The Synthesis and Spectroscopic Identification of $[(\eta^5\text{-}C_5H_5)Re(N_2)_3]$ and $[(\eta^5\text{-}C_5H_5)Re(CO)(N_2)_2]$ in Supercritical Xenon at Room Temperature and in N_2 Matrices at 20 K

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U.v. photolysis of $[(cp)Re(CO)_3]$ (cp = η^5-cyclopentadienyl) in either supercritical xenon heavily doped with N_2 or in solid N_2 matrices at 20 K leads to stepwise substitution of CO by N_2 and formation of $[(cp)Re(CO)_{3-x}(N_2)_x]$ species (x = 1—3), all of which have been characterized by i.r. spectroscopy and $^{15}N_2$ substitution; $[(cp)Re(CO)(N_2)_2]$ is stable at room temperature.

Although a large number of transition metal dinitrogen complexes are now known, relatively few contain more than two dinitrogen groups bound to the same metal centre. One of the simplest routes to such compounds is the photochemical reaction (1) of metal carbonyl compounds with N_2.

$$[M(CO)_x] + y\,N_2 \xrightarrow{\text{u.v.}} [M(CO)_{x-y}(N_2)_y] + y\,CO \qquad (1)$$

This approach has been exploited in a large number of matrix isolation studies and, more recently, in liquefied noble gas solvents to prepare species such as $[Cr(CO)_2(N_2)_4]$.[1] There are two reasons why this route has not been widely used for experiments at room temperature: (i) it is difficult to achieve high concentrations of dissolved N_2 in conventional solvents and (ii) for many metal ligand combinations, even the mono-dinitrogen complex {*e.g.* $[Cr(CO)_5(N_2)]$[2]} is highly unstable at ambient temperatures.

We have already reported how supercritical fluids (*e.g.* Xe, T_c 16.7 °C) provide an excellent environment for such reactions because gases such as H_2 are totally miscible with the supercritical fluids.[3] Thus, for example, u.v. photolysis of $[(cp)Mn(CO)_3]$ (cp = η^5-C_5H_5) and H_2 led to the formation of a previously unknown non-classical dihydrogen complex,[4] $[(cp)Mn(CO)_2(H_2)]$. We now show that supercritical Xe (scXe) can also be highly effective for the synthesis of dinitrogen complexes.‡ We describe the photochemical reaction of $[(cp)Re(CO)_3]$ with N_2. $[(cp)Re(CO)_3]$ is a promising candidate for multiple substitution of CO by N_2 because the mono-dinitrogen compound $[(cp)Re(CO)_2(N_2)]$ is extremely stable.[5]

Figure 1 shows the ν(N–N) region of the i.r. spectrum recorded during the u.v. photolysis of $[(cp)Re(CO)_3]$ and N_2 in scXe. These spectra show the sequential formation of three dinitrogen products: the first product with a single ν(N–N) band (arrowed in Figure 1) and two ν(C–O) bands (not illustrated, see Table 1) is the known compound $[(cp)Re(CO)_2(N_2)]$. The other two products are previously unknown dinitrogen complexes. The second product has two ν(N–N) bands of almost equal intensity (hatched in Figure 1) and one ν(C–O) band, while the third product has two ν(N–N) bands of unequal intensity (coloured black in Figure 1) and no ν(C–O) bands. These spectra suggest that the new compounds are $[(cp)Re(CO)(N_2)_2]$ and $[(cp)Re(N_2)_3]$.

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‡ The miniature supercritical cell at Nottingham has been described previously.[3,4] Matrix experiments were carried out at York and Oxford (Air Products Displex CS202 and Philips HPK 125W Hg arc).[7] Xe and N_2 (BOC) and $^{15}N_2$ (Prochem) were used without further purification.

Safety Note. Experiments in supercritical fluids necessitate high pressures and should be approached with caution.

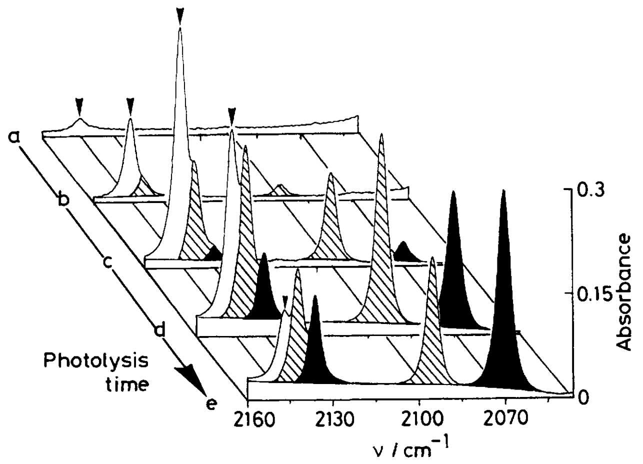


Figure 1. I.r. absorption spectra in the ν(N-N) region showing the effects of progressive u.v. photolysis of $[(cp)Re(CO)_3]$ (*ca.* 10^{-3} M) and N_2 (1350 psi; 3.6 M) in scXe (total pressure 2600 psi).‡ The traces correspond to u.v. photolysis times of (a) 5 s, (b) 4 min, (c) 6 min, (d) 56 min, and (e) 111 min. The bands are labelled as follows: arrowed, $[(cp)Re(CO)_2(N_2)]$; hatched, $[(cp)Re(CO)(N_2)_2]$; coloured black, $[(cp)Re(N_2)_3]$. The slight slope towards higher wavenumber, which appears as the photolysis proceeds, is due to free CO liberated in the photolysis. (Fourier transform i.r. spectra, 2 cm^{-1} resolution, Nicolet Model 730 interferometer with MCT detector; photolysis with Cermax 300 W Xe illuminator, filtered to give 200—400 nm.)

Isotopic substitution with $^{15}N_2$ is an extremely effective way of characterizing dinitrogen compounds.[6] Since the use of high pressures of $^{15}N_2$ would be prohibitively expensive, we have repeated the photolysis of $[(cp)Re(CO)_3]$ in low temperature matrices. The effect of photolysis of $[(cp)Re(CO)_3]$ in a $^{14}N_2$ matrix proves very similar to the scXe/N_2 experiment. However, two factors make the matrix spectra rather more complicated to interpret than those in scXe: (i) the ν(N–N) absorptions of the various dinitrogen species are split into a number of closely spaced bands by different sites in the matrix; (ii) the high frequency N–N stretching modes of all the products of photolysis of $[(cp)Re(CO)_3]$ in $^{14}N_2$ are very close to each other and to the i.r. band of photoejected CO, which is relatively intense. In scXe, the absorption of CO is much less intrusive because it is very broad without resolvable rotational fine structure.

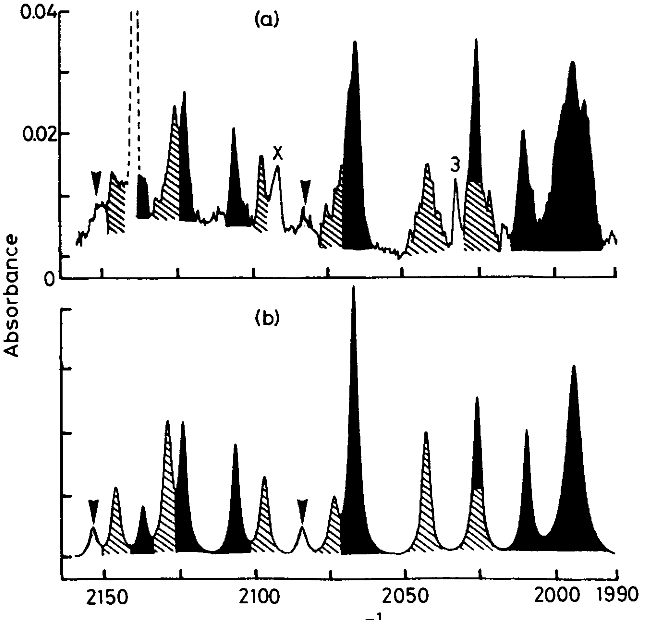
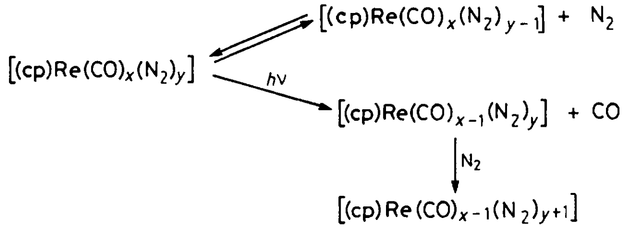


Figure 2. (a) I.r. spectra in the ν(N–N) region obtained after 162 min u.v. photolysis of $[(cp)Re(CO)_3]$ in a mixed $^{14}N_2/^{15}N_2$ (47%/53%) matrix at 20 K and subsequent annealing of the matrix to 32 K. Note the change in the wavenumber scale at 2000 cm^{-1}. The bands are labelled as follows; arrowed, $[(cp)Re(CO)_2(N_2)]$; hatched, $[(cp)Re(CO)(N_2)_2]$; coloured black, $[(cp)Re(N_2)_3]$; 3, the a_1 ν(C–O) band of residual $[(cp)Re(CO)_3]$; dotted, photo-ejected CO; X, an unassigned peak which only appears after the matrix is annealed (i.r. spectra 1.5 cm^{-1} resolution, Perkin-Elmer Model 580B). (b) Simulated i.r. spectrum calculated for a mixture of $[(cp)Re(CO)_{3-x}(N_2)_x]$ species (x = 1—3) using the force constants listed in Table 1. The bands are labelled as in (a).



Scheme 1

Nevertheless, u.v. photolysis of $[(cp)Re(CO)_3]$ in a $^{14}N_2/^{15}N_2$ matrix gives the i.r. spectra of the complete set of isotopomers of the dinitrogen products,§ which can be interpreted with the help of the scXe data¶ and of previous matrix results.[7] Figure 2a shows the experimental spectrum in the ν(N–N) region, while Figure 2b shows the spectrum simulated for a mixture of $[(cp)Re(CO)_{3-x}(N_2)_x]$ (x = 1—3). Given the complexity of the spectra, the agreement between the observed and calculated frequencies is extremely good (see Table 1). In addition, we can eliminate the possibility that the products contain more than one metal atom, since the $[(cp)Re(CO)_3]$ molecules were all well isolated at the start of the matrix experiment. Thus, these matrix experiments provide conclusive evidence that the new photoproducts are indeed $[(cp)Re(CO)(N_2)_2]$ and $[(cp)Re(N_2)_3]$.

The effectiveness of scXe or N_2 matrices in promoting multiple substitution of CO can be understood by considering the two possible photochemical pathways for each mixed carbonyl/dinitrogen complex; loss of N_2 and loss of CO (Scheme 1). In the presence of a high concentration of free N_2, the loss of N_2 becomes in effect reversible. Thus loss of CO and formation of multiply substituted dinitrogen complexes are favoured.

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§ Fortunately, there is rather less matrix splitting for the mixed isotopic speices than for the pure $^{14}N_2$ species. A similar reduction in splitting for isotopic species has previously been found in quite a large number of matrix isolated metal carbonyl compounds.[8]

¶ Most bands were assigned to mono-, bis-, or tris-dinitrogen species by observing their rate of growth during u.v. photolysis. A full assignment of the matrix spectra required additional information from the scXe experiments on the relative ordering of the frequencies of the symmetric stretching modes of the three complexes. A value of the N–M–N bond angle is required for calculations of relative intensities of the ν(N–N) bands.[6] This angle was estimated from the relative intensities of the bands of $[(cp)Re(N_2)_3]$ in scXe; $I(e)/I(a_1) = 2.4 \pm 0.2$, which gives a bond angle of 93.4 ± 1.6°. $[(cp)Re(N_2)_3]$ is probably isostructural with $[(cpRe(CO)_3]$, where the C–M–C angle calculated from ν(C–O) intensities, is identical; $[I(e)/I(a_1) = 2.35]$. The calculated angle is slightly larger than the published *X*-ray value[9] for $[(cp)Re(CO)_3]$, 90.2°. A linewidth of 3 cm^{-1} (f.w.h.m.) was assumed for all bands in Figure 2b.

Table 1. Observed and calculated wavenumbers (cm^{-1}) of $[(cp)Re(CO)_{3-x}(N_2)_x]$ species (x = 0—3) and their $^{15}N_2$ isotopomers in scXe and N_2 matrices.

	scXe[a]	N_2 matrix[b]	Calc.[c]	Assignment
$[(cp)Re(CO)_3]$	2035.0	2032.0	—	a_1 ν(C–O)
	1946.9	1942.5	—	e ν(C–O)
$[(cp)Re(CO)_2(N_2)]$[d]	2146.8	2153.8	2153.6	$\nu(^{14}N{-}^{14}N)$
		2084.4	2084.8	$\nu(^{15}N{-}^{15}N)$
	1978.4	1973.2	1973.3	a′ ν(C–O) $[(cp)Re(CO)_2(^{14}N_2)]$
		1969.4	1969.5	a′ ν(C–O) $[(cp)Re(CO)_2(^{15}N_2)]$
	1925.8	1918.3	1918.3	a″ ν(C–O)
$[(cp)Re(CO)(N_2)_2]$[e]	2142.0	2146.0	2146.1	a′ ν(N–N) $(^{14}N_2)_2$
	2095.1	2097.0	2097.0	a″ ν(N–N) $(^{14}N_2)_2$
	1929	1918.3	—	ν(C–O)
		2127.0	2128.9	ν(N–N) $(^{14}N_2)(^{15}N_2)$
		2043.0	2042.5	ν(N–N) $(^{14}N_2)(^{15}N_2)$
		2075.0	2073.6	a′ ν(N–N) $(^{15}N_2)_2$
		2026.5	2026.1	a″ ν(N–N) $(^{15}N_2)_2$
$[(cp)Re(N_2)_3]$	2135.9	2137.0	2137.1	a_1 ν(N–N) $(^{14}N_2)_3$
	2069.0	2066.0	2066.9	e ν(N–N) $(^{14}N_2)_3$ a″ ν(N–N) $(^{14}N_2)_2(^{15}N_2)$
		2123.5	2123.9	a′ ν(N–N) $(^{14}N_2)_2(^{15}N_2)$
		2010.0	2009.5	a′ ν(N–N) $(^{14}N_2)_2(^{15}N_2)$
		2107.0	2106.7	a′ ν(N–N) $(^{14}N_2)(^{15}N_2)_2$
		2026.5	2025.8	a′ ν(N–N) $(^{14}N_2)(^{15}N_2)_2$
		f	2064.9	a_1 ν(N–N) $(^{15}N_2)_3$
		1997.0	1997.0	e ν(N–N) $(^{15}N_2)_3$ a″ ν(N–N) $(^{14}N_2)(^{15}N_2)_2$

Force constants (k/Nm^{-1}) for the various $[(cp)Re(CO)_{3-x}(N_2)_x]$ species (x = 0—3) in N_2 matrices.

Force constant	$[(cp)Re(CO)_3]$	$[(cp)Re(CO)_2(N_2)]$	$[(cp)Re(CO)(N_2)_2]$	$[(cp)Re(N_2)_3]$
$k(N_2)$	—	1902.5	1857.0	1802.9
$k(N_2, N_2)$	—	—	43.0	40.6
$k(N_2, CO)$	—	39.5	0	—
$k(CO)$	1572.2	1535.0	1486.5	—
$k(CO, CO)$	47.9	48.5	—	—
RMS error (cm^{-1})	—	0.2	1.0	0.5

[a] Room temperature. [b] 20 K. [c] Calculated values based on the matrix data. Each observed frequency was only entered once in the calculation. [d] For this molecule, there is definite experimental evidence for vibrational coupling between ν(N–N) and ν(C–O). This coupling was therefore included in the force field. [e] There is no evidence for coupling between ν(N–N) and ν(C–O) in this molecule. [f] This band is predicted to be weak and was not observed presumably owing to overlap with the stronger band at 2066 cm^{-1}.

In scXe solution, both $[(cp)Re(CO)(N_2)_2]$ and $[(cp)Re(N_2)_3]$ appear to be remarkably inert to substitution. Therefore, when the pressure of N_2 was vented from the cell and 1 atm of CO added in its place, ‖ $[(cp)Re(N_2)_3]$ was converted only slowly ($t_{1/2}$ *ca.* 12 h at 25 °C) into $[(cp)Re(CO)(N_2)_2]$ which, in turn, reacted to form $[(cp)Re(CO)_2(N_2)]$ at *elevated* temperatures ($t_{1/2}$ *ca.* 1 h at 70 °C). Furthermore, $[(cp)Re(CO)(N_2)_2]$ appears to be completely stable at room temperature even in the presence of air.**

Thus, there is the exciting possibility that other dinitrogen complexes, which have so far been observed only in matrices, may also be stable at room temperature.

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‖ The N_2 was vented by freezing the Xe into the cold-finger of our cell[3] using liquid nitrogen. Under these conditions, some of the N_2 appears to be trapped in the solid Xe and so the scXe solution will still contain some N_2, after warming the Xe back to room temperature.

** At the end of one experiment, the supercritical cell was dismantled, cleaned as thoroughly as possible with CH_3CCl_3 and left in the air for two weeks. When the cell was reassembled and refilled with scXe, i.r. bands of $[(cp)Re(CO)(N_2)_2]$ and $[(cp)Re(CO)_2(N_2)]$ were clearly observed. The last vestiges of these compounds could be eliminated only by prolonged u.v. photolysis in scXe doped with O_2.