served two weak visible absorption bands (515 and 620 nm). Even if one isomer of $Fe_2(CO)_8$ had a triplet ground state, spin changes would be unlikely to account for the observed activation barriers for thermal reactions, because previous experiments with $Fe(CO)_4$ have shown that spin-forbidden reactions can proceed thermally in matrices without difficulty.[31]

The characterization of photofragments is clearly more complicated for dinuclear species than for mononuclear. $Fe_2(CO)_9$ is a special case because its physical properties make it difficult to study outside matrices. In general, however, we believe that the problem is best tackled by combining the results of matrix isolation with those of other techniques such as photochemistry in liquefied noble gases[17] or time-resolved IR spectroscopy.[41] Such a combination[42,43] has recently been most successful in the study of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and promises to broaden greatly our understanding of dinuclear compounds.

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Registry No. B, 103671-06-3; U, 100459-39-0; $Fe_2(CO)_9$, 15321-51-4; Fe, 7439-89-6; ^{13}C, 14762-74-4.

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IR Detection and Characterization of $Co(CO)_2NO(\eta^2\text{-1-btn})$ and $Fe(CO)_{2-x}(NO)_2(\eta^2\text{-1-btn})_x$ (x = 1 or 2; 1-btn = 1-Butene) in Liquid Xenon Solution

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UV photolysis of $Co(CO)_3NO$ or $Fe(CO)_2(NO)_2$ dissolved in liquid xenon, doped with 1-butene, at −104 °C, yields the previously unknown species $Co(CO)_2(NO)(\eta^2\text{-1-butene})$ and $Fe(CO)_{2-x}(NO)_2(\eta^2\text{-1-butene})_x$, x = 1 or 2, in solution. The disubstituted species $Fe(NO)_2(\eta^2\text{-1-butene})_2$ is thermally unstable at −55 °C and rapidly reacts with CO to form $Fe(CO)(NO)_2(\eta^2\text{-1-butene})$, which is stable at −30 °C. The absence of IR absorptions due to the solvent allows a complete IR characterization of these compounds. With use of FT-IR techniques, it is even possible to observe IR bands due to the coordinated olefins as well as the intense bands due to CO and NO groups.

Introduction

Olefinic and hydrogen complexes of transition metals are often crucial intermediates in homogeneous catalysis.[1] It is clearly important to obtain the maximum possible information on the structure and stability of such complexes, particularly for those unstable, highly reactive species for which X-ray crystallography is generally inapplicable.

We have recently demonstrated that a combination of liquid noble gases as solvents, photochemical techniques, and sophisticated FT-IR spectroscopy can provide very detailed information on unstable organometallic species. For instance, we have generated[2] $Ni(CO)_3N_2$ by photolysis of $Ni(CO)_4$ in N_2-doped liquid Kr (LKr) at −150 °C, and by monitoring the thermal back-reaction $Ni(CO)_3N_2 \rightarrow Ni(CO)_4$, we have obtained detailed kinetic and energetic information about $Ni(CO)_3N_2$. Further examples include the photogeneration of $Cr(CO)_{6-x}(N_2)_x$[3] in liquid Xe (LXe) and that of $Fe(CO)_{2-x}(NO)_2(N_2)_x$ in LKr.[4] Each of these species possesses excellent, intense IR chromophores, ν(C–O), ν(N–N), and ν(N–O), and thus characterization of photoproduct was generally straightforward.

More recent, and more relevant to catalytic systems, was the production[5] of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$ by photolysis of $Cr(CO)_6$ in LXe under a pressure of H_2 of several atmospheres. The H_2 in $Cr(CO)_5(H_2)$ is *sideways* bonded, as in the analogous stable compound[6] $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$. The bonding of H_2 in $Cr(CO)_5(H_2)$ was proved by observation[5] of the very weak ν(H–H), ν(D–D), and ν(H–D) stretching vibrations. Similar procedures[7] were used to generate $Co(CO)_2(NO)(H_2)$ and $Fe(CO)(NO)_2(H_2)$ in LXe.

Before examining catalytic systems generally, it is necessary to demonstrate whether the IR spectra of *organic* ligands can be probed in the same way.[8] Such IR spectra have been used extensively to characterize organometallic intermediates in noble-gas matrices,[9] but the interpretation of photochemical experiments in solution has relied almost entirely on ν(C–O) bands since the absorptions of conventional solvents obliterate any weak features due to the coordinated organic ligand.

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(8) It could be argued that NMR is an extremely powerful diagnostic tool for such species, and currently we are exploring NMR in liquid xenon (Gregory, M. F. Ph.D. Thesis, Nottingham University, 1985). However, the sensitivity of IR spectroscopy is likely to be greater.

(9) For recent examples see: Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N. *Inorg. Chem.* **1982**, *21*, 3647. Haddleton, D. M.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1985**, 1372.

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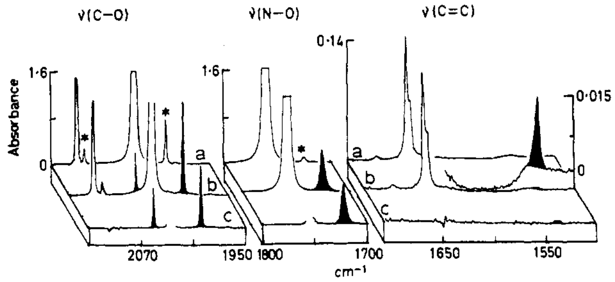

Figure 1. IR spectra illustrating the photolysis of $Co(CO)_3NO$ and 1-butene in LXe at −104 °C: (a) spectrum before photolysis (bands marked with asterisks due to natural-abundance ^{13}C, ^{15}N, and ^{18}O (see Table II)); (b) spectrum after UV photolysis with an unfiltered high-pressure Hg arc (bands colored black due to $Co(CO)_2(NO)(\eta^2\text{-1-btn})$, note weak band in the $\nu(C{=}C)$ region shown as an inset on an expanded absorbance scale; (c) spectrum after computer subtraction of bands due to unreacted $Co(CO)_3NO$ and 1-butene.

In this paper, we show that IR spectroscopy can indeed probe the vibrations of the organic ligands in photogenerated organometallic intermediates, by examining the behavior of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ in LXe doped with 1-butene. These nitrosyl species have a particular advantage over simple carbonyls because they have two intense IR chromophores (ν(C–O) and ν(N–O)) and hence interpretations of the spectra is straightforward. Furthermore, $Fe(CO)_2(NO)_2$, but not $Co(CO)_3NO$, is a known catalyst for the dimerization of dienes[10] and in this paper we establish the basic spectroscopic techniques that will be used in a further paper[11] to interpret the reactions of these nitrosyls with 1,3-butadiene. In brief, we report here that UV photolysis of $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ in LXe doped with 1-butene generates the species $Co(CO)_2(NO)(\eta^2\text{-1-btn})$, $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$, and $Fe(NO)_2(\eta^2\text{-1-btn})_2$ (1-btn = 1-butene). This last compound is thermally unstable and is reconverted to $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$. The rate of this thermal reaction is reduced by increasing the concentration of 1-butene in LXe.

Experimental Section

The use of liquefied noble gases for photochemistry has been described previously,[12] and the design of the IR cell has been published in detail.[13] The cell has an optical pathlength of 2.7 cm. IR spectra were obtained with a Nicolet MX3600 FT-IR interferometer and 1280 data system. Interferograms were recorded with 16K or 32K data points (2- or 0.7-cm⁻¹ resolution) and 32K or 256K points in the Fourier transform. In general, peak heights (absorbance) were used as a quantitative measurement of band intensities. Careful comparison[14] showed that there was no advantage in using numerical integration of band areas for assessing the rate of growth of a band. $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ were prepared by published methods,[15] and 1-butene (BDH) and Xe (BOC Research Grade) were used without further purification.

Results and Discussion

Photoreaction of $Co(CO)_3NO$ with 1-Butene. Figure 1 shows the IR spectra from an experiment in which $Co(CO)_3NO$, dissolved in LXe doped with 1-butene at −104 °C, is photolyzed with a high-pressure Hg arc. It is clear that photolysis has produced two new ν(C–O) bands and one new ν(N–O) band, colored black in Figure 1b. These three bands, which grow in together, are more easily seen in Figure 1c, where computer subtraction has been used to remove the bands of unphotolyzed $Co(CO)_3NO$ from the spectrum. The new bands are assigned to a molecule, $Co(CO)_2NO(X)$, with local C_s symmetry (i.e. ν(C–O) a′ + a″ and ν(N–O) a′). This assignment is justified in more detail below.

The photochemical replacement of CO by X is entirely consistent with the known photochemistry[16] of $Co(CO)_3NO$. It is reasonable to suppose that X is η^2-1-butene, and IR spectroscopy can be used to prove this. First, we consider briefly the spectrum of coordinated ethylene.

In ethylene the coupled $\nu(C{=}C)$ (1623 cm⁻¹) and $\nu(CH_2)_{def}$ (1342 cm⁻¹) vibrations are the most affected when C_2H_4 is coordinated to a low-oxidation-state transition-metal center. On coordination the two vibrations are still extensively mixed and simple labeling of modes is rather imprecise. Nevertheless in, for example, $(C_2H_4)Fe(CO)_4$, a band at 1196 cm⁻¹ is assigned[17] largely to the $\nu(C{=}C)$ vibration, a shift of −427 cm⁻¹ compared to the band in free C_2H_4. Another band at 1508 cm⁻¹ is assigned[17] largely to $\nu(CH_2)_{def}$, a shift of +166 cm⁻¹. Free 1-butene has several bands between 1500 and 1100 cm⁻¹, but the region above 1500 cm⁻¹ is relatively uncongested and so is the most suitable for detecting bands of *coordinated* butene. For convenience we shall refer to this region as "$\nu(C{=}C)$" because the band generally assigned[18] to the $\nu(C{=}C)$ vibration of uncoordinated 1-butene is observed within it.

Apart from the ν(C–O) and ν(N–O) regions already discussed, Figure 1 also includes spectra in this 1700–1500-cm⁻¹ region, but on a greatly expanded absorbance scale. Before photolysis of $Co(CO)_3NO$ and butene (Figure 1a) the uncolored bands at 1642.8 and 1639 cm⁻¹ are the $\nu(C{=}C)$ vibrations of the gauche and cis rotamers of free butene. After photolysis an extremely weak band appears at 1534 cm⁻¹. This band, colored black in Figure 1b, is also illustrated with even greater absorbance expansion. The wavenumber of the band is close to that anticipated for a coordinated alkene.

It is now necessary to *prove* that this weak band is due to coordinated butene and to demonstrate that the band grows in intensity, exactly in parallel to the increase in ν(C–O) and ν(N–O) bands assigned to $Co(CO)_2(NO)(1\text{-btn})$. The difficulty is the huge disparity in intensity between the this band and the ν(C–O) and ν(N–O) bands. This disparity makes accurate intensity comparisons almost impossible, particularly when the ν(C–O) and ν(N–O) bands have an intensity greater than 2 absorbance units. However, an accurate intensity comparison could be achieved by comparing the butene band with the weak features in the spectra due to naturally occurring ^{13}C, ^{15}N, and ^{18}O isotopes and also with the overtone bands of the main ν(C–O) and ν(N–O) vibrations. These are, of course, very weak themselves, and so it is important to justify their assignment before using them for quantitative intensity measurements.

Assignment of Isotopic and Overtone Bands of $Co(CO)_2(NO)(\eta^2\text{-1-btn})$. For both $Co(CO)_3NO$ and $Co(CO)_2(NO)(\eta^2\text{-1-btn})$, we can predict the frequencies of isotopic satellites by use of an energy-factored force field, using force constants[19] k_{CO}, $k_{CO,CO}$, and k_{NO} derived from the main ν(C–O) and ν(N–O) bands (see Table I). The largest error arises for $N^{18}O$, as observed previously,[19] particularly in the full vibrational analysis[20] of $Co(CO)_3NO$. Figure 2 shows the appropriate regions of the IR spectrum of $Co(CO)_2(NO)(\eta^2\text{-1-btn})$. One of the two predicted $\nu(^{13}C\text{–}O)$ bands and the superimposed $\nu(^{15}N\text{–}O)$ and $\nu(N\text{–}^{18}O)$ bands are clearly seen. The other $\nu(^{13}C\text{–}O)$ band (not illustrated) was observed after prolonged photolysis as a weak band at 2039 cm⁻¹ on the high-wavenumber side of the intense ν(C–O) band of $Co(CO)_3NO$. It will be noted that the ^{13}CO satellite of $Co(CO)_2(NO)(\eta^2\text{-1-btn})$, shown in Figure 2, has a shoulder to high frequency. This shoulder is a consequence of the inequivalence of the two CO groups due to the asymmetry of the coordinated

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Table I. Frequencies (cm^{-1}) of IR Bands of $Co(CO)_3NO$ and $Co(CO)_2(NO)(\eta^2\text{-1-btn})$ in Liquid Xenon at −104 °C

obsd	calcd[a,b]	assignt
	$Co(CO)_3NO$	
2101.5		ν(C–O) a_1
2034.4		ν(C–O) e
1810.2		ν(N–O) a_1
2092.5	2091.3	ν(C–O) } (^{13}CO)(^{12}CO)$_2$
1999.1	1998.7	ν(C–O)
1774.4/1773.1	1777.7/1762.6	ν(N–O) (^{15}NO)/(N^{18}O)
4197.7	4203.1	2 × a_1(C–O)
4123.5	4135.9	a_1(C–O) + e(C–O)
4060.3	4068.8	2 × e(C–O)
3596.5	3620.4	2 × a_1(N–O)
3911.6	3911.7	a_1(C–O) + a_1(N–O)
3845	3844.6	a_1(N–O) + a_1(C–O)
	$Co(CO)_2(NO)(\eta^2\text{-1-btn})$	
2053.6		ν(C–O) a′
2000.1		ν(C–O) a″
1776.6		ν(N–O) a′
1534.0		ν(C=C)
2040/2038[c]	2040.0/2038.0	ν(C–O) } (^{13}CO)(^{12}CO)
1970.4/1968.1	1970.4/1968.5	ν(C–O)
1740.6	1744.9/1729.8	ν(N–O) (^{15}NO)/(N^{18}O)
4097.4	4106.0	2 × a′(C–O)
4028.4	4052.6	a′(C–O) + a″(C–O)
3985.3	3999.2	2 × a″(C–O)
3527.1	3553.3	2 × a′(N–O)

[a] Calculated frequencies of isotopic molecules are based on force constants (N m^{-1}) derived from nonisotopic species: for $Co(CO)_3NO$, k_{CO} = 1709.15, $k_{CO,CO}$ = 37.366, k_{NO} = 1441.287; for $Co(CO)_2(NO)(\eta^2\text{-1-btn})$, k_{CO} = 1662.11/1657.20, $k_{CO,CO}$ = 43.735, k_{NO} = 1388.48. [b] Overtone and combination frequencies calculated with anharmonicity being ignored. [c] A detailed explanation of the relative intensities of these ^{13}CO satellites requires two conformers of coordinated 1-butene (see also the assignment of the spectrum of coordinated 1-butene in the supplementary material).

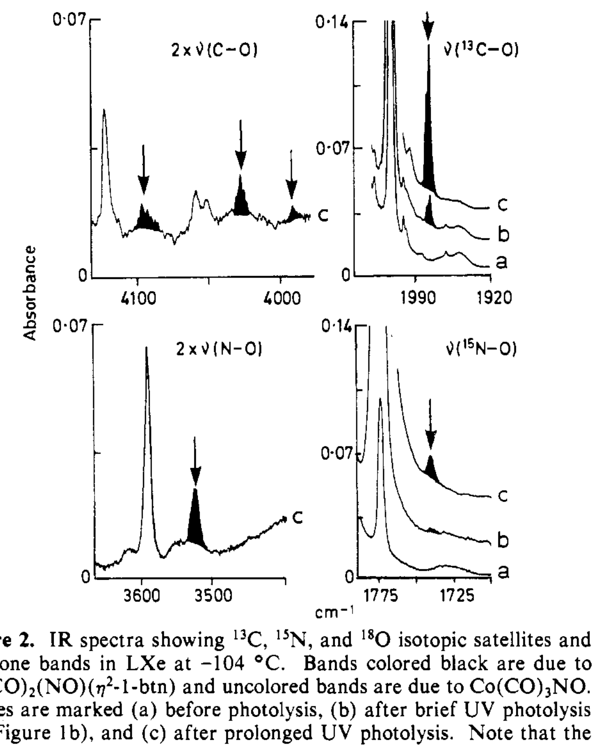

Figure 2. IR spectra showing ^{13}C, ^{15}N, and ^{18}O isotopic satellites and overtone bands in LXe at −104 °C. Bands colored black are due to $Co(CO)_2(NO)(\eta^2\text{-1-btn})$ and uncolored bands are due to $Co(CO)_3NO$. Traces are marked (a) before photolysis, (b) after brief UV photolysis (cf. Figure 1b), and (c) after prolonged UV photolysis. Note that the absorptions of $\nu(^{15}N–O)$ and $\nu(N–^{18}O)$ are overlapped and unresolved (see Table I).

butene molecule. The high-frequency $\nu(^{13}C–O)$ band is also split.[14] The appropriate frequencies and force constants are given in Table I. This force constant analysis confirms that the photoproduct does indeed contain two CO groups and one NO group and precludes the possibility that the photoproduct could be a dinuclear species.

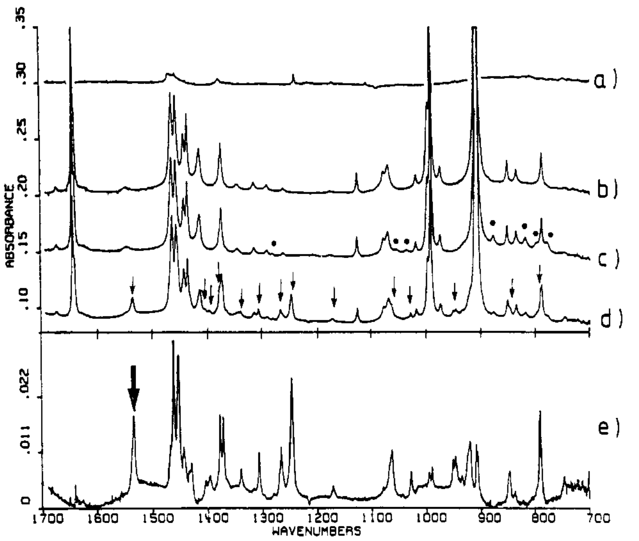

Figure 3. Series of IR spectra illustrating how the absorptions (spectrum e) of coordinated 1-butene were identified: (a) spectrum of LXe before addition of reactants (weak bands due to trace impurities); (b) spectrum after addition of 1-butene; (c) spectrum after addition of $Co(CO)_3NO$ to the butene/LXe mixture (bands due to $Co(CO)_3NO$ marked with ●); (d) spectrum obtained after UV photolysis (bands due to $Co(CO)_2(NO)(\eta^2\text{-1-btn})$ marked with ↓); (e) spectrum of coordinated 1-butene in $Co(CO)_2(NO)(\eta^2\text{-1-btn})$ obtained from spectrum d by computer subtraction of the bands of $Co(CO)_3NO$ and 1-butene (large arrow marks the ν(C=C) band illustrated in Figure 1b; a tentative assignment of this spectrum is given as supplementary material).

Since LXe itself has no IR absorptions, observation of overtone and combination bands of ν(C–O) and ν(N–O) is easy; Table I lists the frequencies and probable assignments for both parent and photoproduct. For purposes of intensity measurement, the best band of $Co(CO)_2(NO)(\eta^2\text{-1-btn})$ is the 2 × ν(N–O) overtone at 3527 cm^{-1}, colored black in Figure 2. That this is the 2 × ν(N–O) overtone is confirmed by a comparison of the anharmonicity (2 × ν(N–O)(calcd) − 2 × ν(N–O)(obsd)), which for $Co(CO)_3NO$ is 24 cm^{-1} and for $Co(CO)_2(NO)(\eta^2\text{-1-btn})$ is 26 cm^{-1}. The observation of *three* bands in the 2 × ν(C–O) region (Figure 2) also confirms that the photoproduct contains *two* CO groups. Two of the bands are assigned to overtones of the ν(C–O) fundamentals (2a′ and 2a″), and the third band is a combination (a′ + a″). In fact, there are sufficient data to permit the calculation of harmonic frequencies and anharmonicity constants (see Table IV in the supplementary material).

IR Bands of Coordinated 1-Butene. It is clear that the band tentatively assigned to coordinated butene (Figure 1) has an extinction similar to those of the isotopic satellites and overtones. A comparison of the absorbance of these bands during photolysis shows that they all belong to the same species. The assignment of the band of coordinated butene is thus confirmed.

Although the ν(C=C) band is likely to be the most diagnostic of the 1-butene ligand vibrations, it is possible to observe further bands due to the coordinated butene. The difficulty is that there is considerable overlap with the bands of free butene, present in considerable excess in LXe solution. However, computer substraction allows reasonable identification of many other vibrations of the 1-butene ligand. As an illustration, Figure 3 shows the derivation of part of the IR spectrum of the coordinated 1-butene. Even without a full assignment, the spectrum in Figure 3e provides an excellent "fingerprint" of coordinated butene. It should be emphasized that most, and probably all, of these bands of coordinated butene would have been obscured in a conventional solvent by IR absorptions of the solvent itself.

Photoreaction of $Fe(CO)_2(NO)_2$ with 1-Butene. Figure 4 illustrates a few of the many IR spectra recorded during the UV

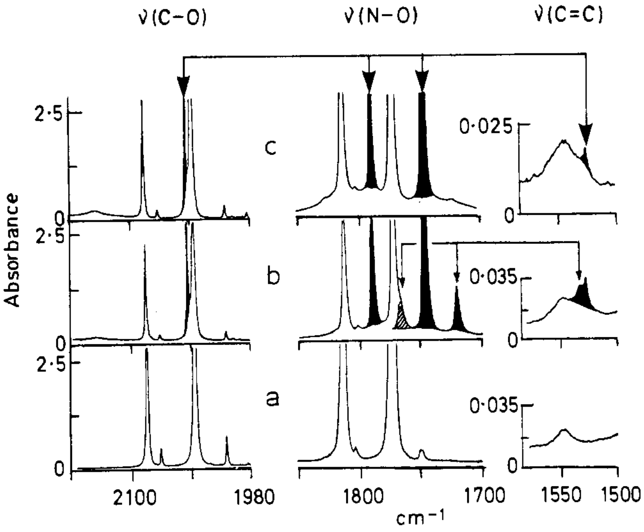

Figure 4. IR spectra illustrating the photolysis of $Fe(CO)_2(NO)_2$ and 1-butene in LXe at −104 °C: (a) before photolysis (weak bands due to ^{13}C, ^{15}N, and ^{18}O satellites, cf. Table II); (b) after UV photolysis (bands marked with ↓ assigned to $Fe(NO)_2(\eta^2\text{-1-btn})_2$); (c) after further UV photolysis, warming the solution to −55 °C, and recooling to −104 °C (bands marked with ↓ due to $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$, note disappearance of bands of $Fe(NO)_2(\eta^2\text{-1-btn})_2$).

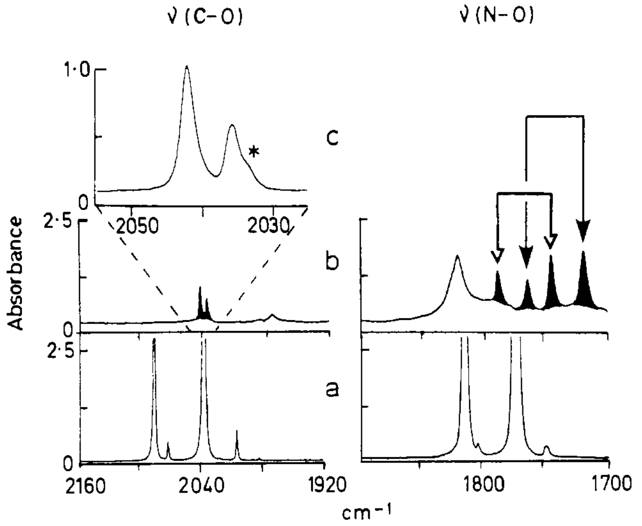

Figure 5. IR spectra showing results of prolonged UV photolysis of $Fe_2(CO)_2(NO)_2$ and 1-butene in LXe at −104 °C: (a) spectrum before photolysis; (b) spectrum after photolysis and addition of further 1-butene (bands colored black due to $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$ and $Fe(NO)_2(\eta^2\text{-1-btn})_2$ (cf. Figure 4) and uncolored bands due to uncoordinated 1-butene); (c) spectrum of ν(C–O) region plotted with expanded absorbance and wavenumber scale to illustrate the unexpected splitting of the band of $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$ (splitting is attributed to different conformers (see text)).

photolysis of $Fe(CO)_2(NO)_2$ and 1-butene in LXe. These spectra show that the photolysis is somewhat more complicated than for $Co(CO)_3NO$ because *two* photoproducts are formed. One photoproduct has *one* ν(C–O) absorption, *two* ν(N–O) bands, and a weak absorption characteristic of coordinated butene in the ν(C=C) region, ~1525 cm⁻¹ (Figure 4c). The second photoproduct has *no* ν(C–O) absorption, two ν(N–O) bands (one overlapping a band of unreacted $Fe(CO)_2(NO)_2$), and a weak absorption in the ν(C=C) region, ~1530 cm⁻¹ (Figure 4b).

A careful analysis of the region 1500–700 cm⁻¹ confirmed that both photoproducts had bands associated with coordinated 1-butene very similar to those shown in Figure 3e. Further evidence that the products do involve the reaction of $Fe(CO)_2(NO)_2$ with the dopant 1-butene comes from monitoring the *decrease* in intensity of IR bands of uncoordinated butene and the concomitant *increase* in the intensity of the bands of the coordinated alkene.

Table II. Frequencies (cm⁻¹) of IR Bands of $Fe(CO)_2(NO)_2$, $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$, and $Fe(NO)_2(\eta^2\text{-1-btn})_2$ in Liquid Xenon at −104 °C

obsd	calcd[a,b]	assignt
	$Fe(CO)_2(NO)_2$	
2084.4		ν(C–O) a_1
2035.0		ν(C–O) b_1
1812.5		ν(N–O) a_1
1770.0		ν(N–O) b_2
2071.1	2070.3	ν(C–O) } (^{13}CO)(^{12}CO)
2004.4	2003.4	ν(C–O)
1802.3	1801.7/1799.2	ν(N–O) } (NO)(^{15}NO)/
1747.3/1745.4	1748.8/1736.1	ν(N–O) } (NO)($N^{18}O$)
4159.9	4168.8[b]	2 × a_1(C–O)
4095.8	4119.4	a_1(CO) + b_1(C–O)
4057.2	4070	2 × b(C–O)
3617.4	3625	2 × a_1(N–O)
3560.3	3582.5	a_1(N–O) + b_2(N–O)
3529.5	3540	2 × b_2(N–O)
	$Fe(CO)(NO)_2(\eta^2\text{-1-btn})$	
2042.3/2035.3/ 2033.1 (sh)		ν(C–O) a′
1789.7		ν(N–O) a′
1745.8		ν(N–O) a″
1525		ν(C=C)
1997.1/1990.5/ 1988.6 (sh)	1996.8/1990.1/ 1987.9	ν(C–O) ^{13}CO
	1778.8/1776.3	ν(N–O) } (NO)(^{15}NO)/
1721.5	1725.1/1712.7	ν(N–O) } (NO)($N^{18}O$)
4056.2/4043.7	4084.6/4070.6[b]	2 × a′(C–O)
3567	3579.4	2 × a′(N–O)
3509.7	3535.5	a′(N–O) + a″(N–O)
3476	3491.6	2 × a″(N–O)
	$Fe(NO)_2(\eta^2\text{-1-btn})_2$	
1766.4		ν(N–O) a_1
1720.3		ν(N–O) b_2
1529.4		ν(C=O)
3459.4	3486.7	a_1(N–O) + b_2(N–O)

[a] Calculated frequencies of isotopic molecules are based on force constants (N m⁻¹) derived from nonisotopic molecules: for $Fe(CO)_2(NO)_2$, $k_{CO} = 1714$, $k_{CO,CO} = 40.97$, $k_{NO} = 1411.6$, $k_{NO,NO} = 33.48$; for $Fe(CO)(NO)_2(\eta^2\text{-1-btn})$, $k_{CO} = 1684.8/1673.3/1669.7$, $k_{NO} = 1374.8$, $k_{NO,NO} = 31.13$; for $Fe(NO)_2(\eta^2\text{-1-btn})_2$, the isotopic bands were too weak to observe. [b] Overtone and combination frequencies calculated with anharmonicity being ignored.

Table III. Frequencies (cm⁻¹) of $Fe(CO)_{2-x}(NO)_2Q_x$ (Q = 1-Butene, *trans*-Cyclooctene; x = 1, 2)

	ν(C–O)	ν(N–O)
$(\eta^2\text{-1-btn})Fe(CO)(NO)_2$[a]	2042	1790, 1746
(η^1-*trans*-cyclooct)$Fe(CO)(NO)_2$[b]	2036	1780, 1736
$(\eta^2\text{-1-btn})_2Fe(NO)_2$[a]		1766, 1720
(η^2-*trans*-cyclooct)$_2Fe(NO)_2$[b]		1762, 1717

[a] This work; in LXe at −104 °C. [b] Reference 21; in hydrocarbon solution at room temperature.

The spectra, therefore, are entirely consistent with the photoreactions

$$Fe(CO)_2(NO)_2 \xrightarrow{h\nu} Fe(CO)(NO)_2(\eta^2\text{-1-btn}) \xrightarrow{h\nu} Fe(NO)_2(\eta^2\text{-1-btn})_2$$

Table II lists the principal bands of $Fe(CO)_2(NO)_2$ and of both Fe/butene complexes. Our assignment of the ν(C–O) and ν(N–O) bands in Table II is supported by the recent work of Grevels et al.[21] They have photochemically synthesized and completely

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(21) Grevels, F.-W., private communication.

characterized the relatively stable alkene compounds (η^2-*trans*-cyclooct)Fe(CO)(NO)$_2$ and (η^2-*trans*-cyclooct)$_2$Fe(NO)$_2$ (cyclooct = cyclooctene), and Table III compares the appropriate frequencies.

After prolonged UV photolysis of Fe(CO)$_2$(NO)$_2$ and 1-butene, all of the Fe(CO)$_2$(NO)$_2$ was destroyed and its ν(C–O) and ν(N–O) bands disappeared from the IR spectrum (Figure 5b). In the absence of these bands of Fe(CO)$_2$(NO)$_2$, the ν(N–O) bands of both photoproducts, colored black in Figure 5b, are easily seen. Most surprisingly, however, Figure 5b also reveals that the ν(C–O) absorption of Fe(CO)(NO)$_2$(η^2-1-btn) is a *doublet*, which on closer inspection has traces of an additional shoulder, marked with an asterisk in Figure 5c. These bands are all due to the same compound, and their relative intensities change reversibly as the solution is warmed. Such band splittings are unusual but are not unprecedented in organometallic compounds. A particularly striking example is the splitting of the a′ ν(C–O) mode of (η^6-C$_6$H$_5$X)Cr(CO)$_3$ compounds,[22] which may be due to different rotamers. Similarly, in the present case the splitting of the ν(C–O) mode of Fe(CO)(NO)$_2$(η^2-1-btn) appears to be due to different conformers of the coordinated 1-butene. This explanation is also consistent with the more detailed analysis of the bands of coordinated 1-butene (see the supplementary material).

Prolonged UV photolysis also resulted in the formation of a reddish solid, insoluble in LXe. It was presumably a polynuclear compound, but unfortunately the amount of material was too small for characterization.

Thermal Stabilities of Fe(CO)(NO)$_2$(η^2-1-btn) and Fe(NO)$_2$(η^2-1-btn)$_2$. There is no evidence for thermal decay of either butene complex on standing for 1 h at −104 °C. However, when the cell is warmed up to −55 °C, the bands assigned to the disubstituted species decayed rapidly ($t_{1/2} \simeq$ 2min). At the same time, there were clear and reproducible increases in the intensities of the ν(^{13}C–O) bands of Fe(CO)(NO)$_2$(η^2-1-btn) and the ν(C=C) band of uncoordinated butene and a decrease in the absorption of due to free CO in the solution. These changes are consistent with the reaction

$$\mathrm{Fe(NO)_2(\eta^2\text{-}1\text{-}btn)_2 + CO \xrightarrow{LXe} Fe(CO)(NO)_2(\eta^2\text{-}1\text{-}btn) + 1\text{-}btn}$$

The rate of this thermal decay is substantially reduced by increasing the concentration of free butene in solution. This observation would be consistent with a dissociative mechanism. However, since the unsubstituted nitrosyl–carbonyl compounds are known to react thermally by both associative and dissociative pathways,[23] it would be unwise to speculate on the mechanism of the thermal decay without further evidence.

In contrast with the thermal decay of Fe(NO)$_2$(η^2-1-btn)$_2$, both Fe(CO)(NO)$_2$(η^2-1-btn) and Co(CO)$_2$(NO)(1-btn) showed no evidence of thermal decay even at −30 °C, the highest temperature currently attainable in our cell. The thermal instability of the disubstituted iron nitrosyl compound is reminiscent of our earlier experiments[4] with N$_2$ ligands, where Fe(NO)$_2$(N$_2$)$_2$ was thermally much less stable than Fe(CO)(NO)$_2$(N$_2$).

Conclusion

In this paper we have demonstrated that IR spectroscopy is a very sensitive technique for characterizing unstable organometallic compounds dissolved in liquefied xenon. In particular, one can observe IR bands due to vibrations of coordinated organic ligands, bands that would be masked by IR absorptions of more conventional solvents. Even the relatively straightforward reaction with 1-butene has revealed striking differences in behavior between Co(CO)$_3$NO and Fe(CO)$_2$(NO)$_2$. The Fe center can coordinate two olefin molecules, while under similar conditions the Co center can only coordinate one. The difference is suggestive of the greater efficiency of Fe(CO)$_2$(NO)$_2$ as a dimerization catalyst,[10] and we shall discuss this reaction in more detail in a separate paper.[11]

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Registry No. Co(CO)$_2$(NO)(η^2-1-butene), 103752-18-7; Fe(CO)(NO)$_2$(η^2-1-butene), 103752-19-8; Fe(NO)$_2$(η^2-1-butene)$_2$, 103752-20-1; Co(CO)$_3$NO, 14096-82-3; Fe(CO)$_2$(NO)$_2$, 13682-74-1.

Supplementary Material Available: Harmonic ν(C–O) and ν(N–O) frequencies for Co(CO)$_3$(NO) and Co(CO)$_2$(NO)(η^2-1-btn) (Table IV) and wavenumbers and tentative assignment of the observed IR bands of coordinated and uncoordinated 1-butene (Table V and Figures 6–10) (9 pages). Ordering information is given on any current masthead page.

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Solid-State Micro-Raman and Fourier Transform Infrared Spectra of Mixed Carbonyl–Isocyanide Dirhenium(0) Complexes, Re$_2$(CO)$_{10-n}$(CNR)$_n$ (n = 1–4)

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Vibrational assignments are proposed for the solid, mixed carbonyl–isocyanide dirhenium(0) derivatives Re$_2$(CO)$_{10-n}$(CNR)$_n$ (R = Me, *t*-Bu, benzyl, n = 1–3; R = 2,6-xylenyl, n = 1–4), on the basis of their room-temperature micro-Raman and FT-IR spectra. Successive replacement of the CO groups by CNR ligands results in a gradual shift of the ν(CO) modes to lower wavenumbers, while the reverse is observed for the ν(Re–C) modes. These shifts are good indicators of the stronger σ-donor and poorer π-acceptor capacities of the CNR ligands compared to those of CO. Moreover, the shifts increase with changes in R in the order Me < benzyl < *t*-Bu < 2,6-xylenyl, presumably reflecting the increased steric hindrance due to the bulkiness of the R ligands. There is no correlation between the position of the strongest Raman peak at 120 cm^{-1} and the Re–Re bond distances in these mixed carbonyl–isocyanide derivatives, demonstrating that this peak cannot be attributed solely to the ν(Re–Re) mode, as had been suggested previously.

Introduction

Decacarbonyldirhenium(0), Re$_2$(CO)$_{10}$, is a particularly simple example of a metal–metal bonded complex in which two, staggered, square-pyramidal Re(CO)$_5$ fragments are held together by a single Re–Re bond.[2,3] In general, the D_{4d} vibrational selection rules are obeyed for the solid and in solution,[4] but the activity

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