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Journal of Organometallic Chemistry 484 (1994) 129–135

Journal of Organometallic Chemistry

# Organometallic photochemistry in supercritical fluids: reactions of cyclopentadienyl carbonyl and phosphine carbonyl complexes of manganese with dinitrogen

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Received 15 March 1994

## Abstract

UV photolysis has been used to generate dinitrogen compounds by substitution of CO groups by $N_2$ in supercritical fluid solvents (scXe, $scCO_2$ and $scC_2H_6$) containing high pressures of $N_2$. Compounds include $Cp'Mn(CO)_2L$ ($Cp' = C_5H_4Me$; $L = PMe_{3-x}Ph_x$, $x = 0$ to 3). A semi-quantitative comparison of the photolysis of $Cp^*Mn(CO)_3$ ($Cp^* = C_5Me_5$) and $N_2$ in scXe and $scCO_2$ indicates that there is little difference between the effectiveness of the photolysis in these two supercritical solvents. The Timney Ligand Effect approach is used to rationalise the fact that some of the $\nu$(C–O) and $\nu$(N–N) bands of $Cp^*Mn(CO)_2(N_2)$ and $Cp^*Mn(CO)(N_2)_2$ are nearly coincident.

*Keywords:* Manganese; Carbonyl; Supercritical fluids; Photochemistry; Dinitrogen; Phosphine

## 1. Introduction

The photochemical substitution of CO groups by $N_2$ is a well-established route to unstable or reactive transition metal carbonyl dinitrogen complexes, (Eq. 1).

$$M(CO)_x + N_2 \xrightarrow{UV} M(CO)_{x-1}(N_2) + CO \qquad (1)$$

Originally devised for use in cryogenic matrices [1], this route has been extensively explored for reactions in liquefied noble gas solvents [2] and, by fast IR measurements, in conventional hydrocarbon solvents at room temperature [3]. More recently, we have shown that supercritical fluids offer particular advantages as solvents for such reactions [4] because the gas-like nature of the fluids provides complete miscibility with permanent gases, such as $N_2$ or $H_2$. This miscibility raises the effective concentration of "dissolved" gas by as much as one order of magnitude compared to that in conventional solvents under similar conditions. We have exploited this effect for the photochemical generation of a range of previously unknown dinitrogen and dihydrogen complexes, e.g. $CpRe(N_2)_3$, from carbonyl precursors in supercritical Xe, scXe [4a]. The high solubility of $H_2$ in supercritical $CO_2$, $scCO_2$, has since been exploited by others for thermal reactions of metal carbonyls [5].

In principle, supercritical fluids offer further advantages. For example, the recovery of solutes from supercritical solution is very simple; all that is required is to lower the pressure of the fluid and the solvent becomes gaseous [6]. Until now, our photochemical experiments have largely been carried out in scXe because of its outstanding spectroscopic properties, total transparency from far UV to far IR. However, scXe is expensive and, for most purposes, $scCO_2$ would be preferable because it is chemically almost as inert as scXe but much cheaper, it also has potential as an environmentally benign solvent. The work described in this paper, therefore, had two aims: (a) to investigate the anecdotal suggestion that photochemical reactions are less efficient in $scCO_2$ than in scXe, and (b) to

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*SSDI* 0022-328X(94)24713-S

investigate the effect of phosphine substituents on the photochemical reactions of $CpMn(CO)_2L$ compounds with $N_2$.

## 2. Experimental details

All photochemical experiments were carried out at Nottingham. The miniature high-pressure cells for photochemistry in supercritical fluids have been described previously [7]. Carbonyl compounds were added to the cell as solids under Ar. The cells were then pressurized with $scCO_2$ using a Lee Scientific model 501 syringe pump, and $N_2$ was then introduced directly from a gas cylinder through a high pressure regulator. Photolysis was carried out with a 300 W Cermax Xe lamp in association either with an OP2 "cold mirror" to filter out visible radiation or with a Lumatec 1 m light guide. The irradiation geometry was similar to that described in Ref. 4b. IR spectra were recorded on a Nicolet Model 730 interferometer (16 K data points, 32 K transform points, 2 $cm^{-1}$ resolution).

Time-resolved IR spectra were obtained using the spectrometer at Nottingham [8]. Briefly, this comprises a Lumonics HyperEx 440 pulsed UV excimer laser (XeCl, 308 nm), a modified Edinburgh Instruments PL3 cw IR carbon monoxide laser, a liquid nitrogen-cooled HgCdTe IR detector and Gould Model 4072 digitiser. *N*-heptane (Aldrich) was distilled over $CaH_2$, and Ar and $N_2$ (BOC Research grade) were used without further purification.

The complexes $Cp'Mn(CO)_2PPh_3$, $Cp'Mn(CO)_2L$ ($Cp' = C_5H_4Me$; $L = PMe_3$, $PMe_2Ph$ & $PMePh_2$) were synthesized by published routes [9]. The complex $Cp^*Mn(CO)_3$ ($Cp^* = C_5Me_5$), from Strem Chemicals, was used as supplied, as were Xe (BOC Research Grade), $N_2$ (BOC) and $CO_2$ (Air Products SFC grade).

The Timney approach is an empirical method for predicting the CO-stretching force constants and associated vibrational frequencies, using the relationships $k_{CO} = k_d + \Sigma\epsilon_L^\theta$ and $k_i = A - Bk_{CO}$ where $k_d$ is the force constant of the fragment, MCO, depending on the number of electrons at the metal centre and $\Sigma\epsilon_L^\theta$ are the Ligand Effect Constants, which are derived values for each ligand in the three main geometries (tetrahedral, trigonal bipyramidal and octahedral) [10]. *A* and *B* are two empirical constants dependent on the angle between the two interacting carbonyl ligands.

## 3. Results and discussion

### 3.1. Comparison of $scCO_2$ and scXe as solvents for photochemical reactions

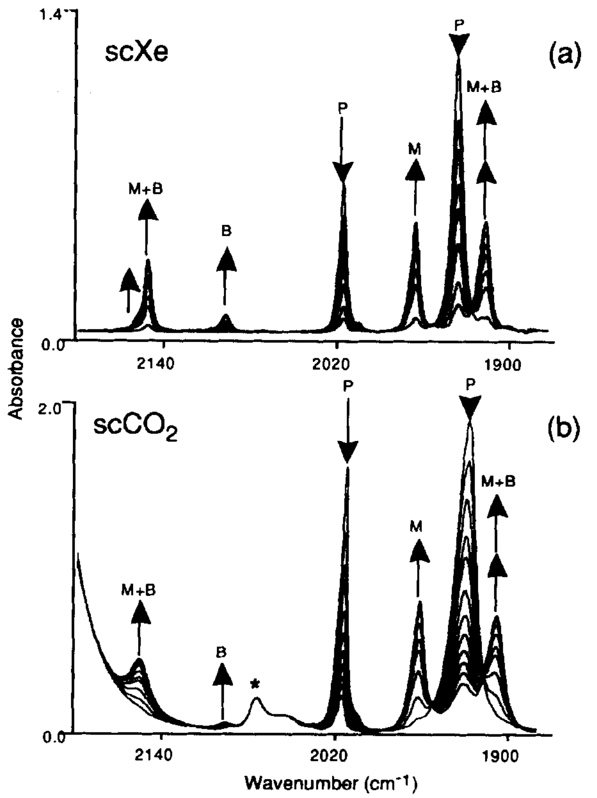


Fig. 1. IR Spectra comparing the effects of UV irradiation of a solution containing $Cp^*Mn(CO)_3$ in (a) scXe and (b) $scCO_2$ doped with a high pressure of $N_2$. In both cases the cell was filled with fluid to a pressure of 1000 psi at 25°C, and then $N_2$ was added to give a total pressure of 3100 psi (scXe) and 3200 psi ($scCO_2$). Spectra were recorded during UV irradiation at regular intervals over a period of ca. 20 min.. The bands are labelled as follows; *P*, parent $Cp^*Mn(CO)_3$; *M*, mono-substituted product, $Cp^*Mn(CO)_2(N_2)$ and *B*, *bis*-substituted $Cp^*Mn(CO)(N_2)_2$. Note that the sloping baseline on the left-hand side of spectrum (b) is caused by the tail of an IR absorption of $scCO_2$ itself.

In principle, any comparison of scXe and $scCO_2$ should be carried out under conditions as nearly identical as possible. However, the two fluids have significantly different critical parameters (Xe; $T_c = 16.9$°C, $P_c = 58$ atm.: $CO_2$; $T_c = 31.6$°C, $P_c = 73$ atm. [11]) and so it is not entirely clear what criteria should be chosen as being "identical" for the two solvents. In the event, we decided that for semi-quantitative studies at least, it was sufficient to ensure that the pressure of $N_2$ was similar in the two solvents, and that the concentrations of dissolved $Cp^*Mn(CO)_3$ were comparable.

Fig. 1 shows a series of IR spectra recorded during photolysis of $Cp^*Mn(CO)_3$ and $N_2$ in (a) scXe and (b) $scCO_2$. Qualitatively, the spectra are strikingly similar, and even a semi-quantitative analysis, as in Fig. 2, shows that there is little difference between rate of formation of $Cp^*Mn(CO)_2(N_2)$ in the two solvents. Thus, $scCO_2$ is clearly an acceptable alternative to scXe for such reactions.

A closer examination of the spectra shows that UV photolysis leads to substitution not just of one but also of two CO groups, to yield small amounts of the

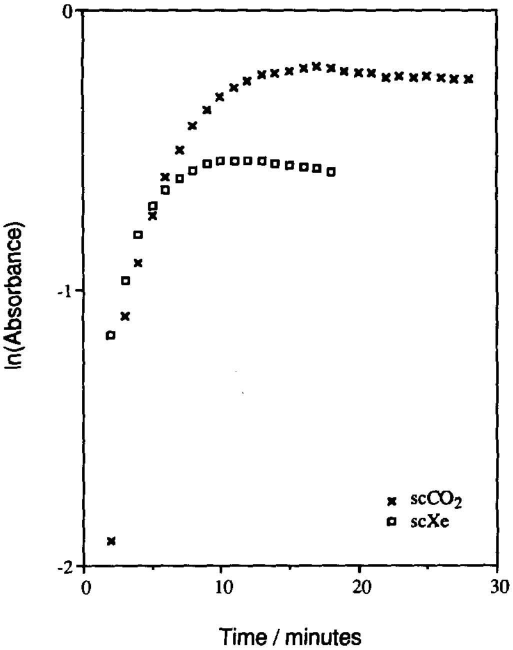


Fig. 2. Plots of ln(*Absorbance*) of the higher wavenumber (*a*′) $\nu$(C–O) band of $Cp^*Mn(CO)_2(N_2)$ against time of UV irradiation. Traces are labelled □, scXe and x, scCO$_2$. It can be seen that the rate of formation of $Cp^*Mn(CO)_2(N_2)$ is similar in the two fluids.

previously unknown $Cp^*Mn(CO)(N_2)_2$, identifiable by analogy with the $(C_5Et_5)Mn(CO)_3/N_2$ system [4b]. This behaviour contrasts with that of $CpMn(CO)_3$, for which substitution of only one CO group is observed under these conditions. It can also be seen from Fig. 1 and from Table 1, that the some of the bands of $Cp^*Mn(CO)(N_2)_2$, **2**, and $Cp^*Mn(CO)_2(N_2)$, **1**, must be assumed to be coincident; in particular, the symmetric $\nu$(N–N) band of **2** and the $\nu$(N–N) band of **1** and the $\nu$(C–O) band of **2** and the antisymmetric $\nu$(C–O) band of **1**. Indeed, such coincidences appear to be quite a common feature in half-sandwich metal carbonyl dinitrogen complexes, and have now been observed for Mn, Re and Fe systems [4a,b]. Table 1 summarizes Timney calculations for the $\nu$(C–O) bands for the $Cp^*Mn(CO)_3$ system, and it can be seen that the relevant $\nu$(C–O) bands of **1** and **2** are predicted to be close but not coincident. In this context, however, the importance of the Timney calculations lies not so much in the precise wavenumbers, but in the overall implications for similar $(C_nR_n)M(CO)_{3-x}(N_2)_x$ species. In terms of the Timney approach and ignoring any coupling between $\nu$(C–O) and $\nu$(N–N) vibrations, the difference in $k_{CO}$, the C–O-stretching force constant, between $(C_nR_n)M(CO)_2(N_2)$ and $(C_nR_n)M(CO)(N_2)_2$ will be given by eq. 2, which suggests that $\Delta k_{CO}$ is not only independent of the nature of the metal but also independent of the nature of the $C_nR_n$ ligand.

$$k_{CO} = k_6 + \epsilon^{\theta}_{C_nR_n} + \epsilon^{\theta}_{N_2} + \epsilon^{\theta}_{CO} \text{ for } (C_nR_n)M(CO)_2(N_2)$$

$$k_{CO} = k_6 + \epsilon^{\theta}_{C_nR_n} + 2\epsilon^{\theta}_{N_2} \text{ for} (C_nR_n)M(CO)(N_2)_2$$

whence

$$\Delta k_{CO} = \epsilon^{\theta}_{N_2} - \epsilon^{\theta}_{CO} \qquad (2)$$

Eq. 3 implies that, if particular bands are nearly coincident for a given pair of $(C_nR_n)M(CO)_{3-x}(N_2)_x$ species, then they are likely to be coincident for any analogous pair with the same metal and the same $C_nR_n$ ring. Any difference between one pair of compounds and another will largely reflect differences in the CO, CO interaction force constant rather than in the stretching force constant.

### 3.2. *Reaction of phosphine-substituted complexes with $N_2$*

The photochemical reactions of $CpMn(CO)_2L$ species with $N_2$ are inherently more complicated than those of $CpMn(CO)_3$ because there are two possible

Table 1
The wavenumbers (cm$^{-1}$) [a] of the observed and calculated $\nu$(C–O) bands and of the observed $\nu$(N–N) bands of $Cp^*Mn(CO)_{3-x}(N_2)_x$ ($x = 0$, 1 or 2) in scXe/N$_2$ solution at 25°C

| Complex | $\nu_{obs}$ | | $\nu_{calc}$ [b] | $\Delta(\nu_{obs} - \nu_{calc})$ [c] | Assignment |
|---|---|---|---|---|---|
| $Cp^*Mn(CO)_3$ | 2015.3 | (2010) [d] | 2029 | −14w. | $a_1$ $\nu$(C–O) |
| | 1936.2 | (1927) [d] | 1926 | 10 | *e* $\nu$(C–O) |
| $Cp^*Mn(CO)_2(N_2)$ | 2150.7 | (2151.8) [d] | | | *a*′ $\nu$(N–N) |
| **1** | 1965.7 | (1958.4) [d] | 1967 | −1.3 | *a*′ $\nu$(C–O) |
| | 1917.5 | (1905.0) [d] | 1918 | 0.5 | *a*″ $\nu$(C–O) |
| $Cp^*Mn(CO)(N_2)_2$ | [2151] [e] | | | | *a*′ $\nu$(N–N) |
| **2** | 2096.8 | (2092.2) [d] | | | *a*″ $\nu$(N–N) |
| | [1917] [e] | | 1922 | −5 | *a*′ $\nu$(C–O) |

[a] Error ± 0.5 cm$^{-1}$.

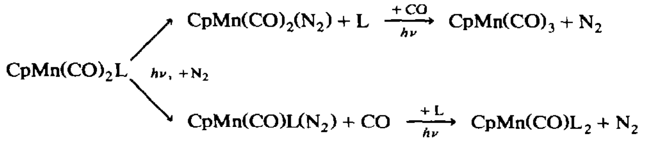
[b] Calculated using the Timney method (see Experimental section) assuming 90° bond angles (which gave the best agreement between observed and calculated wavenumbers) and $\varepsilon^{90}_{N_2} = 6$ Nm$^{-1}$; for $Cp^*Mn(CO)_3$, $k_{CO} = k_6 + 2\varepsilon^{90}_{CO} + \varepsilon^{90}_{Cp^*}$; for $Cp^*Mn(CO)_2(N_2)$, $k_{CO} = k_6 + \varepsilon^{90}_{CO} + \varepsilon^{90}_{N_2} + \varepsilon^{90}_{Cp^*}$; for $Cp^*Mn(CO)(N_2)_2$, $k_{CO} = k_6 + 2\varepsilon^{90}_{N_2} + \varepsilon^{90}_{Cp^*}$.

[c] $\Delta$ for scXe data.

[d] Wavenumbers in scCO$_2$/N$_2$ mixture.

[e] Estimated positions assuming overlap with the bands of $Cp^*Mn(CO)_2(N_2)$.

primary photoproducts, $CpMn(CO)_2(N_2)$ and $CpMn(CO)L(N_2)$ (Eq. 3). In addition, there is the possibility that $CpMn(CO)_3$ and $CpMn(CO)L_2$ could be formed in the later stages of the photolysis by sequestration of free CO and L in the solution.



(3)

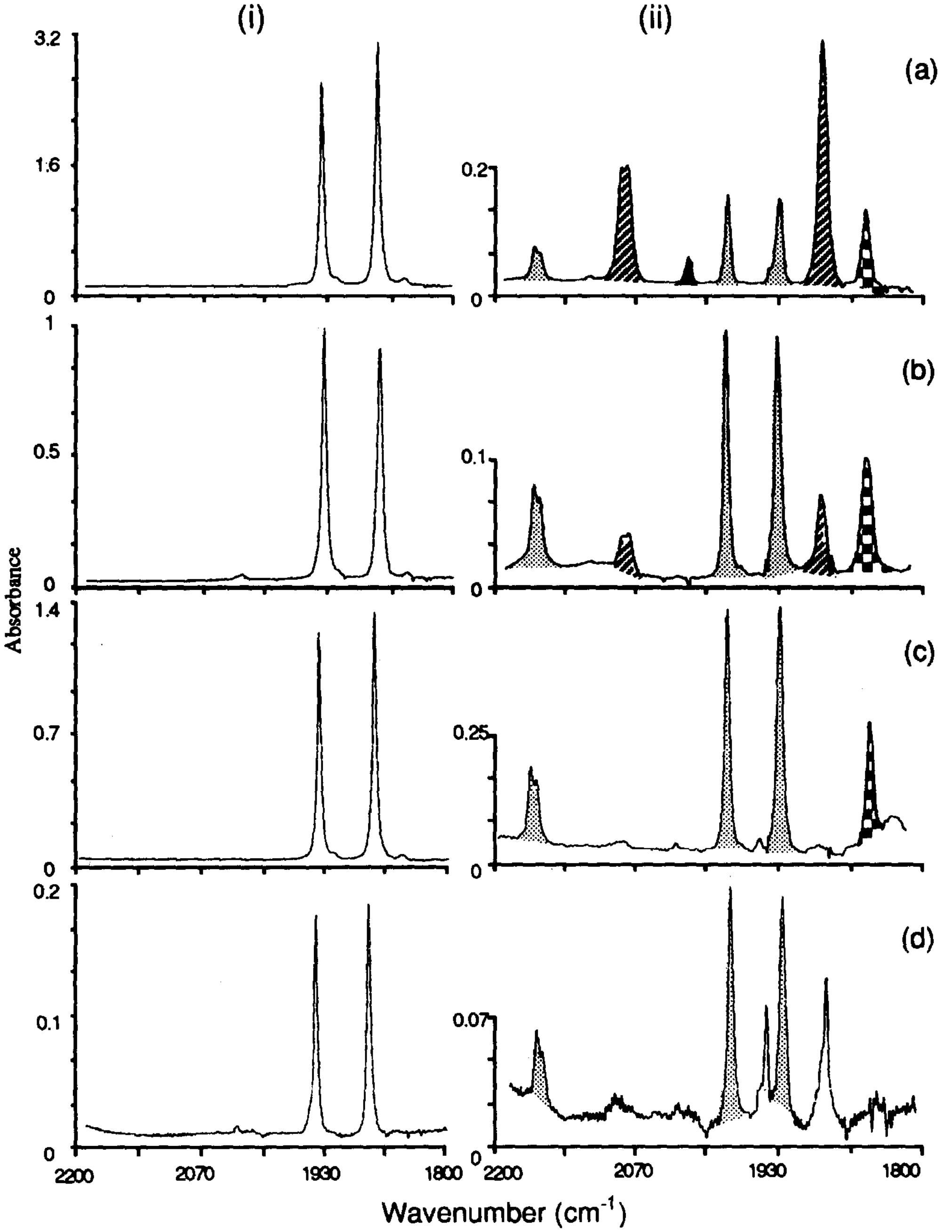


Fig. 3. Comparison of IR spectra recorded (i) before and (ii) after UV irradiation ($\lambda > 300$ nm) of $Cp'Mn(CO)_2PMe_{3-x}Ph_x$ species ($x = 0$–3) and $N_2$ in supercritical fluid solution. (a) $Cp'Mn(CO)_2PMe_3$ in $scXe/N_2$; (b) $Cp'Mn(CO)_2PMe_2Ph$ in $scXe/N_2$; (c) $Cp'Mn(CO)_2PMePh_2$ in $scC_2H_6/N_2$ and (d) $Cp'Mn(CO)_2PPh_3$ in $scC_2H_6/N_2$. The uncoloured bands are those of $Cp'Mn(CO)_2L$ (L = appropriate phosphine) and the other bands are coloured as follows: ■ $Cp'Mn(CO)_3$; ▦ $Cp'Mn(CO)L_2$; ▧ $Cp'Mn(CO)_2(N_2)$; ▨ $Cp'Mn(CO)(N_2)L$. Note that the bands of unreacted $Cp'Mn(CO)_2L$ have been removed by computer subtraction from all of the spectra in (ii) apart from (ii)d, where some absorption resulting from $Cp'Mn(CO)_2PPh_3$ still remains. The $PMePh_2$ and $PPh_3$ compounds have rather lower solubilities than the $PMe_3$ and $PMe_2Ph$ complexes; hence the use of $scC_2H_6$ rather than scXe, because the lower critical pressure of $C_2H_6$ leads to higher solubilities within the pressure limits of our spectroscopic cells.

We now examine the reactions of Cp'Mn(CO)$_2$-PPh$_{3-x}$Me$_x$ ($x$ = 0–3) with N$_2$ under supercritical conditions in order to determine what is the effect of the phosphine on the relative importance of these products. Fig. 3 illustrates the spectra obtained. The bands of the four possible products are easily assigned either by comparison or by analogy with published spectra, in the case of the previously unknown Cp'Mn(CO)L(N$_2$) species, Table 2. The following points are clear from Fig. 3:

(1) Substitution of the Ph groups in the phosphine by Me causes substantial changes in the observed product distribution.

(2) With PPh$_3$, no Cp'Mn(CO)PPh$_3$(N$_2$) is detected in the spectrum

(3) The yield of Cp'Mn(CO)L(N$_2$) increases with increase in the number of Me substituents bonded to the phosphorus atom. In fact, Cp'Mn(CO)PMe$_3$(N$_2$) is the major product of the reaction of Cp'Mn(CO)$_2$PMe$_3$.

(4) Despite the huge excess of N$_2$, detectable amounts of Cp'Mn(CO)$_3$ and Cp'Mn(CO)L$_2$ (L ≠ PPh$_3$) are formed in all of the reactions.

Fig. 4 shows the $\nu$(N–N) bands of Cp'Mn(CO)$_2$(N$_2$) and Cp'Mn(CO)PMe$_3$(N$_2$) with an expanded wavenumber scale. It can be seen that both bands are split into partly resolved doublets. This splitting, similar to that previously reported [4b] for the $\nu$(N–N) band of (C$_6$H$_5$Me)Cr(CO)$_2$(N$_2$), probably indicates the presence of rotamers, a consequence of the Me substituent on the Cp' ring. One might have expected a corresponding splitting in the $\nu$(C–O) bands of these species, but the results with (C$_6$H$_5$-Me)Cr(CO)$_2$(N$_2$) suggest that such splittings would be less than the linewidth of the $\nu$(C–O) bands and would, therefore, be undetectable in this experiment. The overall wavenumber shift in $\nu$(N–N) between Cp'Mn(CO)$_2$(N$_2$) and Cp'Mn(CO)PMe$_3$(N$_2$) is somewhat greater than the corresponding shift in the $\nu$(C–O) bands, underlining the greater sensitivity of $\nu$(N–N) vibrations to substituent effects.

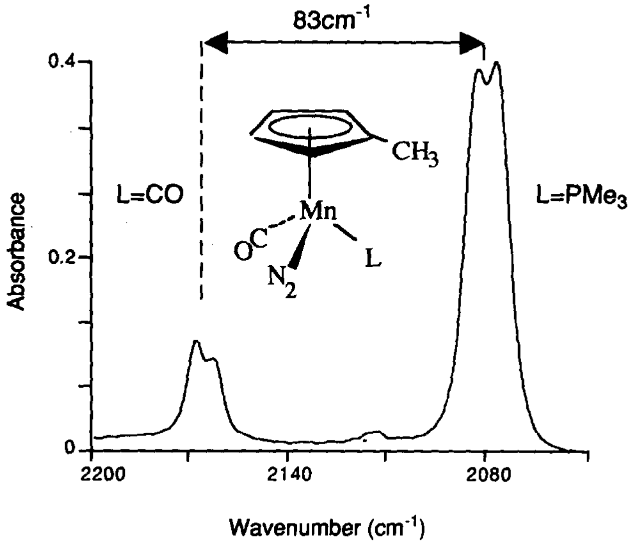


Fig. 4. IR spectrum showing the splitting of the $\nu$(N–N) bands of Cp'Mn(CO)$_2$(N$_2$) and Cp'Mn(CO)(N$_2$)PMe$_3$ in scXe/N$_2$ solution. The splitting is attributed to rotamers arising from the Me group on the C$_5$H$_4$Me ring. The spectrum shows an expanded region of the spectrum shown in Fig. 3a.

There are two possible explanations for our observation that increasing the number of Me substituents on the phosphine ligand increases the photochemical yield of Cp'Mn(CO)(N$_2$)L: (a) the increased yield reflects a genuine change in the branching ratio in the generation from Cp'Mn(CO)$_2$L of the two unsaturated intermediates Cp'Mn(CO)$_2$ and Cp'Mn(CO)L, and (b) the increased yield is the result of differing susceptibility to further photolysis of Cp'Mn(CO)(N$_2$)L during irradiation with the high-intensity UV lamp used in these experiments. To distinguish between these possibilities we can probe the primary photochemistry of Cp'Mn(CO)$_2$L by use of time-resolved IR spectroscopy (TRIR). This technique is a combination of UV flash photolysis and very fast IR detection, and has already proved highly successful in investigating the primary photochemistry of CpMn(CO)$_3$ and its Cp* analogue [12,13]. In both cases, the formally 16-electron dicarbonyl intermediate has been detected, although consid-

Table 2

Observed wavenumbers (cm$^{-1}$) [a] of $\nu$(C–O) and $\nu$(N–N) bands of Cp'Mn(CO)$_2$PMe$_{3-x}$Ph$_x$ ($x$ = 0–3) and their N$_2$ derivatives in supercritical solution.

| L = | CO [b] | PMe$_3$ [b] | PMe$_2$Ph [b] | PMePh$_2$ [c] | PPh$_3$ [c] | |
|---|---|---|---|---|---|---|
| Cp'Mn(CO)$_2$L | 2017 | 1941 | 1939 | 1941 | 1944 | |
| | 1929 | 1880 | 1879 | 1881 | 1886 | |
| Cp'Mn(CO)(N$_2$)L | 2168.8/63.4 | 2083.2/77.8 | 2080.9/75.8 | 2085.6/78.3 | *e* | $\nu$(N–N) [d] |
| | 1979.3 | – | – | – | | – |
| | 1928.7 | 1887.3 | 1887.0 | 1892.7 | [e] | |
| Cp'Mn(CO)L$_2$ | – | 1845 | 1841 | 1843.1 | [e] | |

[a] Error ± 0.5 cm$^{-1}$; [b] scXe/N$_2$ solution; [c] scC$_2$H$_6$/N$_2$ solution.

[d] Splitting of $\nu$(N–N) bands attributed to rotamers arising from the presence of Me on the Cp' ring.

[e] Not observed.

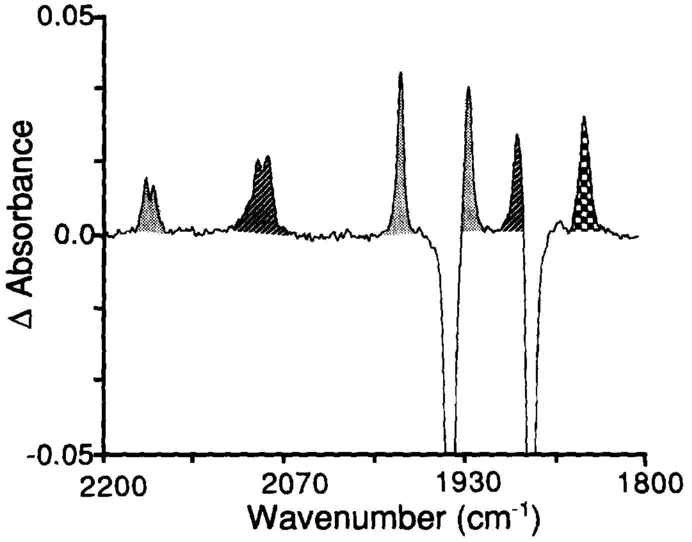


Fig. 5. Changes in IR absorbance of the $\nu$(N–N) and $\nu$(C–O) regions of the spectrum observed after 16 s of UV photolysis of $Cp'Mn(CO)_2PMePh_2$ in $scC_2H_6/N_2$ solution. The spectrum was obtained by computer subtraction of the spectra recorded prior to and immediately after UV photolysis, [cf. the spectrum recorded after prolonged photolysis, Fig. 3c (ii)]. The negative bands are a result of $Cp'Mn(CO)_2PMePh_2$ destroyed by the photolysis. The other bands, which are assigned to photolysis products, have been coloured as in Fig. 3; ▦ $Cp'Mn(CO)(PMePh_2)_2$; ░ $Cp'Mn(CO)_2(N_2)$; ▨ $Cp'Mn(CO)(N_2)PMePh_2$.

erable evidence has now been accumulated to show that these intermediates are indeed solvated by a token solvent ligand, such as $CpMn(CO)_2$(*n*-heptane).

TRIR experiments on $Cp'Mn(CO)_2PPh_2Me$ and $Cp'Mn(CO)_2PPhMe_2$ gave significantly different results. Photolysis of $Cp'Mn(CO)_2PPhMe_2$ at 308 nm led within 500 ns to detectable amounts of both possible primary photoproducts, $Cp'Mn(CO)PPhMe_2$ and $Cp'Mn(CO)_2$, formed respectively by ejection of CO and $PPhMe_2$. By contrast, after photolysis of $Cp'Mn(CO)_2PPh_2Me$ the only detectable reaction intermediate was $Cp'Mn(CO)PPh_2Me$. Surprisingly, the presence of the phosphine ligand greatly increases the reactivity of the Cp'Mn(CO)L intermediate compared with that of $Cp'Mn(CO)_2$; under pressure of $N_2$, the lifetime of Cp'Mn(CO)L is more than an order of magnitude shorter than that of $Cp'Mn(CO)_2$. Presumably, the phosphine ligand weakens the Mn–heptane interaction, but it is not clear if this is a steric or electronic effect.

These TRIR results suggest that substitution of Me by Ph changes the branching ratios between loss of CO and phosphine in the opposite direction from that observed in the final distribution of dinitrogen products in supercritical solution, Fig. 3. There were, of course, differences between the photolysis wavelengths used in the TRIR and supercritical experiments, 308 nm and broadband UV, respectively, but nevertheless the TRIR results suggest that secondary photolysis may be important in the supercritical experiments. Indeed, careful inspection of the FTIR spectra recorded during the prolonged irradiation of the supercritical reaction mixtures confirms that there was a considerable degree of secondary photolysis. This photolysis appears to lead to selective destruction of $Cp'Mn(CO)L(N_2)$. Thus, after brief UV photolysis of the $PPh_2Me$ derivative, the IR spectra show comparable amounts of $Cp'Mn(CO)_2(N_2)$ and $Cp'Mn(CO)L(N_2)$, Fig. 5. This contrasts with longer photolysis times, when the overall conversion to dinitrogen products is greater but almost no $Cp'Mn(CO)L(N_2)$ is observed, Fig. 3(c). Phosphine-substituted dinitrogen products appear to be more labile, both thermally and photochemically, than $Cp'Mn(CO)_2(N_2)$ and therefore do not accumulate in significant concentrations during the prolonged photolysis.

## 4. Conclusions

Our experiments have shown that even minor modifications of the phosphine ligand in the $Cp'Mn(CO)_2$(Phosphine) compounds can have a significant effec on the photochemistry, but that the effect appears t be largely the consequence of secondary, rather tha primary, photolysis. Davies and Watkins have recentl reported [14] a similar effect with $(C_5R_5)Fe(CO)$ (COMe)$PPh_3$, namely a substantial change in phot chemistry with a minor change in molecular structu from R = H to R = Me. In their case, however, th changes occurred in the primary photochemistry rath than in the final distribution of products. As in prev ous studies [4], the use of supercritical fluid solven provides a route to dinitrogen compounds, but t lability of the $Cp'Mn(CO)(N_2)L$ complexes prevents the route from being of value for synthesis of these compounds. The most important outcome of this work is the unequivocal demonstration that photolysis of organometallic compounds in supercritical $CO_2$ is a viable and effective procedure. We are currently exploring the possibility of generating dihydrogen and dinitrogen compounds on a preparative scale in $scCO_2$ using a flow reactor.

## Acknowledgements

We thank the SERC Clean Technology Unit, Grant No. GR/H95464, the Royal Society BP International Ltd, the British Council ARC Programme and the VW Stiftung for supporting this research. We are grateful to Prof. J.J. Turner, Dr J.A. Timney, Mr D.M. Gethin, Mr C.R. Lane, Herr S. Seebald and Mr K. Stanley for their help.

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