (thf), cyclo-octene] generally results in elimination of a CO ligand as the primary photoreaction. The photo-generated complexes were characterised by their i.r. absorptions [ν(CO), ν(NO)] and by their secondary reactions in 'reactive' matrices (^{13}CO, N$_2$) or co-ordinating solvents (thf, cyclo-octene), respectively. Matrix-isolated [V(cp)(CO)(NO)$_2$] (3) is transformed by visible light into a species [V(cp)(CO)(NO)(NO$^{\bullet}$)] where NO$^{\bullet}$ is considered as a one-electron ligand. The photo-induced reactions of (1)—(3) with triethylphosphine were also investigated. In contrast to (1) and (2), [V(cp)(CO)(NO)$_2$] (3) undergoes substitution of the CO ligand in the dark at room temperature.

ALL known members of the series of η^5-cyclopentadienyl compounds [M(cp)(CO)$_{3-n}$(NO)$_n$] (cp = η^5-C$_5$H$_5$; M = Mn, Cr, or V; n = 0—2) are photolabile. Excitation by u.v.–visible light is generally thought to result in photo-elimination of a carbon monoxide ligand and formation of a CO-deficient co-ordinatively unsaturated fragment.† The photo-induced displacement of CO has been extensively used in synthetic solution chemistry to prepare derivatives of [Mn(cp)(CO)$_3$] (1)[1-3,6,‡] and [Cr(cp)(CO)$_2$(NO)] (2).[8-11] While this S_N1 photosubstitution is the only reasonable method to replace CO groups by other two-electron ligands such as phosphines or phosphites in both the manganese and the chromium complexes, the vanadium compound [V(cp)(CO)(NO)$_2$] (3)[12,13] already loses the CO group under ambient conditions in solution, and thermal CO substitution is quite effective at elevated temperatures.

The isoelectronic complexes of the type [M(cp)(CO)$_{3-n}$(NO)$_n$] contain a planar cyclopentadienyl ring. The 'piano-stool' configuration of the diatomic acceptor ligands, CO and/or NO, has been established by *X*-ray crystallography for [Mn(cp)(CO)$_3$] (1)[14] and [Cr(cp)(CO)$_2$(NO)] (2).[15] It is assumed that [V(cp)(CO)(NO)$_2$] (3) possesses an analogous structure. The other member of the series, 'Ti(cp)(NO)$_3$', is as yet unknown.[12]

We have tried to compare the photoreactivity of the isoelectronic and isostructural complexes (1)—(3) both on the basis of solution chemistry and matrix photolysis.

EXPERIMENTAL

The starting materials [Mn(cp)(CO)$_3$] (1),[16] [Cr(cp)(CO)$_2$(NO)] (2),[17] (*cf.* ref. 15) and [V(cp)(CO)(NO)$_2$] (3)[12,13] were prepared according to literature procedures and purified by column chromatography over silica gel.

(*i*) *Solution Studies*.—Photolyses of complexes (1)—(3) in dilute hexane, tetrahydrofuran (thf), or cyclo-octene solutions, respectively, were carried out in both i.r. solution cells with NaCl windows and Duran-glass Schlenk tubes (transparent at $\lambda > 300$ nm) using the unfiltered light of a medium-pressure mercury arc (Hanovia S-200 W). The photoreactions were followed by i.r. spectroscopy in the region 2 100—1 500 cm^{-1} on a Beckman IR 4240 instrument, calibrated by the polystyrene bands at 2 850 and 1 601 cm^{-1}.

The parent complexes (1)—(3) and their solvent-stabilised derivatives were further characterised by u.v.–visible (Zeiss Spektralphotometer DMR 10) and by ^{1}H and ^{13}C n.m.r. spectroscopy (JEOL PMX 60 and FX 90 Q, respectively) (Table 1).

Isolation and identification of side-products. [{Mn(cp)(CO)$_2$}$_2$(C$_5$H$_6$)] (4)[18] is formed in low yield (<1%) during photolysis of [Mn(cp)(CO)$_3$] (1) in thf solution. Samples of (1) (30 mg) in thf (1.5 cm^3) were irradiated in n.m.r. tubes for 5 h and then kept at room temperature overnight. The photoproduct, [Mn(cp)(CO)$_2$(OC$_4$H$_8$)] (1a), decomposes under these conditions to reform (1). The contents of 3—5 tubes were combined and brought to dryness and (1) was removed by high-vacuum sublimation at 50—80 °C. The yellow residue contains an olefin complex which dissolves in thf but is not volatile up to 120 °C, indicating a binuclear compound. The i.r. [ν(CO) 1 955 and 1 895 cm^{-1} in thf] and ^{1}H n.m.r. (δ 4.61 p.p.m. in [^{2}H$_6$]acetone) data agree within experimental error with the literature values given for the μ-η^4-cyclopentadiene complex [{Mn(cp)(CO)$_2$}$_2$(C$_5$H$_6$)] (4).[18] A field desorption mass spectrum § confirms not only the molecular ion at *m/e* 418 (relative intensity, $I_{rel.}$ 100%) but also some of the expected fragments including Mn(cp)(CO)$_2$(C$_5$H$_6$)$^+$ (*m/e* 242, $I_{rel.}$ 8.51%) and C$_5$H$_6^+$ (*m/e* 66, $I_{rel.}$ 1.66%).

[Cr(cp)(NO)$_2$(NO$_2$)] is isolated as a side-product of the photodecarbonylation of [Cr(cp)(CO)$_2$(NO)] (2) in solution. Complex (2) (2.03 g, 10 mmol) in thf (500 cm^3) was irradiated for 1 h in a falling-film photoreactor. The green solution was filtered, brought to dryness, and extracted with acetone. The solvent, acetone, was removed and the residue treated several times with pentane. Evaporation

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† For reviews related to the photochemistry of carbonylmetal complexes see references 1—7.

‡ *Note added at proof:* A review on the co-ordination chemistry of the fragment [Mn(cp)(CO)$_2$] has been published (K. E. Caulton, *Coord. Chem. Rev.*, 1981, **38**, 1).

§ Measured by F. Kreissl, Technische Universität München (Varian MAT 311A).

TABLE 1

Spectroscopic data for the complexes (1)—(3) and their solvent-stabilised derivatives

Compound	$[Mn(cp)(CO)_3]$ (1)		$[Cr(cp)(CO)_2(NO)]$ (2)		$[V(cp)(CO)(NO)_2]$ (3)	
Colour	Yellow		Orange		Red-brown	
(*a*) Infrared ($\bar{\nu}$/cm^{-1})	ν(CO)		ν(CO)	ν(NO)	ν(CO)	ν(NO)
Hexane	2 030, 1 942 (1)		2 029, 1 955	1 714 (2)	2 051	1 735, 1 651 (3)
thf	2 015, 1 930 (1)		2 015, 1 947,	1 700 (2)	2 046	1 725, 1 637 (3)
	1 928, 1 852 (1a)		1 906	1 643 (2a)		1 686, 1 578 (3a)
Cyclo-octene	2 022, 1 944 (1)		2 018, 1 954,	1 708 (2)	2 043	1 730, 1 642 (3)
	1 963, 1 902 (1b)		1 965	1 675 (2b)		
				1 665 (2b)		
(*b*) U.v.–visible (λ/nm) [a]	$\lambda_{max.}$ (ε/dm^3 mol^{-1} cm^{-1})		$\lambda_{max.}$ (ε/dm^3 mol^{-1} cm^{-1})		$\lambda_{max.}$ (ε/dm^{-3} mol^{-1} cm^{-1})	
Hexane	328 (1 150) (1) [b]		*ca.* 360 (sh) (*ca.* 860) (2)		498	
thf	328 (1 200) (1) [b]		*ca.* 355 (sh) (*ca.* 700) (2)		495 (*ca.* 1 300)	
	ca. 290, *ca.* 390, 510 (*ca.* 380)		*ca.* 550			
(*c*) N.m.r. (δ/p.p.m.)	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
C_6D_6	3.98	82.7 (1)	4.25	90.3 (2)	4.81	97.7 (3)
[$^2H_8$]thf (−30 °C) [c]	4.93	84.1 (1)	5.26	91.6 (2)	5.71	99.3 (3)
	4.43	82.5 (1a)	4.94	93.1 (2a)	5.54	101.2 (3a)

[a] Absorptions at the long-wavelength end of the spectrum. [b] Literature values: ref. 21, $[Mn(cp)(CO)_3]$ (1) $\lambda_{max.}$ 330 nm (ϵ 1 100) in 1-octane, $[Mn(cp)(CO)_2(OC_4H_8)]$ (1a) $\lambda_{max.}$ 400 nm (ϵ 1 400) and 510 nm (ϵ 990) in thf (N. J. Gogan and C.-K. Chu, *J. Organomet. Chem.*, 1975, **93**, 363); (1) $\lambda_{max.}$ 216 nm (ϵ 11 600) and 331 nm (ϵ 860) in hexane (R. T. Lundquist and M. Cais, *J. Org. Chem.*, 1962, **27**, 1167), (1) $\lambda_{max.}$ 328 nm (ϵ 1 120) in ethanol. [c] The thf complexes (1a)—(3a) decompose slowly under ambient conditions, therefore the ^{13}C n.m.r. spectra were accumulated at −30 °C.

of pentane from the combined extracts leads to green crystals on the wall of the Schlenk tube. The crystals (40—50 mg, *ca.* 2% yield) were sublimed under high vacuum at 50 °C and identified by their i.r. [ν(NO) 1 817 and 1 712 cm^{-1} in CH_2Cl_2], n.m.r. {$\delta(^1H)$ 5.88, $\delta(^{13}C)$ 103.9 p.p.m. in [$^2H_8$]-thf at −30 °C}, and mass spectra [$Cr(cp)O^+$, *m/e* 133, most intense peak]. These data agree reasonably well with data published by Legzdins and co-workers.[19]

TABLE 2

Spectroscopic characterisation of triethylphosphine complexes derived from (1)—(3)

	Infrared spectrum [a]		^1H N.m.r. spectrum [b,c]	
Complex	ν(CO)/cm^{-1}	ν(NO)/cm^{-1}	δ (C_5H_5)/p.p.m.	$J(^{31}P-^1H)$/Hz
(1)	2 030, 1 942		3.98(s)	
(1c)	1 937, 1 873		4.17(d)	1.8
(1d)	1 836		4.08(t)	1.8
(2)	2 029, 1 955	1 714	4.25(s)	
(2c)	1925	1 659	4.47(d)	1.9
(2d)		1 603	4.36(t)	2.0
(3)	2 051	1 735, 1 651	4 81(s)	
(3b)		1 692, 1 597	5.06(d)	1.6

[a] Hexane. [b] C_6D_6. [c] s = Singlet, d = doublet, t = triplet.

Reactions with triethylphosphine. The photo-induced reactions of complexes (1)—(3) with triethylphosphine, PEt_3, were investigated in C_6D_6 solution by ^1H n.m.r. spectroscopy. In a series of semi-quantitative n.m.r. tube experiments, the solutions containing 0.05 mmol of the metal complex and PEt_3 (0.05 mmol) in C_6D_6 (0.4 cm^3) were checked periodically for the disappearance of the cyclopentadienyl singlet of the parent compound (1)—(3) and for growth of new cyclopentadienyl patterns which are doublets or triplets depending on the number of PEt_3 ligands (one or two) in the newly formed substitution products.

(*ii*) *Matrix Studies.*—Cryogenic temperatures (*ca.* 12 K) were obtained using a Displex CSA-202 closed-cycle helium refrigeration system (Air Products and Chemicals Inc.). Matrices containing (1), (2), and (3) were prepared by the slow spray-on technique [20] and the vapour from the cooled solid (*ca.* −5, 0, and 10 °C respectively) was co-condensed with matrix gas onto the cold LiF window. Monomer isolation (1 : 2 000—1 : 5 000) was ensured by having substantially higher gas flow for the host matrix gas than for the complex to be isolated. Deposition was monitored throughout by running i.r. spectra of the matrix and checking that the half-width at half-height of the terminal CO stretching bands did not exceed *ca.* 2 cm^{-1} and that there was no tailing of bands to lower wavenumbers.

Infrared spectra in the region 2 200—1 550 cm^{-1} were recorded on a Grubb-Parsons Spectromajor grating spectrometer modified to suppress the grating change to 1 850 cm^{-1}. Calibration in the terminal CO and NO stretchings was carried out regularly using the gas phase bands of CO, DCl, and H_2O. Resolution was better than 1 cm^{-1} and the reproducibility of measurements was ±0.5 cm^{-1}.

The photolysis source was a medium-pressure mercury arc lamp (Philips HPK 125 W). Wavelength-selective photolysis was achieved by using the following filters: (A) $460 < \lambda < 540$ nm, Ilford colour filter (gelatin film, thickness 2 mm); (B) $\lambda > 330$ nm, sodaglass disc (thickness 5 mm); (C) $\lambda < 370$ and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing Br_2 gas (300 Torr *); (D) $\lambda < 280$ and $\lambda > 550$ nm, quartz gas cell (pathlength 25 mm) containing 3 atm * of Cl_2 gas + quartz gas cell (pathlength 25 mm) containing 200 Torr of Br_2 gas; and (E) $\lambda > 290$ nm, Pyrex glass disc (thickness 5 mm).

Matrix gases (Ar, CH_4, CO, and N_2) were BOC ' Grade X '

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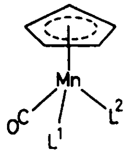
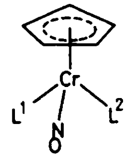
* Throughout this paper: 1 atm = 101 325 Pa; 1 Torr = (101 325/760) Pa.

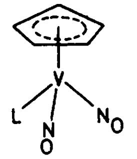
purity and ^{13}CO (95% enriched) was obtained from BOC Prochem Limited.

RESULTS

(*i*) *Studies in Solution.*—Compounds (1)—(3) and their photo-generated derivatives are best characterised in solution by their i.r. absorptions in the carbonyl and nitrosyl stretching region (2 200—1 500 cm^{-1}) and by their ^{1}H and ^{13}C n.m.r. chemical shifts of the cyclopentadienyl ring ligand; the relevant data are collected in Tables 1 and 2. The structures of the complexes (1)—(3) and their photoproducts are given below; OC_4H_8 = tetrahydrofuran, C_8H_{14} = *cis*-cyclo-octene.







	L^1	L^2		L^1	L^2		L
(1)	CO	CO	(2)	CO	CO	(3)	CO
(1a)	CO	OC_4H_8	(2a)	CO	OC_4H_8	(3a)	OC_4H_8
(1b)	CO	C_8H_{14}	(2b)	CO	C_8H_{14}	(3b)	PEt_3
(1c)	CO	PEt_3	(2c)	CO	PEt_3	(3c)	N_2
(1d)	PEt_3	PEt_3	(2d)	PEt_3	PEt_3		
(1e)	CO	N_2	(2e)	CO	N_2		

Within the series of the isoelectronic complexes (1)—(3) the electronic absorptions (Figure 1) are shifted into the visible range (towards lower energies). The recording of the u.v.-visible spectrum of [V(cp)(CO)(NO)$_2$] (3) is hampered by the light-induced decarbonylation of the complex, and only approximate absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) have been obtained. Only a single strong absorption (log ε *ca.* 4) is observed in the 'photochemical region' where excitation by mercury arcs can take place (λ ⩾ 254 nm). This absorption at the long-wavelength side of the u.v.-visible spectrum is well resolved in (1) and (3) but appears as a shoulder in (2). In the case of [Mn(cp)(CO)$_3$] (1), this lowest transition has been interpreted as a charge-transfer (c.t.) transition with substantial Mn→(η^5-C_5H_5) character but with additional Mn→(CO)π* c.t. contributions (*cf.* refs. 7 and 21). The characteristic absorptions of (1) and (3) disappear if a CO group is replaced by a thf ligand which has no low-lying orbitals for metal-to-ligand back-bonding.

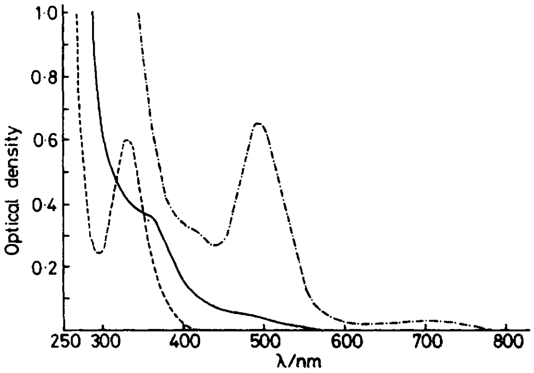
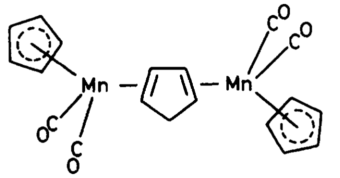


FIGURE 1 Electronic absorption spectra of complexes [Mn(cp)(CO)$_3$] (1) (— — —), [Cr(cp)(CO)$_2$(NO)] (2) (——), and [V(cp)(CO)(NO)$_2$] (3) (— · —) in thf solution (5 × 10^{-4} mol dm^{-3})

(*a*) [Mn(cp)(CO)$_3$] (1). In the closed system of an i.r. solution cell the photolysis of a yellow thf solution of (1) [ν(CO) 2 015 and 1 930 cm^{-1}] leads to partial formation of (1a) [ν(CO) 1 928 and 1 852 cm^{-1}]; at the same time free carbon monoxide [ν(CO) 2 128 cm^{-1} in thf] appears in the spectrum. The equilibrium mixture of (1) and (1a) which is formed in the course of a few minutes remains unchanged under prolonged irradiation although (1) is reformed from (1a) upon standing of the wine-red solutions in the dark at room temperature. Complete transformation of (1) into (1a) is possible in the open system of a Schlenk tube, and solutions of (1a) in thf are therefore generally used for the synthesis of complexes containing the Mn(cp)(CO)$_2$ unit. There is no indication that a further CO ligand can be eliminated from thf solutions of (1a), not even in the course of 6 h of photolysis; *i.e.*, irradiation of (1a) in thf solution does not lead to further thf incorporation into the Mn(cp)(CO)$_2$ fragment. The only side-product is an olefin complex which, on the basis of the i.r., ^{1}H n.m.r., and mass spectral data, is identified as the known [18] binuclear compound [{Mn(cp)(CO)$_2$}$_2$(C_5H_6)] (4) containing a cyclopentadiene bridge.



(4)

Irradiation of (1) in cyclo-octene solution gives the yellow monosubstituted derivative (1b).[22,23] Again, no indication of photo-induced substitution of a second CO ligand to give the unknown '[Mn(cp)(CO)(C_8H_{14})$_2$]' can be found in the i.r. spectra.

Exposure of C_6D_6 solutions containing (1) together with PEt_3 (1 : 1) to the unfiltered emission of the high-pressure mercury lamp leads to the expected photosubstitutions to form (1c) and (1d). The formation of the di-substituted derivative (1d) begins as soon as the mono-substituted complex (1c) is available, but the concentration of (1d) remains small due to the limited amount of PEt_3. Estimated amounts of the original complex (1) converted into PEt_3-substituted derivatives as a function of time are presented in Figure 2, while the formation of PEt_3 complexes within a given period of time may be seen from Figure 3. The effect of the phosphine concentration upon the photo-induced CO substitution is presented in Figures 4 and 5. No reaction is observed of (1) with PEt_3 in solution in the dark at ambient temperature.

(*b*) [Cr(cp)(CO)$_2$(NO)] (2). In contrast to (1), the nitrosylchromium complex (2) loses two CO ligands successively upon irradiation in either thf or cyclo-octene solution. In the i.r. cell, the thf solution of (2) [ν(CO) 2 015 and 1 947, ν(NO) 1 700 cm^{-1}] is partially converted to the mono-substituted derivative (2a) [ν(CO) 1 906, ν(NO) 1 643 cm^{-1}] which slowly reforms (2) after the high-pressure mercury lamp has been switched off. Continued irradiation leads to loss of the second CO ligand. As expected, the complete decarbonylation of (2) and (2a) is much more rapid in the Schlenk tube where the liberated CO can escape. However, by a suitable choice of both concentration of (2) and irradiation time, thf solutions containing a relatively high amount of (2a) can be prepared and used for synthetic purposes.[19]

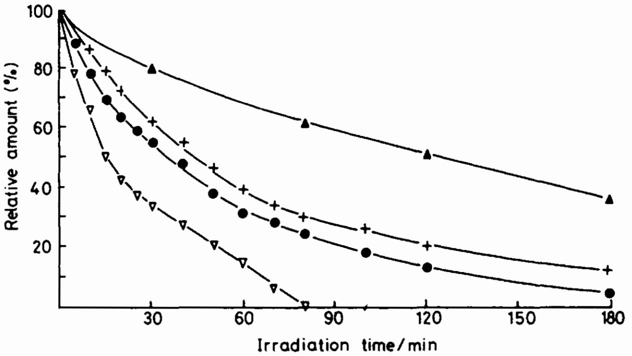


FIGURE 2 Reaction of the complexes (1) (●), (2) (+), (3) (▽), and (3) [dark reaction (▲)] with equimolar amounts of PEt_3: disappearance of the starting cyclopentadienyl complex with time, as followed by ^1H n.m.r. The solutions (and those in Figure 3) contained initially 0.125 mol dm^{-3} of both starting complex and PEt_3 in C_6D_6; the sum of all cyclopentadienyl complexes is taken as 100%

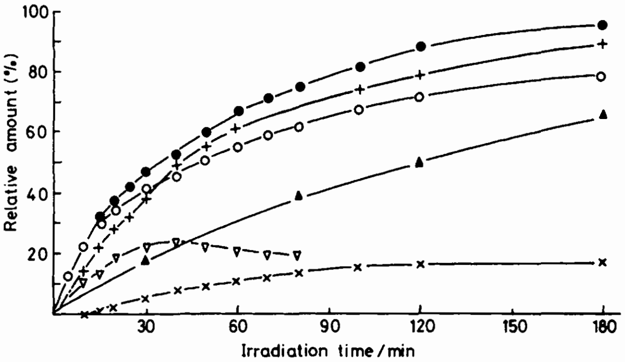


FIGURE 3 Photo-induced reaction of the complexes (1), (2), and (3), respectively with equimolar amounts of PEt_3: extent of formation of triethylphosphine complexes (1c) (○), (1d) (×), (1c + 1d) (●), (2c) (+), (3b) (▽), (3b) [dark reaction (▲)] with time, as followed by ^1H n.m.r.

The green thf solutions obtained by complete decarbonylation of (2) show an i.r. absorption at 2 205 cm^{-1} and a more complex band pattern in the nitrosyl stretching region with bands at 1 780w, *ca.* 1 682 (sh), 1 662s, and *ca.* 1 650 (sh) cm^{-1}; the solution is not affected by free carbon monoxide.* The band at 2 205 cm^{-1} might be due to isocyanate groups or indicate solvated nitrosyl cations (*cf.* ref. 10). If the photodecarbonylation of (2) in a concentrated [$^2H_8$]thf solution is monitored in the ^1H n.m.r. spectrum at room temperature, only the cyclopentadienyl signals of (2) [$\delta(C_5H_5)$ 5.17 p.p.m.] and (2a) [$\delta(C_5H_5)$ 4.89 p.p.m.] can be observed. Although the concentration of both compounds gradually decreases in the solution, the parent complex (2) is always in excess over (2a).

Some side-products, which could be formed during the photoinduced decarbonylation of (2) in thf solution and which are consistent with the observation of new terminal nitrosyl bands and the band at 2 205 cm^{-1}, include complexes of the type [Cr(cp)$(NO)_2$X] (X = NCO or NO_2). Their presence, albeit in small quantities, clearly shows that nitrosyl transfer reactions take place in the irradiated solution. The nitrite complex [Cr(cp)$(NO)_2(NO_2)$] has been previously prepared both by photo-induced nitrosylation of (2) in thf solution [10,19] and by dark reaction between (2a) and NO; [19] its physical and spectroscopic properties have been described.[19] Although the molecular composition [Cr(cp)$(NO)_2(NO_2)$] is also confirmed by the mass spectrum, the mode of co-ordination of the NO_2 ligand (*via* N or O) appears not to have been clearly established. A similar problem is encountered in the case of [Cr(cp)$(NO)_2$(NCO)] which was also identified by the mass spectrum.

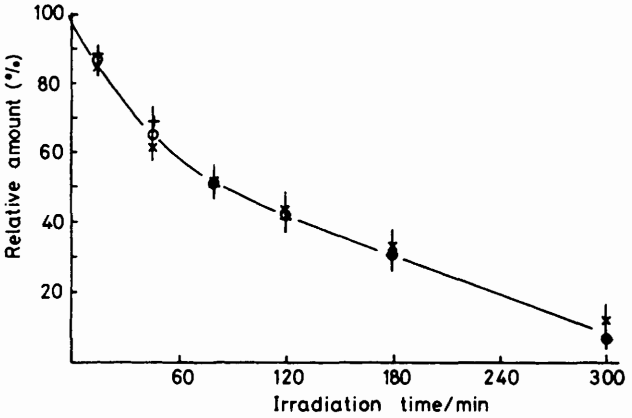


FIGURE 4 Photo-induced reaction of [Mn(cp)$(CO)_3$] (1) with PEt_3 in molar ratios [Mn(cp)$(CO)_3$] : PEt_3, 1 : 0.5 (+); 1 : 3 (○); 1 : 5 (×): disappearance of (1) with irradiation time, as followed by ^1H n.m.r. The solutions (and those in Figure 5) contained initially 0.25 mol dm^{-3} of (1) and varying amounts of PEt_3. The sum of all cyclopentadienyl complexes is taken as 100%

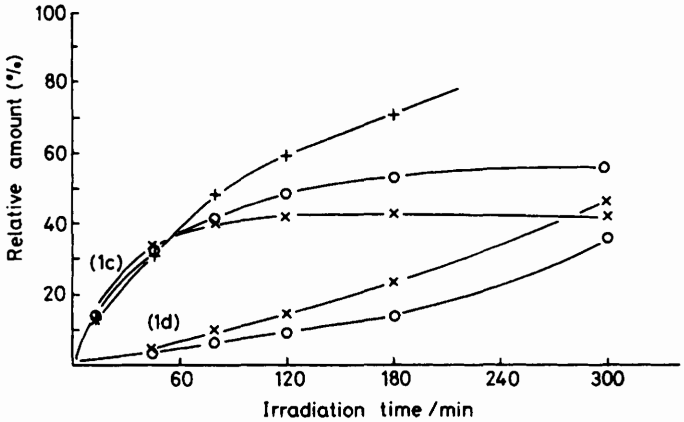


FIGURE 5 Photo-induced reaction of [Mn(cp)$(CO)_3$] (1) with PEt_3 in molar ratios [Mn(cp)$(CO)_3$] : PEt_3, 1 : 0.5 (+); 1 : 3 (○); 1 : 5 (×): extent of formation of the complexes [Mn(cp)$(CO)_2(PEt_3)$] (1c) and [Mn(cp)(CO)$(PEt_3)_2$] (1d) with irradiation time, as followed by ^1H n.m.r.

In cyclo-octene solution, complex (2) loses CO to give the reddish brown cyclo-octene complex (2b) which is easily isolated from the solution.[9,11] Upon prolonged irradiation of (2b) [ν(CO) 1 965, ν(NO) 1 675 cm^{-1} in cyclo-octene], the colour changes to green, the ν(CO) absorption disappears, and only a single ν(NO) band remains at 1 665 cm^{-1}. We ascribe these changes to the formation of a green, disubstituted complex '[Cr(cp)$(C_8H_{14})_2$(NO)]' which, however, has not been isolated so far. The formation of di- or polynuclear species by aggregation of Cr(cp)(NO) units under these conditions might also be possible.

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* The i.r. spectrum (KBr) of the residue remaining after evaporation of the solvent thf from the decarbonylated solutions contains absorptions at 2 200s, 1 767w, and 1 645s cm^{-1}.

Similar to (1), complex (2) upon photolysis in C_6D_6 solution in the presence of excess PEt_3 is converted into the substituted products (2c) and (2d). The bis(phosphine) complex (2d) can only be observed in the n.m.r. spectra after all the complex (2) has been converted into the monophosphine compound (2c), *i.e.* in the presence of excess PEt_3. Comparatively, [Mn(cp)(CO)$_3$] (1) undergoes the photoreaction with PEt_3 slightly faster than does [Cr(cp)(CO)$_2$(NO)] (2) if the molar ratio is 1 : 1 (*cf.* Figures 2 and 3). However, the photo-induced consumption of (2) is faster than that of (1) in the presence of excess triethylphosphine. In the dark no reaction is observed between (2) and PEt_3.

(*c*) [V(cp)(CO)(NO)$_2$] (3). Under ambient conditions in the dark, the red-brown thf solution of (3) [ν(CO) 2 046, ν(NO) 1 725 and 1 637 cm^{-1}] slowly releases CO to give the red derivative (3a) [ν(NO) 1 686 and 1 578 cm^{-1}]. The solution of (3a) tends to disintegrate at room temperature even in the dark, but is stable at −30 °C. The thf complex (3a) is also formed under photolytic conditions, although it decomposes rapidly as a result of irradiation. Studies using the closed system of the i.r. cell indicate that the photo-induced substitution of the labile CO ligand in (3) by the solvent thf is partially reversible in the dark. The slow formation of a secondary derivative, having ν(NO) absorptions at 1 672 and 1 562 cm^{-1}, was also observed. Similar i.r. absorptions (1 677 and 1 571 cm^{-1}) are found for thf solutions of the brown material which has been obtained by nitrosylation of [V(cp)$_2$] in diethyl ether solution at 0 °C and formulated as the binuclear [{V(cp)(NO)$_2$}$_2$].[24] We therefore assume that the mononuclear thf complex [V(cp)(OC$_4$H$_8$)(NO)$_2$] (3a) formed initially is slowly transformed into thf-solvated aggregates consisting of V(cp)(NO)$_2$ units.

There are indications that the photolysis of (3) in cyclooctene solution also leads to a primary displacement of CO by the solvent. The i.r. spectra show new, broad absorptions centred near 1 688 and 1 583 cm^{-1}.

While neither [Mn(cp)(CO)$_3$] (1) nor [Cr(cp)(CO)$_2$(NO)] (2) reacts with PEt_3 in C_6D_6 solution in the absence of light, the dark reaction of [V(cp)(CO)(NO)$_2$] (3) with PEt_3 (1 : 1) leads to (3b) in a clean and almost quantitative process which is considerably accelerated at higher PEt_3 concentrations. However, irradiation of C_6D_6 solutions containing (3) and PEt_3 results in rapid photodecarbonylation which overruns the thermal CO elimination and also causes decomposition of (3b) (Figures 2 and 3).

TABLE 3

Observed and calculated[a] band positions (cm^{-1}) of terminal CO stretching bands in ^{13}CO enrichment experiments of [Mn(cp)(CO)$_3$] (1) isolated in ^{13}CO doped CH_4 matrices at 12 K

Compound	Symmetry	ν(CO)	Observed (calc.)
[Mn(cp)(^{12}CO)$_3$] (1)	C_{3v}	A_1	2 025.8 (2 025.3)
		E	1 940.7 (1 939.9)
[Mn(cp)(^{12}CO)$_2$(^{13}CO)]	C_s	A'	2 014.7 (2 014.5)
		A''	1 940.7 (1 939.9)
		A'	1 907.0 (1 906.9)
[Mn(cp)(^{12}CO)(^{13}CO)$_2$]	C_s	A'	2 001.6 (2 001.0)
		A'	1 920.5 (1 919.8)
		A''	1 895.9 (1 896.7)
[Mn(cp)(^{13}CO)$_3$]	C_{3v}	A_1	1 979.8 (1 980.3)
		E	1 895.9 (1 896.7)
[Mn(cp)(^{12}CO)$_2$]	C_{2v}	A_1	1 959.2 (1 958.4)
		B_1	1 889.2 (1 889.4)
[Mn(cp)(^{12}CO)(^{13}CO)]	C_s	A'	[b] (1 942.8)
		A''	1 861.5 (1 862.2)
[Mn(cp)(^{13}CO)$_2$]	C_{2v}	A_1	1 914.1 (1 914.9)
		B_1	1 847.5 (1 847.4)

[a] Refined energy-factored CO stretching and interaction force constants (N m^{-1}) are for [Mn(cp)(CO)$_3$], K = 1 565.9, k_i = 45.6; and [Mn(cp)(CO)$_2$], K = 1 495.8, k_i = 53.7. [b] Band obscured by overlap.

(*ii*) *Matrix Isolation Studies*.—(*a*) [Mn(cp)(CO)$_3$] (1). The result of the photolysis of (1) in Ar, CH_4, and N_2 matrices to give [Mn(cp)(CO)$_2$] and [Mn(cp)(CO)$_2$(N$_2$)] has been reported earlier.[25] Photolysis of (1) in a pure CO matrix with even unfiltered light from the medium-pressure mercury lamp failed to cause any observable photoreaction. However, an experiment with a ^{13}CO doped (5%) CH_4 matrix showed that on photolysis (filter C) enrichment of the complex takes place to form [Mn(cp)(^{12}CO)$_2$(^{13}CO)], [Mn(cp)(^{12}CO)(^{13}CO)$_2$], and [Mn(cp)(^{13}CO)$_3$]. Prolonged photolysis results in the formation of the co-ordinatively unsaturated fragments [Mn(cp)(^{12}CO)$_2$], [Mn(cp)(^{12}CO)(^{13}CO)], and [Mn(cp)(^{13}CO)$_2$]. All species mentioned are

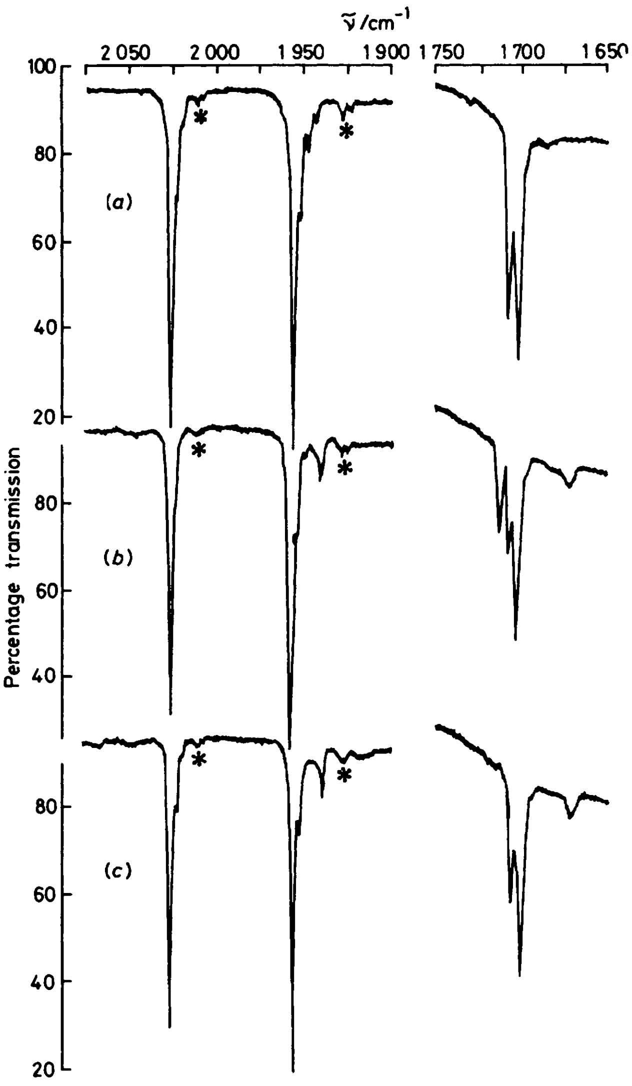

FIGURE 6 Infrared spectra from an experiment with [Cr(cp)(CO)$_2$(NO)] (2) isolated at high dilution in a CH_4 matrix at 12 K: (*a*) after deposition; (*b*) after 40 min photolysis using filter B; (*c*) after annealing to *ca.* 30 K. Bands marked (*) are due to [Cr(cp)(^{12}CO)(^{13}CO)(NO)] in natural abundance

confirmed by the excellent agreement of the observed band positions with the calculated [26-28] values (Table 3).

(*b*) $[Cr(cp)(CO)_2(NO)]$ (2). *Photolysis in* Ar *and* CH_4 *matrices.* The i.r. spectra from an experiment with (2) in methane are shown in Figure 6. The spectrum after deposition [Figure 6(*a*)] shows the three strong bands expected for the symmetric *A′* (2 025.2 cm^{-1}) and asymmetric *A″* (1 955.3 cm^{-1}) terminal carbonyl-stretching modes of the (C_s) $[Cr(CO)_2]$ fragment, and the single terminal nitrosyl-stretching *A′* (1 709.5 cm^{-1}) which is matrix-split (Table 4). Natural-abundance ^{13}CO enrichment is indicated by the presence of weak bands (marked with an asterisk) corresponding to $[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$.

TABLE 4

Band positions (cm^{-1}) for $[Cr(cp)(CO)_2(NO)]$ (2) and its photoproducts in various matrices at 12 K

		Matrix					
Compound		CH_4		Ar		CO	N
$[Cr(cp)(CO)_2(NO)]$ (2)	*A′* [ν(CO)]	2 025.2		2 029.2		2 023.9	2 027.7
	A″ [ν(CO)]	1 955.3		1 959.5		1 955.3	1 957.2
	A′ [ν(NO)]	1 712.8 1 706.2	1 709.5 *	1 718.2 1 693.7	1 706.0 *	1 712.9	1 714.2
$[Cr(cp)(CO)(NO)]$	*A* [ν(CO)]	1 944.8					
	A [ν(NO)]	1 678.8					
$[Cr(cp)(CO)(NO)(N_2)]$ (2e)	*A* [ν(NN)]						2 196.6
	A [ν(CO)]						1 967.5
	A [ν(NO)]						1 701.9

* Weighted mean position.

Long-wavelength photolysis (filter B) using the mercury arc produced four new high-frequency bands at the expense of the parent complex [Figure 6(*b*)]. A weak absorption at 2 138.0 cm^{-1} (not illustrated) corresponds to the formation of ' free ' CO, suggesting that an ejection of CO from the complex has occurred. The band at 1 944.8 cm^{-1} is due to a new terminal CO-stretching frequency. The bands at 1 720.2 and 1 678.8 cm^{-1} represent two new terminal NO-stretching vibrations. Changing photolysis conditions and annealing the matrix caused all bands to vary in intensity. A short period of annealing (small temperature rise) caused the band at 1 720.2 cm^{-1} to disappear while the bands at 1 944.8 and 1 678.8 cm^{-1} sharpened [Figure 6(*c*)]. Annealing to a higher temperature (not illustrated) caused the latter bands to decrease while the parent bands increased. The relative band intensities of the single terminal carbonyl band (1 944.8 cm^{-1}) and the equally weak nitrosyl band (1 678.8 cm^{-1}) remained constant under the varying conditions thus suggesting that they arise from a single photoproduct which is likely to be $[Cr(cp)(CO)(NO)]$. The other terminal nitrosyl-stretching frequency (1 720.2 cm^{-1}) might be due to some photochemical alterations of the parent species within the matrix, or could be due to the formation of $[Cr(cp)(NO)]$, or could arise from a change in the matrix environment of the parent molecule as a result of a forward and reverse photolysis step. Of these three possibilities the first two would give rise to a large shift (*ca.* 40—100 cm^{-1}) of ν(NO) to low wavenumbers whereas the latter would give a change in the matrix splitting pattern.[29] The behaviour of the nitrosyl band is very similar to that of the nitrosyl band of $[Ni(cp)(NO)]$ which on deposition is a triplet, becomes a doublet after photolysis, and returns to being a triplet after reversal and annealing of the matrix.[29] The change in the nitrosyl band for (2), therefore, probably indicates a facile forward and reverse photoreaction (see below) rather than a change in the mode of NO co-ordination or ejection of a second CO ligand. The i.r. spectrum of (2) isolated in Ar is similar to that in CH_4 (Table 4) but there is no evidence for any photoreaction under the various photolysis conditions used.

Photolysis in ^{13}CO *doped* (5%) Ar *and* CH_4 *matrices.* An experiment with (2) isolated at high dilution in a ^{13}CO doped (5%) CH_4 matrix shows two strong bands of the bis(^{12}CO) species [Figure 7(*a*)] together with bands marked (†) corresponding to isotopic bands of CO. Irradiation of the matrix (filter B) caused rapid growth of the bands corresponding to $[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$ and $[Cr(cp)(^{13}CO)_2(NO)]$ [Figure 7(*b*)]. Prolonged photolysis showed the presence of the bands corresponding to $[Cr(cp)(^{12}CO)(NO)]$ and $[Cr(cp)(^{13}CO)(NO)]$ [Figure 7(*c*)] as confirmed by the excellent agreement between observed and calculated [26-28] band positions (Table 5). A similar experiment in ^{13}CO doped (5%) Ar matrix only showed the enriched

TABLE 5

Observed and calculated * band positions (cm^{-1}) of terminal CO stretching bands in ^{13}CO enrichment experiments of $[Cr(cp)(CO)_2(NO)]$ (2) isolated in ^{13}CO doped methane and argon matrices at 12 K

			Matrix	
			CH_4	Ar
Compound	Symmetry		Observed (calc.)	Observed (calc.)
$[Cr(cp)(^{12}CO)_2(NO)]$ (2)	C_s	*A′*	2 024.7 (2 024.2)	2 025.2 (2 024.5)
		A″	1 955.5 (1 955.2)	1 954.7 (1 955.5)
$[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$	C_s	*A′*	2 008.9 (2 008.3)	2 009.4 (2 008.6)
		A″	1 926.3 (1 927.0)	1 927.5 (1 927.2)
$[Cr(cp)(^{13}CO)_2(NO)]$	C_s	*A′*	1 978.8 (1 979.3)	1 978.8 (1 979.5)
		A″	1 911.5 (1 911.8)	1 912.8 (1 912.0)
$[Cr(cp)(^{12}CO)(NO)]$	C_1	*A*	1 939.7 (1 940.1)	
$[Cr(cp)(^{13}CO)(NO)]$	C_1	*A*	1 896.5 (1 896.1)	

* Refined energy-factored CO stretching and interaction force constants (N m^{-1}) are for $[Cr(cp)(CO)_2(NO)]$, K = 1 600.0, k_i = 55.5; and $[Cr(cp)(CO)(NO)]$, K = 1 520.0.

species $[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$ and $[Cr(cp)(^{13}CO)_2(NO)]$ (Table 5).

Photolysis in N_2 *matrices.* The i.r. spectrum of (2) isolated in a N_2 matrix [Figure 8(*a*)] exhibits the same two

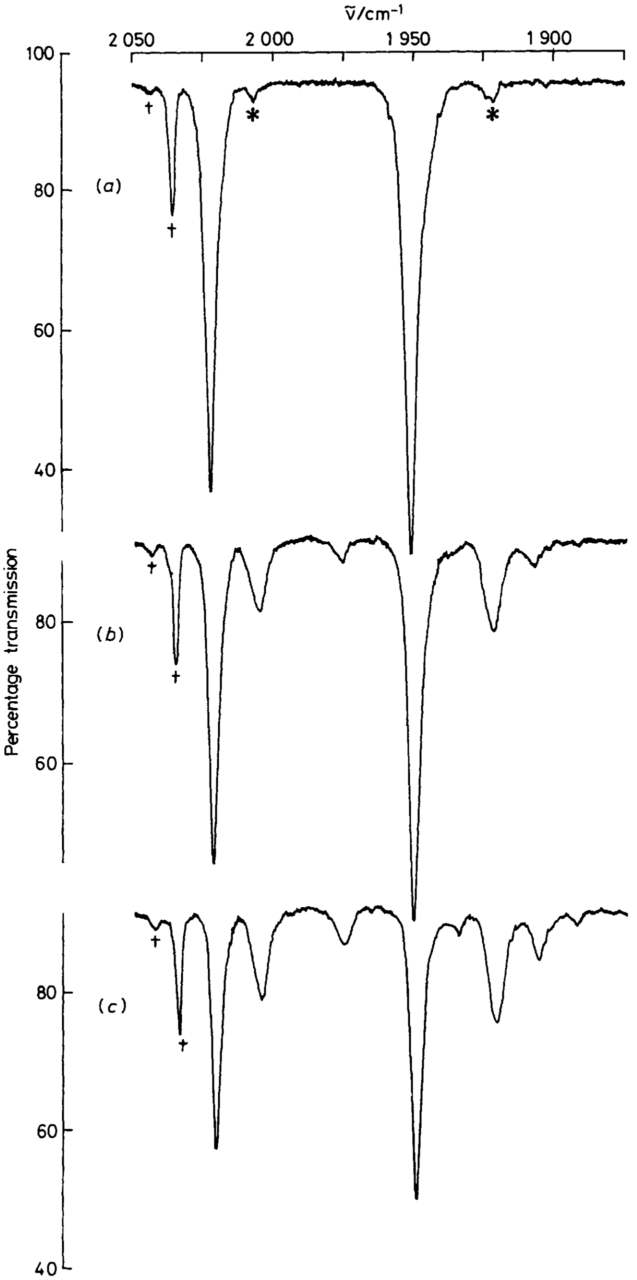

FIGURE 7 Infrared spectra from an experiment with $[Cr(cp)(CO)_2(NO)]$ (2) isolated in a ^{13}CO doped (5%) CH_4 matrix at 12 K: (*a*) after deposition; (*b*) after 40 min photolysis using filter B; (*c*) after further 40 min photolysis using filter B. Bands marked (*) are due to $[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$ in natural abundance and those marked (†) to $^{13}C^{17}O$ and $^{13}C^{18}O$

high-frequency bands corresponding to the symmetric A' (2 027.7 cm^{-1}) and asymmetric A'' (1 957.2 cm^{-1}) modes of the C_s $[Cr(CO)_2]$ fragment, and a single terminal nitrosyl absorption, A' (1 714.2 cm^{-1}) (Table 4). The weaker bands (marked with an asterisk) result from the natural abundance $[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$.

Photolysis using the long-wavelength radiation from the mercury lamp (filter B) produced new bands at 2 196.6, 2 138.0, 1 967.5, and 1 701.9 cm^{-1} [Figure 8(*b*)]. The band at 2 196.6 cm^{-1} appears in the region expected for co-ordinated N_2. With the formation of ' free ' CO at 2 138.0 cm^{-1} (not illustrated) it is likely that loss of CO has occurred with the formation of a dinitrogen complex. The apparent analogous behaviour of all bands under various photolysis conditions suggests that the photoproduct bands belong to a single species. The presence of a single terminal CO (1 967.5 cm^{-1}) and terminal NO (1 701.9 cm^{-1}) fundamentals and the absence of any liberated NO suggests that the photoproduct must be $[Cr(cp)(CO)(NO)(N_2)]$ (2e), where isoelectronic N_2 has replaced CO.

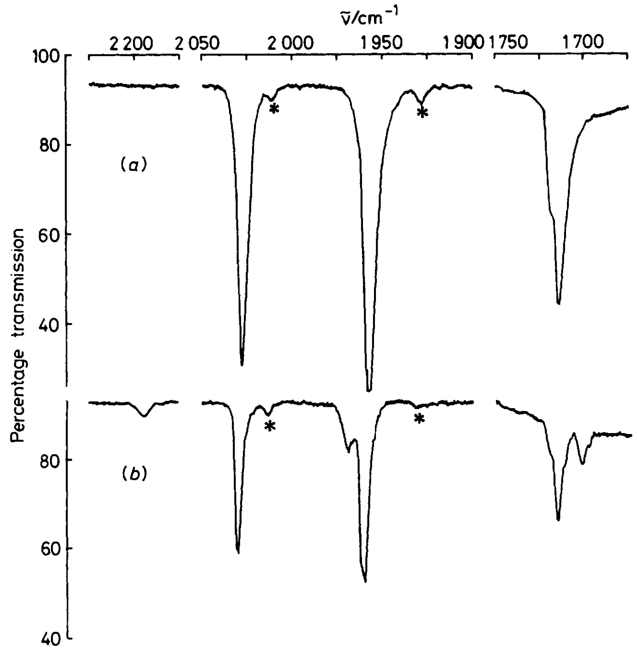

FIGURE 8 Infrared spectra from an experiment with $[Cr(cp)(CO)_2(NO)]$ (2) isolated at high dilution in a N_2 matrix at 12 K: (*a*) after deposition; (*b*) after 60 min photolysis using filter B. Bands marked (*) are due to $[Cr(cp)(^{12}CO)(^{13}CO)(NO)]$ in natural abundance

Photolysis in CO *matrices.* The i.r. spectrum of (2) isolated in carbon monoxide is very similar to that in methane, argon, and dinitrogen matrices (Table 4). However, there is no evidence for any photoreaction under the various photolysis conditions available.

(*c*) $[V(cp)(CO)(NO)_2]$ (3). *Photolysis in* Ar *and* CH_4 *matrices.* The vanadium complex (3) has a much more intense visible absorption (Figure 1) compared to $[Cr(cp)(CO)_2(NO)]$ (2) which only tails into the visible region of the electronic spectrum. Consequently, (3) is expected to be photochemically more reactive with visible light than the other members of the series. A coated germanium interference filter (Ocli Optical Coatings Ltd.) was, therefore, used to prevent any possible visible photolysis of the matrix sample by visible radiation of the glowbar of the i.r. spectrometer.[29]

The i.r. spectrum of (3) isolated in a methane matrix at high dilution is shown in Figure 9. The spectrum of the parent complex [Figure 9(*a*)] consists of a single terminal carbonyl-stretching A' (2 054.0 cm^{-1}) mode and two strong bands in the terminal nitrosyl-stretching region corresponding to the A' (1 731.0 cm^{-1}) and A'' (1 649.2 cm^{-1}) modes of the (C_s) [V(NO)$_2$] fragment (Table 6). The weaker band (marked with an asterisk, Figure 9) is due to [V(cp)(^{13}CO)(NO)$_2$] present in natural abundance.

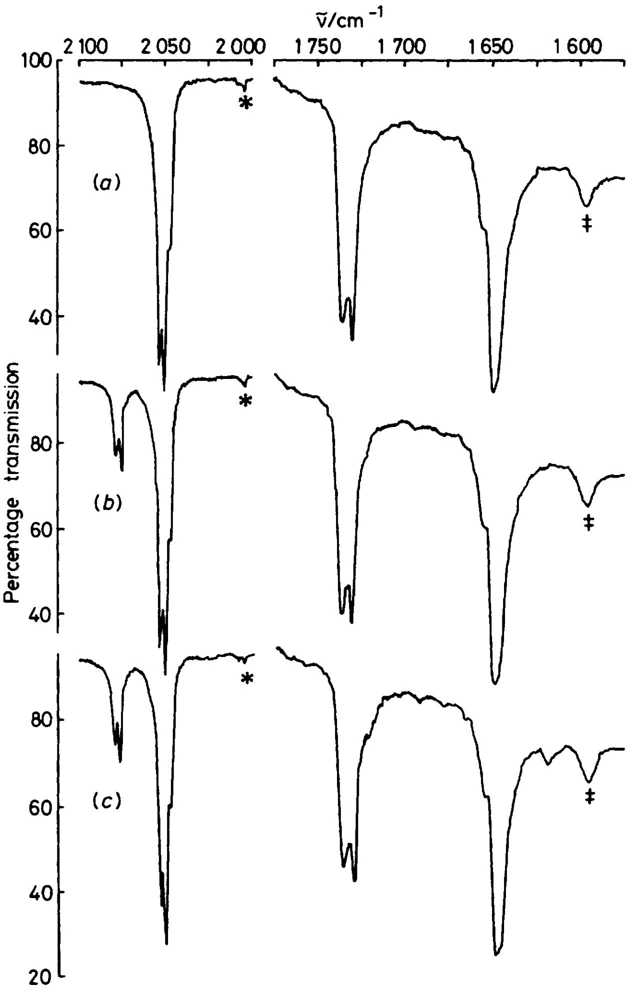

FIGURE 9 Infrared spectra from an experiment with [V(cp)(CO)(NO)$_2$] (3) isolated at high dilution in a CH$_4$ matrix at 12 K: (*a*) after deposition; (*b*) after 15 min photolysis using filter A; (*c*) after further 15 min photolysis using filter C. Bands marked (*) are due to [V(cp)(^{13}CO)(NO)$_2$] in natural abundance and those marked (‡) to a trace of matrix isolated H$_2$O

Irradiation of the matrix at longer wavelengths (filter A) for *ca.* 10 min produced little change in the intensity of the parent bands, but a new carbonyl absorption band at 2 080.0 cm^{-1} [Figure 9(*b*)] was produced without the apparent formation of any new terminal nitrosyl absorptions.* Further photolysis with the filtered medium-pressure mercury arc (filter C) produced the i.r. spectrum shown in Figure 9(*c*). There is little further formation of the band at 2 080.0 cm^{-1}, but new terminal NO bands were visible at 1 720.0 and 1 618.7 cm^{-1} together with a weak band at 2 138.0 cm^{-1} due to photochemically generated ' free ' CO.

The relative intensity of the two new terminal NO bands remained constant under a variety of photolyses indicating that they arose from a single product species. The dilution used (*ca.* 1 : 2 000) and the thermal reversibility (annealing) of the matrix reaction rule out the possibility of any polynuclear aggregate formation. The most probable formulation for the product species is [V(cp)(NO)$_2$] with the new bands assigned as the A_1 (1 720.0 cm^{-1}) and B_1 (1 618.7 cm^{-1}) terminal NO-stretching modes of a [V(NO)$_2$] fragment having local C_{2v} symmetry. Annealing the matrix caused some regeneration of the parent with partial loss of [V(cp)(NO)$_2$] and virtually the total disappearance of the band at 2 080.0 cm^{-1}.

A repeat experiment at much higher dilution (>1 : 5 000) failed to eliminate the formation of the high-frequency band (2 080.0 cm^{-1}), and the reversibility of the forward photoprocess indicates that aggregation is unlikely. With the absence of a terminal NO absorption for ' free ' NO, the presence of the band at 2 080.0 cm^{-1} could be due to the species [V(cp)(CO)(NO)(NO*)]. The weak bands at 1 652.9 and 1 393.9 cm^{-1} may be assigned to ν(NO) and ν(NO*) respectively, *cf.* ν(NO*) for [Ni(cp)(NO*)] at 1 390 cm^{-1}.[29] In these species (NO*) represents some type of co-ordinated NO ligand, where electron transfer to the nitrosyl ligand has occurred.[29]

Analogous results were obtained using an argon matrix (Table 6) although the rate of conversion to [V(cp)(NO)$_2$] was slower.

Photolysis in N$_2$ *matrices.* The i.r. spectra from an experiment with (3) in N$_2$ matrix are shown in Figure 10. At a dilution of *ca.* 1 : 2 000 the spectrum of the parent complex [Figure 10(*a*)] is very similar to that in argon and methane matrices (Table 6) but the bands are quite broad even

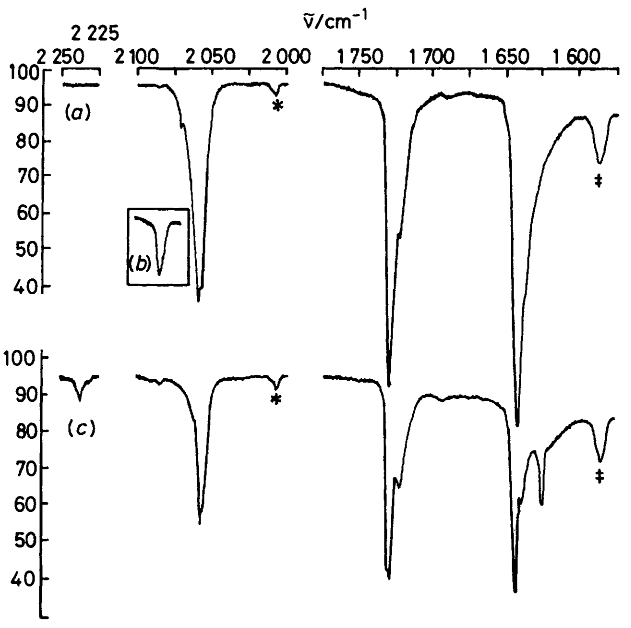

FIGURE 10 Infrared spectra from an experiment with [V(cp)(CO)(NO)$_2$] (3) isolated at high dilution in a N$_2$ matrix at 12 K: (*a*) after deposition; (*b*) after 10 min photolysis using filter A; (*c*) after further 10 min photolysis using filter C. Bands marked (*) are due to [V(cp)(^{13}CO)(NO)$_2$] in natural abundance and those marked (‡) are due to a trace of matrix isolated H$_2$O

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* A very recent experiment using a Nicolet 7199 FTIR spectrometer revealed two further weak bands at 1 652.9 and 1 393.9 cm^{-1} on computer subtraction of spectra.

TABLE 6

Band positions (cm^{-1}) for [V(cp)(CO)(NO)$_2$] (3) and its photoproducts in various matrices at 12 K

Compound		Matrix				
		CH$_4$		Ar	CO	N$_2$
[V(cp)(CO)(NO)$_2$] (3)	A' [ν(CO)]	2 055.1 2 052.9	2 054.0 [a]	2 050.9	2 056.6	2 057.8
	A' [ν(NO)]	1 734.0 1 728.0	1 731.0 [a]	1 741.7	1 732.0	1 732.8
	A'' [ν(NO)]	1 649.2		1 660.2	1 648.9	1 648.3
[V(cp)(CO)(NO)(NO*)]	[ν(CO)]	2 081.9 2 078.0	2 080.0 [a]	2 078.6	2 085.5 [b]	2 085.3
	[ν(NO)]	1 652.9		*c*	*c*	*c*
	[ν(NO*)]	1 393.9		*c*	*c*	*c*
[V(cp)(NO)$_2$]	A_1 [ν(NO)]	1 720.0		1 732.0	1 721.9	
	B_1 [ν(NO)]	1 618.7		1 630.2	1 620.5	
[V(cp)(NO)$_2$(N$_2$)] (3c)	A' [ν(NN)]					2 232.0
	A' [ν(NO)]					1 733.0
	A'' [ν(NO)]					1 637.0
[V(cp)(CO)$_2$(NO)(NO*)]					2 009.4	

[a] Weighted mean position. [b] Band partially coincident with matrix $^{13}C^{16}O$ band. [c] Weak bands not observable using Grubb-Parsons Spectromajor.

under the most carefully controlled spray-on conditions. This behaviour seems to be characteristic of vanadium complexes as previously observed in the studies of [V(CO)$_6$] isolated in frozen matrices.[30] Again, a weak band (marked with an asterisk) is observed in the initial spectrum due to natural abundance [V(cp)(^{13}CO)(NO)$_2$].

Photolysis with the medium-pressure mercury lamp and filter A produced a spectrum [Figure 10(*b*)] containing one new band at 2 085.3 cm^{-1} corresponding to the same species [V(cp)(CO)(NO)(NO*)] as observed in argon and methane. The possibility of [V(cp)(CO)(NO)(NO*)] formation in both reactive and inert matrices is suggested by the failure to detect the presence of a high-frequency band corresponding to co-ordinated dinitrogen (> 2 150.0 cm^{-1}), *i.e.* no ligand loss is occurring. Further photolysis, using filter C, produced four new bands [Figure 10(*c*)] at 2 232.0, 2 138.0, 1 733.0, and 1 637.0 cm^{-1} at the expense of the parent absorptions. The band at 2 138.0 cm^{-1} (not illustrated) corresponds to the position of ' free ' CO. Formation of ' free ' CO and a co-ordinated dinitrogen band (2 232.0 cm^{-1}) indicate some replacement of CO in the complex by N$_2$ has now taken place. The assignment of the bands at 1 733.0 and 1 637.0 cm^{-1} as terminal NO-stretching modes (Table 6) leads to the identification of the primary photoproduct as [V(cp)(NO)$_2$(N$_2$)] (3c). Annealing the matrix made no visible difference to the intensity of both parent and product absorption bands.

Photolysis in CO *matrices*. The i.r. spectrum of (3), isolated in a pure CO matrix at a dilution of *ca.* 1 : 2 000, in the terminal CO- and NO-stretching regions is shown in Figure 11(*a*). The single absorption at 2 056.6 cm^{-1} is the terminal CO-stretching A' mode band and the two strong bands at 1 732.0 and 1 648.9 cm^{-1} are the terminal NO-stretching A' and A'' modes respectively (Table 6). The natural abundance [V(cp)(^{13}CO)(NO)$_2$] band is observed at 2 009.2 cm^{-1} (marked with an asterisk, Figure 11). A short duration of photolysis using filter A produced a new band at *ca.* 2 085 * cm^{-1} [Figure 11(*b*)], assigned to the same species, [V(cp)(CO)(NO)(NO*)], which had been observed earlier in argon, methane, and dinitrogen matrices. The failure to observe ν(NO*) is probably due to weakness of the band in a region masked by bands of H$_2$O vapour. Further photolysis using filter C produced three new bands [Figure 11(*c*)] at 2 009.4,‡ 1 721.9, and 1 620.5 cm^{-1} (Table 6). The bands at 1 721.9 and 1 620.5 cm^{-1} correspond to the terminal NO-

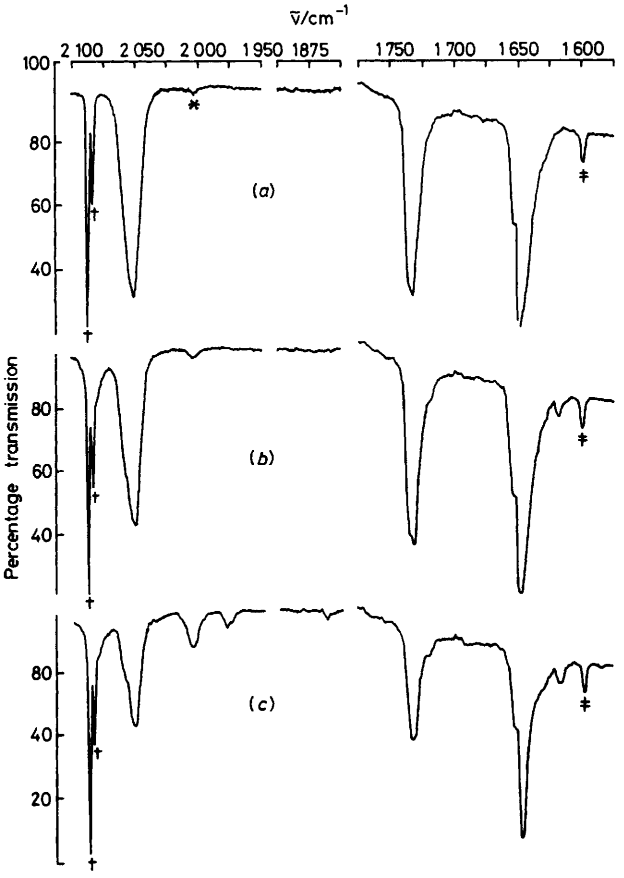

FIGURE 11 Infrared spectra from an experiment with [V(cp)(CO)(NO)$_2$] (3) isolated at high dilution in a CO matrix at 12 K: (*a*) after deposition; (*b*) after 10 min photolysis using filter A; (*c*) after further 30 min photolysis using filter C. The band marked (*) is due to [V(cp)(^{13}CO)(NO)$_2$] in natural abundance, those marked (†) are due to natural abundance isotopes of CO, and those marked (‡) due to a trace of matrix isolated H$_2$O

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* The exact position of this band is unobtainable due to partial coincidence with the matrix absorption.

‡ This band coincides with the natural abundance [V(cp)(^{13}CO)(NO)$_2$] absorption.

stretching bands of the photoproduct [V(cp)$(NO)_2$]. A possible explanation for the band at 2 009.4 cm^{-1} is that incorporation of CO into the species [V(cp)(CO)(NO)(NO*)] has occurred to form a new photoproduct ' [V(cp)$(CO)_2$(NO)(NO*)] '.

Continued irradiation of this system using filter C afforded the formation of two bands at 1 982.7 and 1 865.9 cm^{-1} [Figure 11(*c*)]. The band at 1 865.9 cm^{-1} may be assigned to the ' free ' NO absorption.[31] In separate matrix isolation experiments on photolysis of [V(cp)$(CO)_4$] [ν(CO) 2 031.7 and 1 933.1 cm^{-1}] in a CO matrix the possible formation of [V(η^3-C_5H_5)$(CO)_5$] [ν(CO) 2 056.1, 1 981.5, and 1 946.2 cm^{-1}] has been observed.[32] With the ejection of NO from the photoproduct [V(cp)$(CO)_2$(NO)(NO*)] it is plausible to assign the band at 1 982.7 cm^{-1} to [V(η^3-C_5H_5)$(CO)_5$] with the other bands obscured by the parent absorption or too weak to be observed.

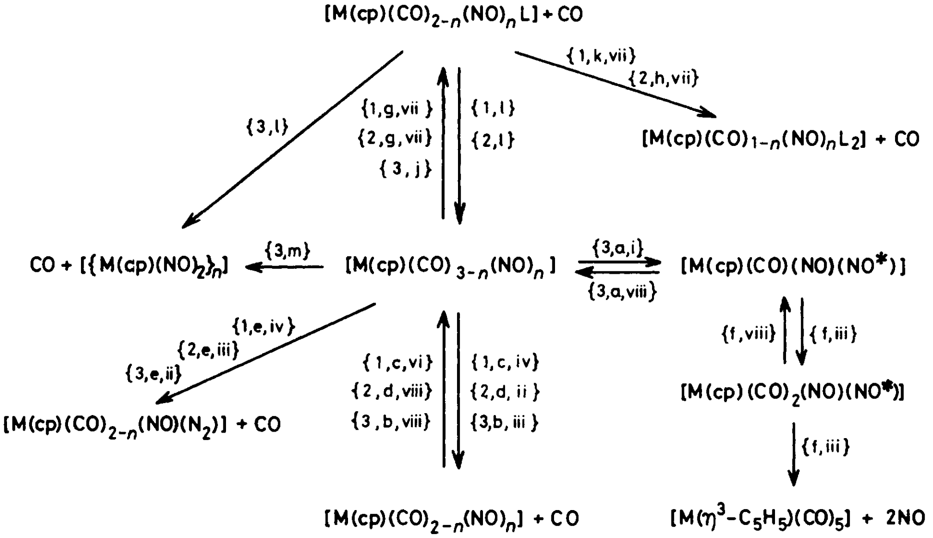
DISCUSSION

The combined investigation of both solution and matrix photochemistry has the advantage that the nature of the photogenerated primary intermediates can be deduced both indirectly from their reactivity in solution and directly from the characteristic i.r. bands of the mononuclear species trapped in the rigid matrix. The two approaches complement each other.

The isoelectronic complexes [Mn(cp)$(CO)_3$] (1), [Cr(cp)$(CO)_2$(NO)] (2), and [V(cp)(CO)$(NO)_2$] (3) were photolysed in both inert solvents (hexane) and inert matrices (methane or argon). In addition, the fate of the primary photoproducts was investigated in co-ordinating solvents (thf, cyclo-octene) and co-ordinating matrices (carbon monoxide, dinitrogen). The photo-induced reactions are summarised in Scheme 1.

Photochemical substitution reactions of metal carbonyls in solution generally proceed with high quantum yields and are independent of the nature and concentration of the incoming nucleophile.[1-7] For example, the quantum yield for replacement of a CO ligand by diphenylacetylene in [Mn(cp)$(CO)_3$] has been reported to be 1.0.[33] The primary photochemical reaction, therefore, involves the dissociative loss of CO. The sequence of processes for such dissociative reactions of [M(cp)$(CO)_{3-n}(NO)_n$] complexes can be represented as in Scheme 2, where the asterisk denotes an excited state species.

The only detailed study of a photochemical substitution reaction of a metal carbonyl nitrosyl is that for [Mn$(CO)_4$(NO)] in solution.[34] In this case the quantum yields for the replacement of a CO ligand by PPh_3, $AsPh_3$, and $PBu^n{}_3$ were less than unity and were found to depend both on the entering group and, for PPh_3, on its concentration. These two facts were interpreted as indicative of an associative contribution to the overall photoreaction. This could possibly take place *via* a change in the M–NO interaction from one where the NO ligand is a three-electron donor to one where the NO



SCHEME 1

Complexes

(1) M = Mn, *n* = 0
(2) M = Cr, *n* = 1
(3) M = V, *n* = 2

Gas matrices

a. Ar, CH_4, CO, or N_2
b. Ar, CH_4, or CO
c. Ar or CH_4
d. CH_4
e. N_2
f. CO

Ligands (*L*)

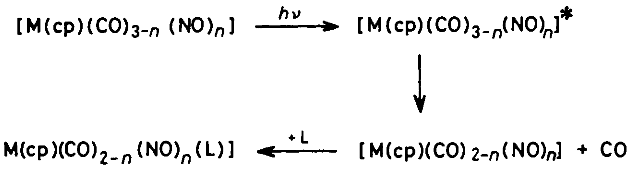
g. PEt_3 in C_6D_6 solution, C_8H_{14} or thf solution
h. PEt_3 in C_6D_6 solution or C_8H_{14} solution
j. PEt_3 in C_6D_6 solution or thf solution
k. PEt_3 in C_6D_6 solution
l. thf solution
m. n-hexane solution, daylight

Reaction conditions

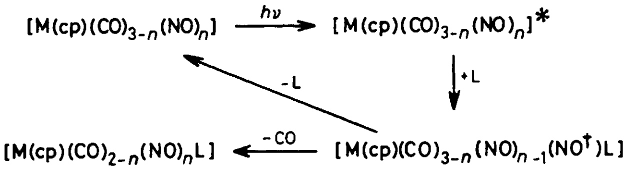
i. *hν* (filter A)
ii. *hν* (filter B)
iii. *hν* (filter C)
iv. *hν* (filter D)
v. *hν* (filter E)
vi. *hν* (filter E) or anneal
vii. *hν* (unfiltered)
viii. anneal

ligand is a one-electron donor, as denoted by NO† in Scheme 3.

The photo-induced substitution of CO ligands by PEt_3 was studied in order to compare the reactivity of complexes (1)—(3). The integration of the n.m.r. signals of the cyclopentadienyl ring protons is only of limited accuracy, but the method nevertheless gives a rapid estimate of the amount of the original complex converted into PEt_3-substituted derivatives within a given period of time (Figures 2 and 3). In all cases the cyclopentadienyl signals of the products are sufficiently separated from that of the parent complex (Table 2). Within the series (1)—(3), only $[V(cp)(CO)(NO)_2]$ (3) reacts with PEt_3 at ambient temperatures in the dark; the product is (3b). Complexes (1) and (2) require photo-excitation for the substitution of CO ligands to take place, and stepwise replacement of one or two CO ligands by PEt_3 leads to the mono- or di-substituted derivatives (1c), (1d) and (2c), (2d) respectively. The analogous compounds $[Mn(cp)(CO)_2(PPh_3)]$, $[Mn(cp)(CO)(PPh_3)_2]$ [35] and $[Cr(cp)(CO)(PPh_3)(NO)]$, $[Cr(cp)(PPh_3)_2(NO)]$ [8,10] respectively have also been prepared photochemically. If the molar ratio of parent complex [(1) or (2), respectively] to triethylphosphine is kept at 1 : 1, the formation of the disubstituted derivative $[Mn(cp)(CO)(PEt_3)_2]$ (1d) is limited (<15%) and that of $[Cr(cp)(PEt_3)_2(NO)]$ (2d) remains almost negligible (Figures 2 and 3). With increasing PEt_3 concentration the relative amounts of the disubstituted complex increase. As shown in Figure 4, the rate of disappearance of $[Mn(cp)(CO)_3]$ (1) is not significantly influenced by excess PEt_3. However, the ratio of the products (1c) and (1d) depends strongly on the concentration of PEt_3 (Figure 5). It appears, therefore, that the reactivity of the photo-excited species $[Mn(cp)(CO)_3]^*$ is nearly unaffected by the presence of PEt_3 which is only required for secondary chemical reactions. Complexes (1) and (2) undergo dissociative loss of CO to give $[Mn(cp)(CO)_2]$ and $[Cr(cp)(CO)(NO)]$ as the first chemical products (Scheme 2). For $[V(cp)(CO)(NO)_2]$, however, the facile dark reaction and the fact that photosubstitution is considerably accelerated at higher PEt_3 concentrations indicates that there could be a contribution from the associative photochemical path, *i.e.* involving [V(cp)(CO)(NO)(NO†)L] (Scheme 3).



SCHEME 2



SCHEME 3

The primary photoproduct $[Mn(cp)(CO)_2]$ cannot be observed during photolysis of (1) in the inert solvent hexane at room temperature where photodecomposition and loss of all CO ligands predominates. However, photolysis of (1) in the donor solvent thf leads to stabilisation of the $[Mn(cp)(CO)_2]$ fragment in the form of $[Mn(cp)(CO)_2(OC_4H_8)]$ (1a); the thf solution of (1a) is stable when kept at −30 °C. The red complex (1a) has been isolated from its thf solution at temperatures below 0 °C.[22] The i.r. frequencies of (1a) (1 928 and 1 852 cm^{-1}) agree well with the mean values of the ν(CO) frequencies reported [36] for the two rotamers of (1a) in methylcyclohexane–isopentane (4 : 1) glasses doped with 5% thf [1 942/1 865 (minor rotamer) and 1 916/1 834 cm^{-1} (major rotamer)], respectively. The photochemical substitution of more than just one CO ligand in (1) by the solvent is not observed in thf solution. This is in contrast to the results of the photolysis of (1) in methylcyclohexane–isopentane (4 : 1) glasses doped with 5% thf where the formation of a disubstituted derivative $[Mn(cp)(CO)(OC_4H_8)_2]$ has been found.[36] In contrast to (1), complex (2) loses two CO ligands successively upon prolonged irradiation in thf solution, forming a side-product identified as $[Cr(cp)(NO)_2(NO_2)]$ from the mass spectrum. Loss of the CO ligand occurs also in solutions of (3) in daylight at room temperature. The brown product precipitating from hexane solutions of (3) has the approximate composition $\{V(cp)(NO)_2\}_n$.[37] This material shows spectra similar to those of the thf-soluble product obtained by Morán and Gayoso [24] and formulated as the binuclear $[\{V(cp)(NO)_2\}_2]$. In thf solution (3) slowly loses CO even in the dark to give the thermolabile derivative (3a) initially. The direct thermal substitution of the carbonyl group in (3) by two-electron ligands (Lewis bases) co-ordinating through lone pairs at a phosphorus,[13,38] nitrogen, sulphur, or oxygen atom has been accomplished in various solvents.[38]

Similarly, CO substitution reactions are observed for (1), (2), and (3) upon photolysis in cyclo-octene solutions. The only product formed by photolysis of (1) in cyclo-octene is the known [22,23] η^2-olefin complex $[Mn(cp)(CO)_2(C_8H_{14})]$ (1b). However, (2) forms both mono- and di-substituted complexes and it turns out that the η^2-cyclo-octene derivative $[Cr(cp)(CO)(C_8H_{14})(NO)]$ (2b) is a more attractive intermediate [10] for the synthesis of [Cr(cp)(CO)(L)(NO)] complexes (L = two-electron ligand) than the thf derivative (2a).[19] Complex (2b) has been characterised in the solid state [9,11] and used for the attachment of the [Cr(cp)(CO)(NO)] fragment to potential two-electron ligands (see, for example, refs. 9—11 and 39).

In general, the photolysis of (1), (2), and (3) in gas matrices at 12 K leads to the ejection of a CO ligand and the formation of co-ordinatively unsaturated species $[M(cp)(CO)_{2-n}(NO)_n]$ (Scheme 1). Such species are in accordance with the proposals for the dissociative path for photochemical substitution reactions (Scheme 2). The i.r. band positions for [Mn(cp)$(CO)_2$] in argon and methane matrices agree well with those for hydrocarbon glasses at 77 K.[36] In contrast with (1) and (2), irradiation of (3) with visible light produces an additional species [V(cp)(CO)(NO)(NO*)], where (NO*) represents a type of co-ordinated NO ligand in which electron transfer to the ligand has taken place.[29] Similar behaviour has been noted on photolysis of [Mn(CO)$(NO)_3$] [40] and [Mn$(CO)_4$(NO)] [41] in gas matrices at 12—20 K. By analogy with the known associative path of photosubstitution reactions of [Mn$(CO)_4$(NO)] [34] (Scheme 3), it seems probable that the photosubstitution reactions of [V(cp)(CO)$(NO)_2$] have a contribution from an associative process. In this context photolysis of [V(cp)(CO)$(NO)_2$] in a matrix containing a good nucleophile, *e.g.* CO, would be expected to yield [V(cp)$(CO)_2$(NO)(NO*)] as a preliminary process prior to loss of NO. On extended photolysis in a CO matrix, evidence is seen for ' free ' NO but as yet only a tentative assignment of a product species as [V(η^3-C_5H_5)$(CO)_5$] can be made. Future experiments with a Fourier-transform i.r. spectrometer will aim to detect other species and thereby clarify the details of the associative path of photosubstitution reactions in metal nitrosyl complexes.

The reactivity of matrix-isolated [M(cp)$(CO)_{2-n}(NO)_n$] species is demonstrated by recombination with CO on annealing the matrices and on longer wavelength photolysis, by the facile exchange of ^{12}CO ligands with ^{13}CO doped into matrices, and by the reaction with N_2 to give [M(cp)$(CO)_{2-n}$(NO)(N_2)] species. The formation of [Mn(cp)$(CO)_2(N_2)$] (1e) in reactive N_2 matrices [25] is not surprising since this complex has been characterised following reaction of N_2 with a thf solution of (1a).[42-44] The band positions of matrix-isolated (1e) [25] agree well with those for (1e) in n-hexane.[42] As yet the other N_2 species [Cr(cp)(CO)(NO)(N_2)] (2e) and [V(cp)$(NO)_2(N_2)$] (3c) have not yet been isolated as molecular complexes. Comparison of ν(NN) for these species [(2e), 2 196 cm^{-1}; (3c), 2 232 cm^{-1}] with ν(NN) for (1e) (2 175 cm^{-1}) [25] suggests that in (2e) and (3c) the N–N bond gets progressively stronger in the series Mn < Cr < V, while in the same series the M–N bond will get progressively weaker, *i.e.* Mn–N > Cr–N > V–N. While the Cr–N bond may be strong enough to allow characterisation of [Cr(cp)(CO)(NO)(N_2)] it seems unlikely that the vanadium species would be stable as a molecular complex.

The very facile exchange of bound CO ligands with ^{13}CO doped in the matrices, often in circumstances when no detectable quantities of the co-ordinatively unsaturated species [M(cp)$(CO)_{2-n}(NO)_n$] are observed, indicates that within the solution solvent cage there must also be the distinct possibility of recombination of [M(cp)$(CO)_{2-n}(NO)_n$] with ejected CO. Therefore, quantum yields of unity for photosubstitution reactions would not be expected and should be viewed with caution. Indeed, the quantum yield for photosubstitution in [Cr$(CO)_6$] has recently been re-determined as 0.67 (ref. 45) rather than unity.[1]

No evidence was obtained for the ejection of the cyclopentadienyl ligand from [M(cp)$(CO)_{3-n}(NO)_n$] complexes, not even on prolonged photolysis in ' reactive ' CO matrices. This is in contrast to the formation of [Ni$(CO)_4$] on photolysis of [Ni(cp)(NO)] in CO matrices.[29]

Matrix and solution experiments with the nitrosylmetal complexes [M(cp)$(CO)_2$(NO)] [M = Cr (2), Mo, or W) and [V(cp)(CO)$(NO)_2$] (3) are in progress which indicate that upon charge-transfer photoexcitation (200—300 nm) the generation of a ' nitrene ' species is possible. This is expected to lead to isocyanate complexes, as observed in the formation of [Mo(cp)$(CO)_2$$(PPh_3)$(NCO)] [46] from [Mo(cp)$(CO)_2$(NO)].

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