Preliminary communication

PHOTOCHEMICAL GENERATION AND REACTIONS OF RHODIUM (η^5-CYCLOPENTADIENYL) (ETHENE) (DINITROGEN) IN LIQUID XENON

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Summary

Photolysis of $CpRh(C_2H_4)_2$ dissolved in N_2-doped liquid xenon at 173 K causes dissociation of ethene and production of $CpRh(C_2H_4)N_2$ (FTIR detection); when CO is dissolved in the xenon, the dinitrogen complex may be converted to $CpRh(C_2H_4)CO$ by brief photolysis ($Cp = \eta^5$-C_5H_5).

Although many ethene complexes are thermally labile, a substantial number are inert to dissociation. In recent studies of $Cp_2W(C_2H_4)$ and $CpRh(C_2H_4)_2$ ($Cp = \eta^5$-C_5H_5), we have demonstrated the mechanistic and synthetic value of photodissociation of coordinated ethene [1,2]. Photolysis of $CpRh(C_2H_4)_2$ (I) in argon matrices at 20 K leads to reversible loss of ethene (identified by its IR absorptions); in reactive matrices (e.g. CO, N_2) substitution products $CpRh(C_2H_4)L$ ($L = N_2$, II; $L = CO$, III) are identified. When I is photolysed at room temperature in benzene solution with added ligands, ethene is lost (identified by NMR) and a variety of stable substitution and oxidative addition products are formed [2].

Liquid xenon, LXe, is now established as an effective medium for studying the photochemical generation and reactions of labile metal carbonyls such as $Cr(CO)_5N_2$ and $Cr(CO)_5(H_2)$ by IR spectroscopy [3,4]. In this communication we show that the technique is equally applicable to non-carbonyl organometallics. We present IR spectra which provide unequivocal evidence for the formation of both II and uncoordinated C_2H_4, when I is photolysed in the presence of N_2 in LXe solution at 173 K.

$CpRh(C_2H_4)_2$ is surprisingly soluble in LXe. Its IR spectrum (Fig. 1) shows fundamental vibrations across the range 3150–400 cm^{-1} and even overtone/combination modes up to 4500 cm^{-1}. Figure 2 shows the changes in selected spectral regions which were observed on photolysis of I in the presence of dissolved N_2.
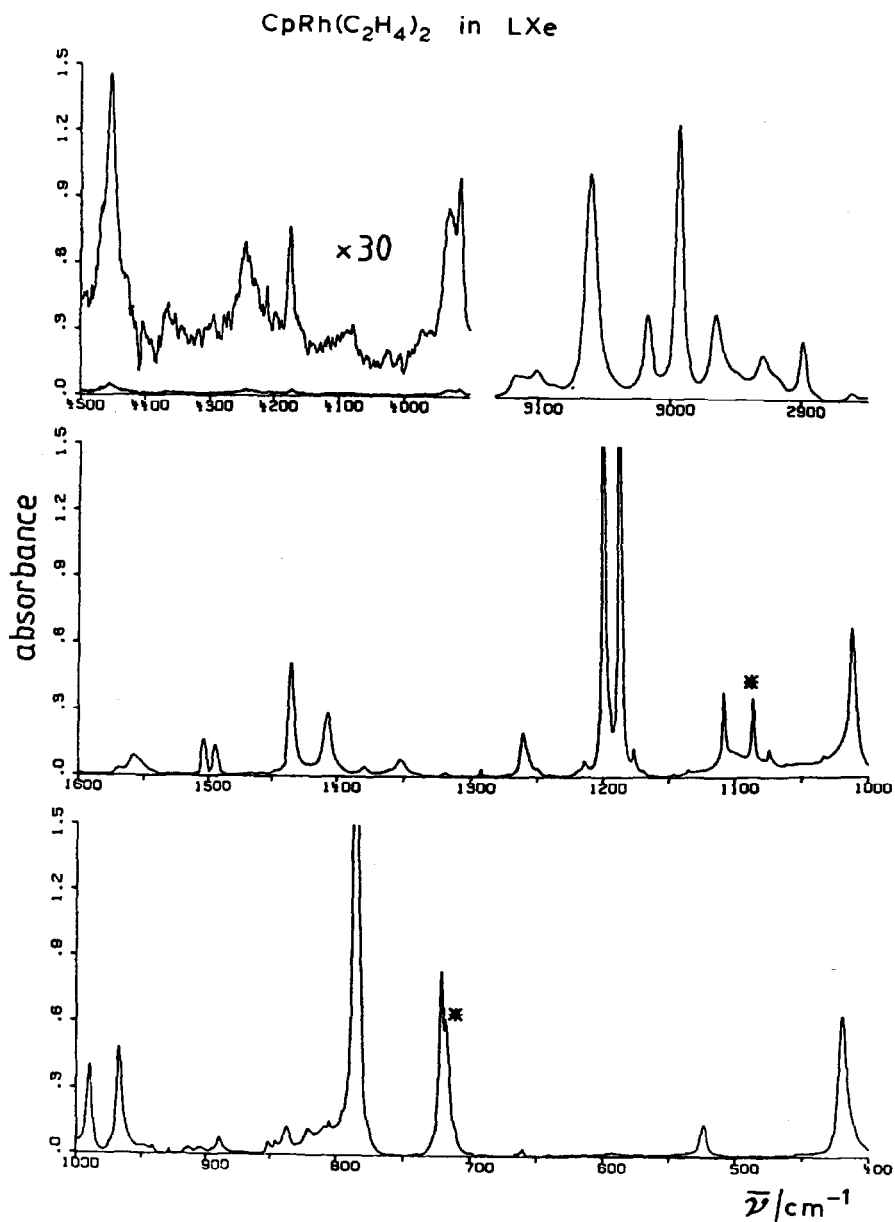
CpRh(C$_2$H$_4$)$_2$ in LXe

Fig. 1. IR spectrum of CpRh(C$_2$H$_4$)$_2$ (I) dissolved in LXe at 173 K. Spectra were obtained using a Nicolet MX-3600 interferometer (16 K data points, 32 K transform points, 2 cm^{-1} resolution) and a low-temperature cell (25 mm path-length) described previously [11]. The region 2850–1600 cm^{-1} has been omitted since there are no bands of significant intensity. Bands marked* are due to impurities. The region above 3900 cm^{-1} is shown with 30× ordinate expansion and is digitally smoothed (16 pt).

These spectra demonstrate that photolysis generated the dinitrogen complex, II, with an intense ν(NN) mode only 7.4 cm^{-1} lower in position than observed for II in a N$_2$ matrix [2]. In spectrum c, the band is so intense that it is possible to observe
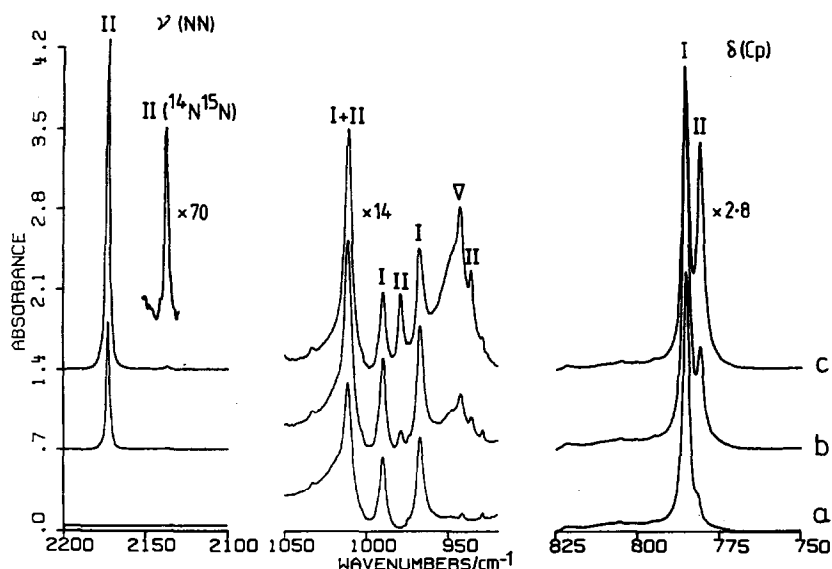
Fig. 2. IR spectra showing formation of CpRh(C_2H_4)N_2 (II) and C_2H_4 during photolysis of I in LXe doped with N_2 (100 psi): (a) before photolysis, unlabelled bands are due to I, cf. Fig. I which was recorded in a different experiment; (b) after 140 s photolysis, note the growth in ν(NN) region; (c) after 650 s photolysis, bands are labelled due to II and C_2H_4 $\triangledown$. Note the different absorbance scales in the three spectral regions and the ×70 expansion of the ν($^{15}N^{14}N$) band. The photolysis source is an AEI 250 W high-pressure Hg arc, output $\lambda > 280$ nm.

ν($^{14}N^{15}N$) of CpRh(C_2H_4)($^{14}N^{15}N$) in natural abundance. The isotopic shift of 35.6 cm^{-1} compares very well to that calculated for an isolated NN oscillator: 36.4 cm^{-1}. Even though the ν($^{14}N^{15}N$) band is quite sharp ($\sim$ 3.5 cm^{-1} FWHM), we were unable to resolve the bands of the two isotopomers, Rh$^{14}N^{15}N$ and Rh$^{15}N^{14}N$ (compare better resolved spectra of matrix-isolated dinitrogen complexes [5]). Many other bands of II were observed throughout the spectrum (Table 1). The growth of the most intense of these bands, 781.0 cm^{-1}, assigned to a δ(CH) vibration of the C_5H_5 ring, is shown in Fig. 2.

TABLE 1

PRINCIPAL IR BANDS OF PHOTOPRODUCTS OF CpRh(C_2H_4)$_2$ IN LIQUID XENON AT 173 K ($\bar{\nu}$ (cm^{-1}))

II	III	IV
2172.6vs	1990.3vs	2049.3vs
2137.0vw		1985.5vs
1426.2w		
1179.6m	1188.3w	
1010.5w		
979.0w		
935.9w		
780.9s	785.4s	
444.0w	553.7m	

Equally clear from Fig. 2 is the growth of a broad band at 943 cm^{-1} due to the ν_7 vibration of uncoordinated C_2H_4 formed during the photolysis of I [6]. The ν_{12} band (1437 cm^{-1}) of C_2H_4 was also observed to grow in during photolysis. The bands of C_2H_4 are broader than those of I or II, because small molecules such as this rotate and librate in LXe [7]. This effect is observed most clearly for H_2 and D_2 which even display ro-vibrational IR spectra when dissolved in LXe [8]. Thus, in these experiments the IR spectra provide definite evidence for the reaction:

$$CpRh(C_2H_4)_2 + N_2 \xrightarrow[LXe]{h\nu} CpRh(C_2H_4)N_2 + C_2H_4 \qquad (1)$$
$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$
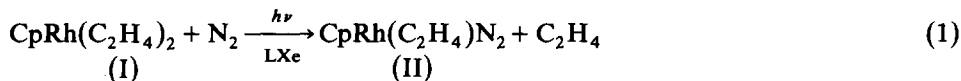
We were therefore somewhat surprised by a recent claim that IR spectroscopy could not be used to detect the photoejection of C_2H_4 because the molecular symmetry renders the $\nu(C{=}C)$ stretching mode IR-inactive [9]. This assertion is invalid because the five IR-active modes are characteristic of C_2H_4, regardless of the inactivity of the remainder.

The criteria for using IR spectra to prove ligand expulsion from organometallics are: (i) the growth of bands due to free ligand at a comparable rate to loss of precursor and formation of organometallic product; (ii) the matching of the IR bands of expelled ligand to spectra of the free ligand obtained under similar conditions (with the caveat that mutual perturbation of product and expelled ligand within the cage may cause slight shifts in matrix-isolation experiments [10]); (iii) observation, in cases of doubt, of the correct shifts in the bands of expelled ligand on isotopic labelling of the precursor complex.

All three criteria were met in our previous study of matrix-isolated I and there can be no doubt that C_2H_4 was photo-ejected in the matrix, just as we have now observed in LXe solution. The short photolysis times suggest that the quantum yield for reaction 1 is higher in solution than in the matrix.

The high-pressure IR cell enables LXe to be used over a relatively wide temperature range (163–235 K), allowing thermal reactions to be studied [8,11]. II was stable indefinitely at 173 K under pressure of N_2 and did not decompose over 1 h at 203 K. On venting the N_2 and replacing it with a N_2/CO mixture, two bands appeared in the ν(CO) region, readily assignable to $CpRh(CO)_2$ (IV) (Fig. 3a, b). (Although the CO was dissolved by warming to 223 K and recooling, the thermal
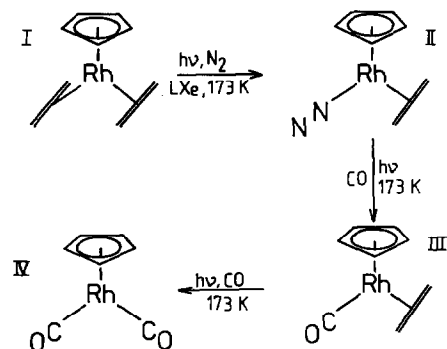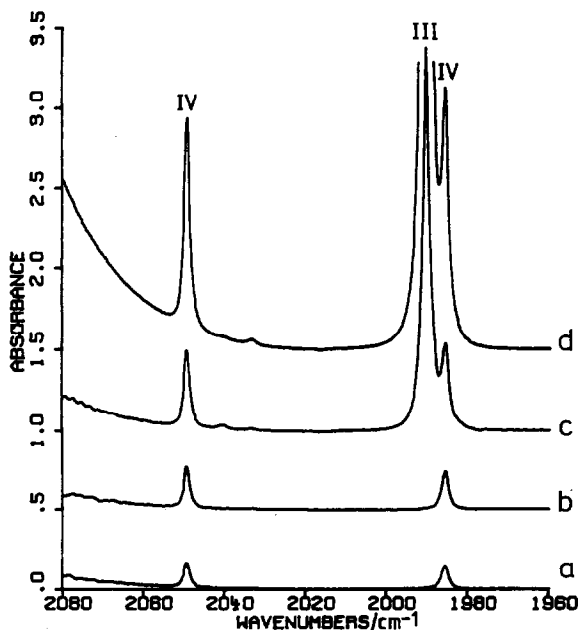

SCHEME 1

Fig. 3. IR spectra in the ν(CO) region showing formation of carbonyl products on reaction with CO: (a) after addition of CO/N_2; (b) after 10 min without photolysis to allow thermal reaction with CO; (c) after 46 s photolysis; (d) after a total of 255 s photolysis. The products are CpRh(C_2H_4)CO (III) and CpRh(CO)$_2$ (IV). Note that most of the absorption of dissolved CO has been subtracted digitally, but increased CO concentration accounts for the sloping baseline in (d).

reaction occurred at 173 K). Conversion to IV was so slight that it is uncertain whether IV is generated by reaction of II, or of some other species present in very low concentration. In contrast, subsequent photolysis converted all the remaining II to carbonyl products. For the first 105 s photolysis only CpRh(C_2H_4)CO (III) is formed (Fig. 3c). Further photolysis generated IV, but it remained the minor product of the photochemical reaction (Fig. 3d). Compound III has been synthesised independently and is stable at room temperature [12].

The experiments described here show how liquid xenon acts as a solvent which bridges the gap between low-temperature matrices and room-temperature solutions (Scheme 1) [2,12]. Although CpRh(C_2H_4)N_2 has a high ν(NN) mode [13], it is thermally stable at temperatures as high as 203 K, suggesting that it may be a synthetically useful reaction intermediate. In current experiments we are studying the reactions of I with H_2 and D_2.

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