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A New Approach To Studying the Mechanism of Catalytic Reactions: An Investigation into the Photocatalytic Hydrogenation of Norbornadiene and Dimethylfumarate Using Polyethylene Matrices at Low Temperature and High Pressure

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Abstract: This paper presents a new method for investigating the mechanisms of homogeneously catalyzed reactions involving gases, particularly H_2. We show how the combination of polyethylene (PE) matrices and high pressure−low temperature (HPLT) experiments can be used to provide new mechanistic information on hydrogenation processes. In particular, we show how we are able to generate reaction intermediates at low temperature, and then to extract the contents of the PE film at room temperature to characterize the organic products using GC-MS. We have used our new technique to probe both the hydrogenation of dimethyl fumarate (DF), using $Fe(CO)_4(\eta^2\text{-DF})$ as the catalytic species, and the hydrogenation of norbornadiene (NBD), using $(NBD)M(CO)_4$ (M = Cr or Mo) as the catalytic species. Irradiation of $Fe(CO)_4(\eta^2\text{-DF})$ in a PE matrix at 150 K resulted in the formation of an intermediate complex tentatively assigned $Fe(CO)_3(\eta^4\text{-DF})$. Warming this complex to 260 K under H_2 leads to the formation of $Fe(CO)_3(\eta^2\text{-DF})(\eta^2\text{-}H_2)$. Further warming of the reaction system results in the hydrogenation of the coordinated DF, to generate dimethyl succinate (DS). Characterization of the intermediate species was obtained using FTIR spectroscopy. Formation of DS was confirmed using both FTIR spectroscopy and GC-MS analysis. UV photolysis of $(NBD)M(CO)_4$ in PE under H_2 in the presence of excess NBD results in the formation of the hydrogenated products norbornene (NBN) and nortricyclene (NTC), with trace amounts of norbornane (NBA) being observed. These products were in similar ratios to those observed in fluid solution. However, for $(NBD)Mo(CO)_4$, the relative amounts of the organic products change considerably when the reaction is repeated in PE under H_2 *in the absence* of free NBD, with NBA being the major product. The use of our HPLT cell allows us to vent and exchange high pressures of gases with ease, and as such we have performed gas exchange reactions with H_2 and D_2. Analysis of the reaction products from these exchange reactions with GC-MS provides evidence for the mechanism of formation of NBA, in both the *presence* and *absence* of excess NBD, a reaction which has been largely ignored in previous studies.

Introduction

This paper presents a new method for investigating the mechanisms of homogeneously catalyzed reactions involving gases, particularly H_2. Reactions between transition metal complexes and gases are a recurrent feature of organometallic chemistry, particularly in catalytic processes.[2−6] A detailed understanding of the mechanism of such reactions is essential to improve the efficiency and selectivity of the processes. In principle, spectroscopic studies can provide valuable information needed to elucidate such mechanistic pathways.[7,8] However, since most catalytic intermediates are short-lived at room temperature, it is usually necessary to employ special methods to study these species.

The most common approach is to use low-temperature matrix isolation,[9−11] slowing the reaction down so that the intermediates can be studied using conventional spectroscopic methods. In matrix isolation, the organometallic is frozen in a noble gas matrix or a hydrocarbon "glass" at temperatures in the range 10−77 K. However, the temperature range accessible in conventional matrix isolation is limited by the melting point of the matrix material. It is, therefore, usually very difficult to study the thermal steps involved in a catalytic process. Furthermore, reactions between organometallic complexes and H_2 are difficult to study because of the problems involved in trapping sufficient quantities of the gaseous reagent within the matrix.[12−14] Experi-

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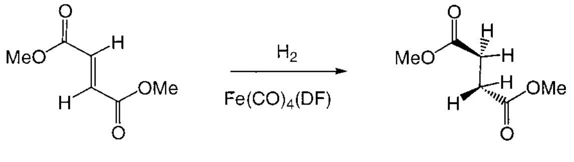
ments with liquefied noble gas solvents have overcome some of these problems,[15,16] but although this technique allows reactions to be studied in solution at low temperature, the accessible temperature range remains relatively narrow. Room temperature time resolved IR spectroscopy (TRIR), a combination of UV flash photolysis and fast IR detection, has been extensively used for the study of short-lived organometallic intermediates with lifetimes ranging from femto- to milliseconds.[17−19] The key advantage of TRIR is that it allows the study of fast chemical processes under reasonably realistic conditions (e.g., at room temperature). However, this technique cannot always provide all of the information required to understand a particular reaction.

Ideally, a single technique is needed that can span a broad temperature range *and* allow the study of reactions between organometallic compounds and gases. Building on studies by Rest and co-workers,[20] we have shown that polyethylene (PE) is a versatile matrix material for investigating organometallic reactions which can be used over a broad temperature range (10−300 K). Initially, we investigated PE as a matrix material for studying the hydrogen bonding of highly acidic fluorinated alcohols to metal centers, e.g. in $Cp^*Ir(CO)_2$.[21] In an extension of this, we developed a miniature high-pressure cell that can operate at pressures of up to 300 bar over a very broad temperature range (20−300 K).[22] This cell was used to study the photochemical reaction between $Fe(CO)_5$ and N_2 at low temperatures.[23] The thermal stability of the PE matrix and the ability to easily exchange gases inside the reactor allowed us to study the *thermal* reaction of $Fe(CO)_4N_2$ with H_2. Subsequently,[24] we have also used our technique to study the reaction of a range of d^6 metal centers with H_2 and N_2, generating $(\eta^6\text{-}C_6H_3Me_3)M(CO)_{3-n}(N_2)_n$ ($n = 1−3$), $(\eta^6\text{-}C_6H_3Me_3)M(CO)_2(H_2)$ (M = Cr or Mo), *cis*-$W(CO)_4(H_2)CS$, and *trans*-$W(CO)_4(H_2)CS$ and monitoring their reaction chemistry.

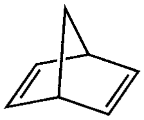
In this paper, we describe how polymer matrix isolation can be combined with both FTIR spectroscopy and GC-MS detection, for the study of complicated catalytic mechanisms. In particular, we show that our new method allows a surprisingly high level of control over the manipulation of thermally unstable organometallic reaction intermediates, and that this can lead to an enhanced understanding of complicated reaction mechanisms. We illustrate the use of our new technique with two studies, the hydrogenation of dimethyl fumarate (DF) and norbornadiene (NBD).

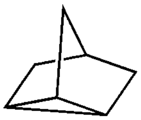
In the first example, we have simplified the hydrogenation of DF catalyzed by $Fe(CO)_5$ by merely studying the photochemistry of $Fe(CO)_4(DF)$ and its reaction with H_2. The advantage of this hydrogenation as a test reaction is that the organic compound has strong IR chromophores, the C═O groups. These can be used to detect the hydrogenation spectroscopically because the ν(C−O) bands of DF and the hydrogenated product dimethyl succinate, DS, are shifted significantly relative to each other.

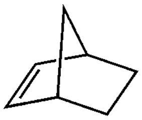


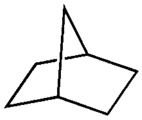
DF DS

Our second example, the catalytic hydrogenation of dienes involving Group 6 transition metal compounds, is mechanistically far richer. The reaction has been studied in detail for more than 30 years,[25−32] but still has unsolved problems, particularly in the hydrogenation of NBD, where both 1,2- and 1,4-addition can occur, giving two possible hydrogenation products, norbornene (NBN) and nortricyclene (NTC). Early investigators[33,34] proposed that the catalytic cycle for this hydrogenation reaction included an intermediate with a classical dihydride bonded to the same metal center as the diene. However, the discovery of nonclassical dihydrogen complexes[35,36] prompted our group to reinvestigate this reaction using a combination of both low-temperature techniques[37] (liquefied noble gases) and TRIR spectroscopy.[38] These studies demonstrated that the key catalytic intermediates in the hydrogenation of NBD are most probably the nonclassical dihydrogen complexes of the type $(NBD)M(CO)_3(\eta^2\text{-}H_2)$ (M = Cr, Mo or W). The mechanism proposed following these studies[39] is shown in Scheme 1. The different ratios of NBN and NTC observed in the reactions catalyzed by $(NBD)M(CO)_4$ (M = Cr or Mo) were rationalized by assuming that the two metals give rise to different distributions of *mer* and *fac* intermediates (i.e., the Mo complex gives rise to more NBN because the *mer* intermediate is more favored than for Cr).


NBD


NTC


NBN


NBA

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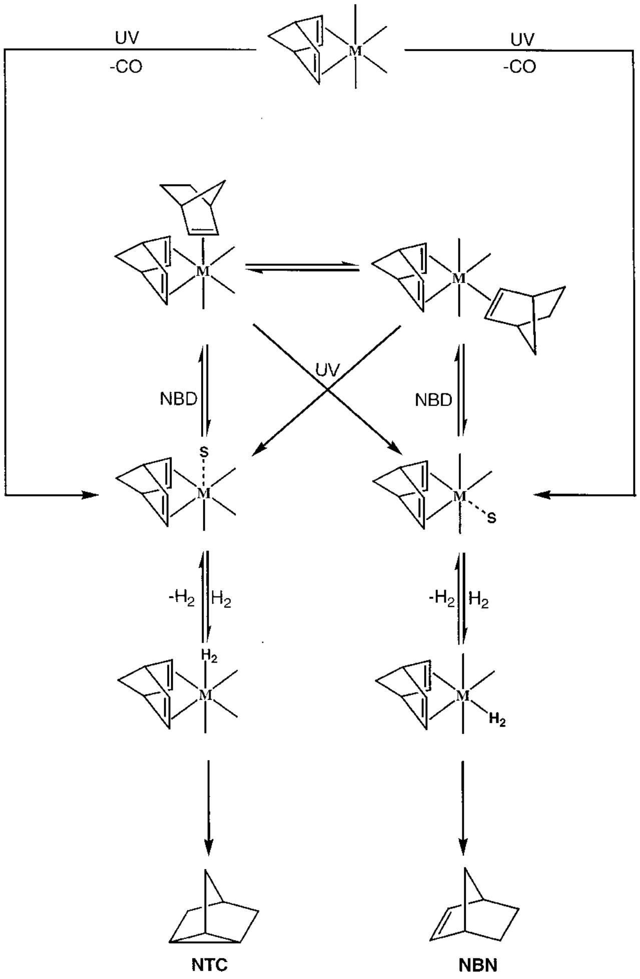
[39] In this scheme, and in subsequent schemes, carbonyl groups are represented by lines without labels. All other ligands are shown explicitly.

Scheme 1. Reaction Scheme for the Catalytic Hydrogenation of Norbornadiene (NBD) Using (NBD)M(CO)$_4$ (M = Cr, Mo or W)[a]



[a] Adapted from Hodges et al.[38]

There are still fundamental, but as yet unanswered, questions concerning this catalytic cycle. For example, the formation of the doubly hydrogenated species, norbornane (NBA), as a minor product in these reactions has not been satisfactorily explained. In addition, while it was possible to detect and identify a wide range of intermediates, it was never possible to observe *directly* the crucial step, i.e., the transfer of hydrogen from the metal to the organic substrate.

We now explain the principles of our technique before describing the results in detail.

Experimental Section

The apparatus used for polymer matrix isolation studies has been described in detail elsewhere (see Figure 1).[22,23] Briefly, a 250 μm thick polyethylene disk (Hostalen GUR-415 PE (Hoechst)) was impregnated with the organometallic compound under investigation. Clarke et al.[40] have shown that this form of PE has a very low degree of unsaturation, and have demonstrated that interaction between olefinic double bonds in the PE and unsaturated photofragments is negligible. Impregnation was achieved either by gentle warming of the PE and organometallic compound under reduced pressure or by placing the PE disk in an alkane solvent saturated with the organometallic compound. Once impregnated, the disk was clipped into the high pressure−low temperature (HP-LT) copper cell.[22,23] The cell was filled with reactant gas (typically H_2 or N_2) and was cooled to the required temperature using an Air Products Displex CS-202 cooler. Temperatures were measured accurately using a Scientific Instruments Inc. 9600-1 silicon diode temperature controller. Once at the required temperature, reactions were initiated using broadband UV from a Phillips HPK 125W medium-pressure Hg arc. Reactions were monitored using a Nicolet 730 IR interferometer interfaced to a PC running OMNIC software. Polyethylene (PE) has very weak temperature-dependent IR absorptions in the ν(CO) region, therefore background spectra were recorded with unimpregnated PE disks over the range of temperatures required for the experiments.

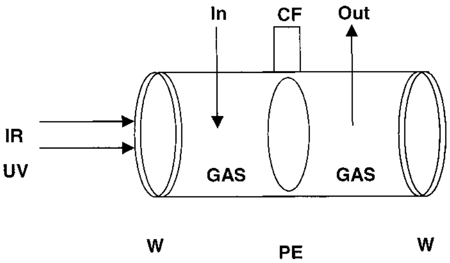


Figure 1. Schematic representation of the HP-LT Cu cell used in the experiments described here. A high pressure of gas can be introduced (or removed) from the cell, which is connected to a coldfinger (CF). The gas can freely permeate around the PE film. Reactions can be initiated using a UV lamp, and monitored using in situ FTIR. Irradiation and spectroscopy use the same CaF_2 windows (W) in the Cu cell body.

GC-MS analysis was performed using a Hewlett-Packard 5890A gas chromatograph fitted with a splitless injection system and interfaced to a Trio 2000 quadrupole mass spectrometer (VG Biotech) with a GC column (SE-54 stationary phase, methylpolysiloxane, 5% phenyl substituted, 30 m, 0.32 mm (i.d)). Positive electron impact ionization (electron energy = 70 V) was used to induce fragmentation. The mass spectrum associated with each GC peak was compared with the American National Bureau of Standards (NBS) Library for identification. GC-MS data were initially obtained using the full scanning mode, which scanned the entire mass range (30−300 amu) throughout the entire chromatographic run. Single ion monitoring (SIM), which detects distinctive and diagnostic ions, was used to obtain GC spectra with improved signal-to-noise ratio. The products from the norbornadiene experiments were eluted using an oven temperature of 303 K for 5 min rising to 308 K at 5 K per minute. The extracts from the hydrogenation of DF were eluted using an oven temperature of 323 K for 5 min rising to 473 K at 10 K per minute. The injector temperature was 523 K in all cases.

Fe(CO)$_4$(DF) and (NBD)M(CO)$_4$ (M = Cr and Mo) were gifts from Prof. F.-W. Grevels (Max Planck Institut für Strahlenchemie, Müllheim) and were used as supplied. Norbornadiene (Aldrich), norbornene (Aldrich), norbornane (Aldrich), dimethyl fumarate (Aldrich), dimethyl succinate (Aldrich), helimatricesum (Air Products), hydrogen (Air Products), and deuterium (BOC, Research Grade) were used as supplied.

Results and Discussion

Hydrogenation of Dimethyl Fumarate (DF) in PE Matrices at Low Temperature. Fe(CO)$_4$(DF) (**1**) has four characteristic IR bands in the ν(CO) region due to the Fe(CO)$_4$ moiety, with an additional band at 1741 cm^{-1} due to the carbonyl groups on the coordinated DF (see Table 1). Irradiation of **1** in PE at 150 K under a pressure of He resulted in a decay in the five parent bands accompanied by the growth of three new bands (Figure 2). These new bands, at wavenumbers slightly lower than parent, suggest that a tricarbonyl species was being formed. Upon warming the PE, the new peaks remained unchanged up to temperatures of ca. 260 K. Thus, it is unlikely that these new bands were due to an unsaturated 16-electron Fe(CO)$_3$(DF) species, which would be expected to be highly reactive toward the photoejected CO in the PE. It seems more likely

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Table 1. ν(C−O) Band Positions (cm^{-1}) of the Products Observed Following UV Irradiation of Fe(CO)$_4$(DF) in PE

complex	ν(C−O)
Fe(CO)$_4$(DF) **(1)**	2109
	2046
	2039
	2005
	1713
Fe(CO)$_3$(η^4-DF) **(1A)**	2075
	2011
	1998
Fe(CO)$_3$(DF)(η^2-H$_2$) **(1H)**	2060
	1977
Fe(CO)$_3$(DF)(η^2-D$_2$) **(1D)**	2058
	1979
Fe(CO)$_5$ **(1P)**	2021
	1999
uncoordinated DF	1733
uncoordinated DS	1748

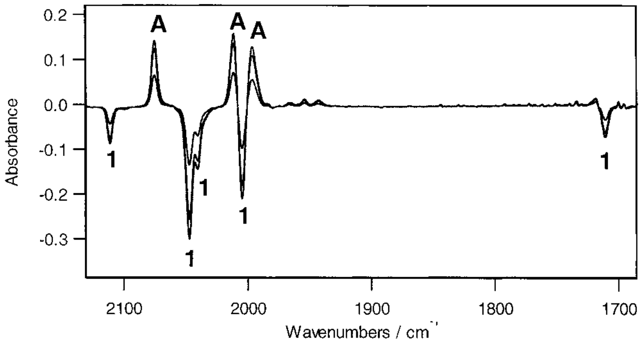

Figure 2. FTIR difference spectrum obtained following UV irradiation of Fe(CO)$_4$(η^2-DF) (**1**) under high pressures of both He and H$_2$ at 150 K in a PE disk. Positive peaks are due to generation of Fe(CO)$_3$(η^4-DF) (**1A**), negative peaks are due to depletion **1**.

that the coordinated DF has shifted its coordination mode to saturate fully the metal center, either through the π cloud of the C═O bond or perhaps by dative bond formation from one of the lone pairs on the carbonyl oxygen. Fe is known to prefer coordination to conjugated dienes, to form complexes such as Fe(CO)$_3$(η^4-butadiene).[41,42] This behavior extends to π-hetero-1,3-diene complexes[43,44] where the hereroatom is either O or N, with coordination through π clouds of the double bond rather than lone pairs. The relative intensities of the new bands are similar to the spectra of Fe(CO)$_3$(η^4-hetero-1,3-diene) complexes.[45,46] Thus we have assigned tentatively these three new bands to Fe(CO)$_3$(η^4-DF) (**1A**).

Warming the PE matrix further to ambient temperature led to regeneration of the parent tetracarbonyl, **1**, at the expense of the η^4 species, **1A**. The reaction was then repeated under 900 psi of H$_2$. Photolysis of **1** at 150 K again resulted in the formation of **1A**. However, warming the matrix to 260 K resulted in the growth of two additional bands (see Figure 3), which were not seen in the absence of H$_2$, and can therefore be assigned to a hydrogen-containing species. Fe(CO)$_3$(η^2-DF)-(η^2-H$_2$) (**1H**) seems more likely than the classical dihydride complex, Fe(CO)$_3$(η^2-DF)H$_2$, which would be expected to have ν(C−O) bands occurring at wavenumbers higher than those of **1**, due to oxidation of the metal center. Thus, we have been able to detect the thermal reaction of **1A** with H$_2$, most probably to form **1H**. Further warming of the PE to room temperature resulted in a decay of the bands of **1H** and the growth of two new bands (see Figure 4), which could be shown to be due to Fe(CO)$_5$ (**1P**). We were unable to detect the unsaturated Fe species (possibly metallic Fe) which, by stoichiometry, must have been formed at the same time as Fe(CO)$_5$. An additional band was also observed at 1748 cm^{-1}, which was identified as the hydrogenated product, DS, by comparison with the IR spectrum of pure DS impregnated into a PE film. The presence of this band indicates that the hydrogenation reaction of DF to DS had occurred within the PE film.

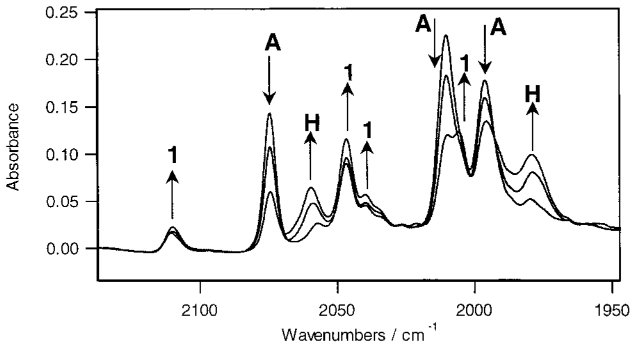

Figure 3. FTIR spectrum obtained following warming of a PE disk containing Fe(CO)$_3$(η^4-DF) (**1A**) from 150 to 260 K under a high pressure of H$_2$. Upon warming, a decrease in bands due to **1A** is observed, concurrent with a growth in bands due to the parent species, Fe(CO)$_4$(η^2-DF) (**1**), and a new species, Fe(CO)$_3$(DF)(η^2-H$_2$) (**1H**). Note that these spectra cover a time period shorter than that needed to take the conversion of **A** to completion.

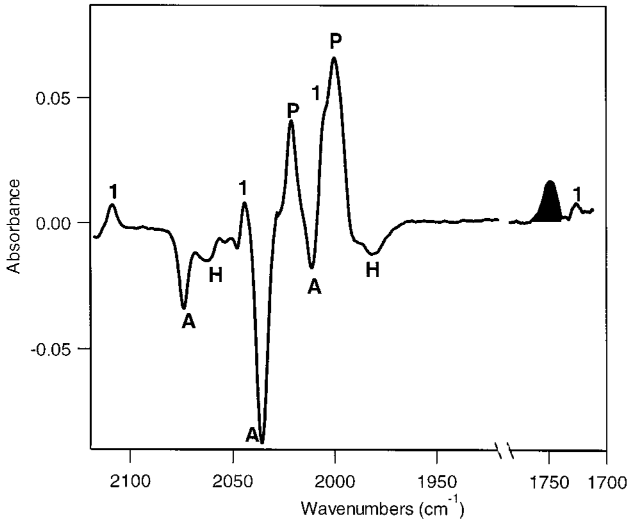

Figure 4. FTIR difference spectrum obtained upon warming the reaction products formed in Figure 3 to 298 K. A decrease in Fe(CO)$_3$-(DF)(η^2-H$_2$) (**H**) and Fe(CO)$_3$(η^4-DF) (**A**) is observed, along with an increase in Fe(CO)$_5$ (**P**), Fe(CO)$_4$(η^2-DF) (**1**), and the hydrogenated product, DS (solid band) at 1748 cm^{-1}.

The advantage of PE over more conventional matrices is that the PE film remains intact up to and indeed above room temperature. Therefore, it is possible to extract stable reaction products and to analyze them off-line. In this experiment, extraction of the PE disk with CCl$_4$ followed by GC-MS analysis revealed two peaks (not illustrated) which could be assigned to unhydrogenated DF and the hydrogenated product, DS, by

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Table 2. Wavenumbers (cm^{-1}) of the Photoproducts of $(NBD)Mo(CO)_4$ under Various Conditions

	Ar matrix/10 K[a]	lXe/190 K[b]	*n*-heptane/298 K[b]	PE/low T	PE/298 K
$(\eta^4\text{-NBD})Mo(CO)_4$ **(2)**		2044	2044	2042	2041
		1959	1958	1954	1954
		1914	1912	1906	1907
mer-$(\eta^2\text{-NBD})(\eta^4\text{-NBD})Mo(CO)_3$ **(2M)**			2015	2011	2011
			1938	1943	1943
			1932	1933	1933
fac-$(\eta^2\text{-NBD})(\eta^4\text{-NBD})Mo(CO)_3$ **(2F)**			1994[c]		1993
			1927[c]		*e*
			1900[c]		1903
mer-$(\eta^4\text{-NBD})Mo(CO)_3(H_2)$ **(2H′)**	2029[d]	2029	*e*	2025	
	1952[d]	1952	1952	1947	
fac-$(\eta^4\text{-NBD})Mo(CO)_3(H_2)$ **(2H)**	1997[d]	1997	1998	1993	
	1930[d]	1930	1930	1927	
	1898[d]	1898	1900	1891	
cis-$(\eta^2\text{-NBD})Mo(CO)_4(H_2)$ **(2C)**	2060[d]	2060		2056	
	1964[d]	1964		1958	
	1941[d]	1941		1937	
fac-$(NBD)Mo(CO)_3(s)$ **(2U)**	1985		1988	1977	
	1899		1900	1891	
	1889		1893	1878	
mer-$(NBD)Mo(CO)_3(s)$ **(2U′)**	2024		2016	*e*	
	1950		1944	1946	
	(1900)		1884	*e*	
$(\eta^2\text{-alkene})Mo(CO)_5$ **(2X)**			*e*	2076	2076
			1958	1954	1955
			e	1942	1943
$Mo(CO)_6$ **(2P)**		1986	1985	1985	1985

[a] See ref 50. [b] See refs 37 and 38. [c] These band positions are for the W analogue as the data for the equivalent Mo complex have not been reported. [d] IR band positions for the deuterated complex. [e] Band position obscured. Band positions shown in parentheses are tentative assignments.

comparison with GC-MS analysis of commercially available standards.

Repeating the photolysis of **1** in the presence of D_2 rather than H_2 gave identical results, apart from the expected isotopic shift in the $\nu(C-O)$ bands (Table 1) of $Fe(CO)_3(DF)(\eta^2\text{-}D_2)$ (**1D**). GC-MS analysis of the deuterated extract also gave two peaks, one of which was assigned to d_2-DS from its mass spectrum.

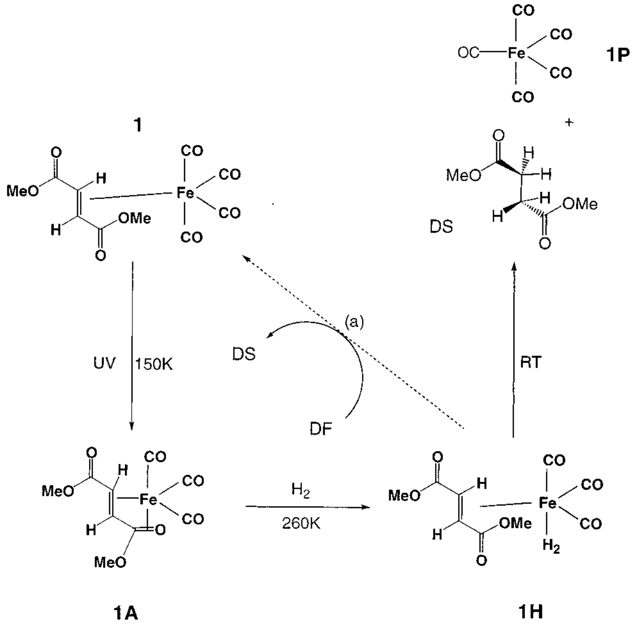
Therefore, by using polymer matrix isolation, we have been able to probe the intermediates in the stoichiometric hydrogenation of DF to DS using $Fe(CO)_4(DF)$. We have shown that not only can we characterize the reaction products using IR spectroscopy, but also we are able to extract the products from the PE disk and identify them using GC-MS analysis.

These hydrogenation experiments were performed under artificial conditions, with no free DF in the reaction mixture. As such, the catalytic cycle could not continue once the hydrogenated product had been formed. However, when we repeated the reaction in the presence of free DF, identical results were obtained. It seems therefore that DS can be formed from coordinated DF, but once hydrogenation has occurred, uncoordinated DF does not react with the unsaturated metal center. This may be due to the poor mobility of free DF in the PE matrix, or simply because it is more favorable to form $Fe(CO)_5$ rather than $Fe(CO)_4(DF)$ once the hydrogenated product has been released.

The reaction scheme for the hydrogenation of DF is shown in Scheme 2. Although we have not been able to observe the catalytic reaction, we have been able to follow the hydrogen transfer from the metal center to the coordinated olefin to form the hydrogenated product.

Hydrogenation of Norbornadiene (NBD). As explained in the Introduction, the hydrogenation of norbornadiene by Group 6 metal centers has been the subject of intense study. In the context of these experiments the hydrogenation is interesting, first because there are at least three possible hydrogenation products (NBN, NTC, and NBA), and second because none of the products has a strong IR chromophore for in situ detection. Furthermore, in the case of the molybdenum catalyzed reaction, previous work in this area has provided a surprisingly complete IR library of the $\nu(C-O)$ bands of the various compounds and intermediates involved in the catalytic cycle (see Table 2). Therefore, it is unnecessary to carry out a detailed study of the

Scheme 2. Reaction Scheme for the Hydrogenation of DF Using $Fe(CO)_4(DF)$[a]



[a] For the reaction to be catalytic, step (a) needs to occur, a process that seems unfavorable under the conditions of our reaction. Spectroscopic evidence has been obtained for all the species shown in the scheme.

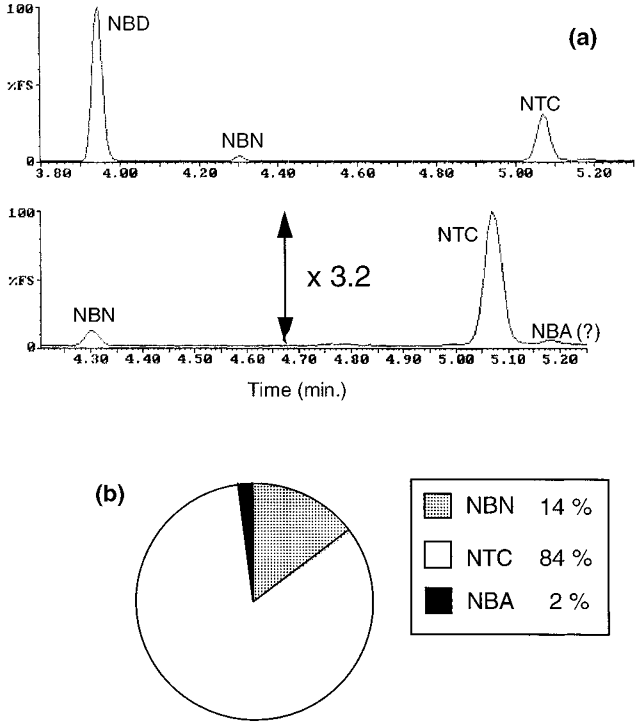


Figure 5. (a) GC analysis of the compounds extracted from PE following the irradiation of (NBD)Cr(CO)$_4$ under H_2 (500 psi) at room temperature. (b) Chart showing the relative ratios of the products.

type needed to identify the intermediates in the reactions of Fe(CO)$_4$(DF) above.

UV photolysis at 296 K of (NBD)Cr(CO)$_4$ impregnated into PE under 500 psi of H_2 resulted in a decrease in the intensity of the ν(C−O) bands of the starting material and the formation of no easily detectable metal carbonyl products. The dilution of the compounds in the matrix also meant that no IR bands could be observed which were attributable to hydrogenated products. However, subsequent extraction of the PE disk with CH_2Cl_2 (0.1 cm^3) and GC-MS analysis revealed the formation of NBN, NTC, and a trace of NBA, see Figure 5. The ratio of the three products (see Figure 5b) was very similar to that reported for the photocatalytic reaction at room temperature.

When the photolysis of (NBD)Cr(CO)$_4$ was repeated in PE saturated with NBD under a pressure of D_2, IR bands were seen to grow in the ν(C−D) region (see Figure 6a). The wavenumbers of these bands are summarized in Table 3. They can be assigned to d_2-NBN, and more tentatively to d_2-NTC, by comparison with data from earlier studies in fluid solution,[37,38] where remarkably similar IR spectra were observed. Extraction of the PE disk, followed by GC-MS analysis, revealed a broadly similar ratio of products to those in Figure 5, but with somewhat more NBN relative to NTC and NBA. These chromatographic results also confirmed the assignment of the ν(C−D) IR bands.

Repeating the experiment with (NBD)Mo(CO)$_4$, **2**, in the presence of NBD and D_2 again generated bands in the ν(C−D) region, but with quite different relative intensities from those observed for the Cr analogue, see Figure 6b. Thus, even from the IR, it is immediately clear that the product distributions from the Cr and Mo catalysts are different. This difference mirrors the literature reports of the product distributions from these reactions in conventional solutions. Again, GC-MS of the extracted products allowed the product distribution to be quantified more precisely, and Figure 7 shows the difference in product distribution between Cr and Mo for the catalytic hydrogenation of NBD in the presence of excess D_2 (or H_2). Broadly, the major difference between the metals is that Mo generates NBN as the principal product and relatively little NTC. The amount of fully hydrogenated product, NBA, is similar for the two metals under these conditions.

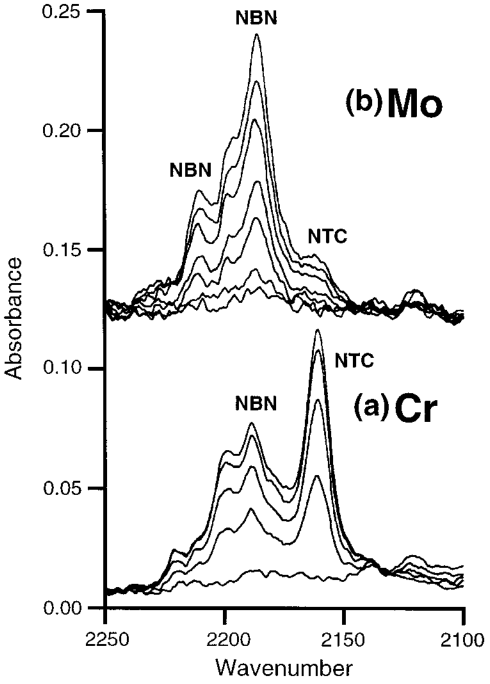


Figure 6. FTIR spectra obtained following the UV irradiation of (NBD)M(CO)$_4$ (M = (a) Cr or (b) Mo) under D_2 (500 psi) at room temperature in PE.

Table 3. ν(C−D) Band Positions (cm^{-1}) of the Products Observed Following the Photocatalytic Deuteration of NBD at Room Temperature

complex	*n*-heptane[a]	CCl_4 [a]	PE[b]
NBN	2212	2212	2210
	2188	2188	2186
NTC	2163	2202	2199
		2163	2160

[a] See ref 38. [b] This study.

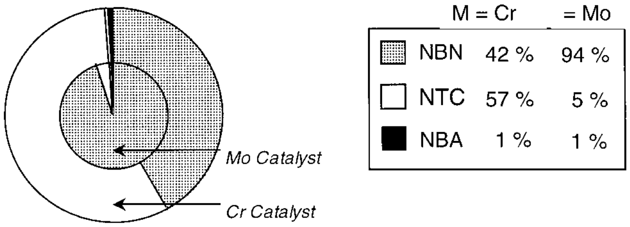


Figure 7. Distribution of the hydrogenated products (NTC, NBN, or NBA) following irradiation of (NBD)M(CO)$_4$ (M = Cr or Mo) in the presence of excess NBD and D_2 in PE at room temperature.

Figure 8 shows IR spectra recorded during the UV photolysis of **2** in PE under a pressure of D_2 and in the presence of excess NBD. Unlike the Cr system, new ν(C−O) bands were observed to grow in as the photolysis proceeded, see Figure 8a. After a total of 50 min of irradiation, most of the starting material was destroyed and computer subtraction of the IR spectra revealed five clearly resolved ν(C−O) bands (Figure 8b). By comparison with the "library" data for this system, four of these bands could be assigned to the *mer*-(**2M**) and *fac*-(**2F**) isomer of (η^2-NBD)(η^4-NBD)Mo(CO)$_3$. These compounds were identified by previ-

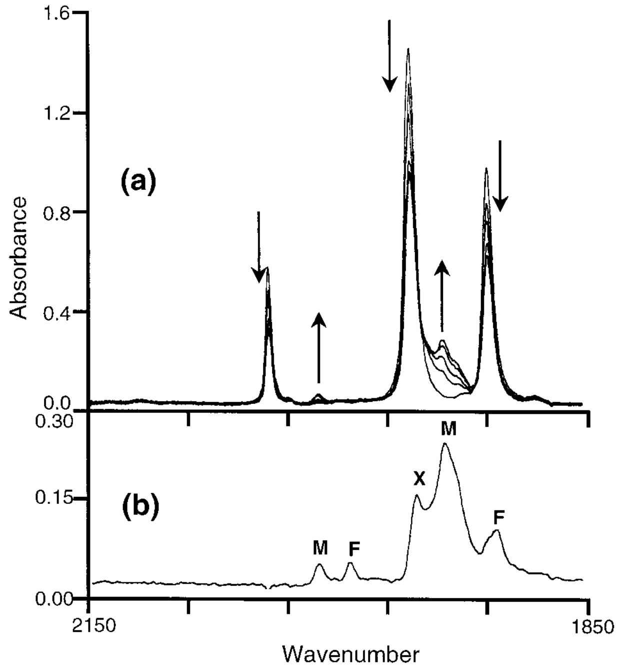


Figure 8. (a) FTIR spectra recorded during the UV irradiation of (NBD)Mo(CO)$_4$ (**2**) under D_2 in the presence of excess NBD in PE at room temperature. The ν(C−O) bands due to **2** decrease in intensity, with new bands due to *mer*-(**M**) and *fac*-(**F**) (η^2-NBD)(η^4-NBD)Mo(CO)$_3$ observed to grow in. (b) Scaled subtraction spectrum showing the IR bands of only the photoproducts. The band marked **X** can be assigned to (η^2-C=C)Mo(CO)$_5$ where C=C is either NBD or NBN.

ous workers[36,37] as being the resting state of the Mo catalyst in fluid solution at room temperature. The fifth band, labeled **X** in Figure 8b, is assigned to (η^2-C=C)Mo(CO)$_5$ (where C=C is either NBD or NBN), and is discussed in more detail below.

The kinetics of this reaction are interesting because the apparent rate of growth in intensity of the bands of the *mer* isomer is significantly faster than that of the *fac* isomer. However, this disparity could be due, at least in part, to the growth of underlying bands due to other reaction products. The rate of growth of the bands due to NBN (see Figure 6b) is approximately linear with time, as might be expected for a photocatalytic reaction that does not proceed at an appreciable rate in the dark at room temperature. The overall conclusions from the results shown in Figures 5−8 indicate that the behavior of these catalysts is very similar in PE and in other hydrocarbon solvents at room temperature.

By contrast, striking differences in behavior are observed when **2** is irradiated under a pressure of hydrogen, but *in the absence of excess NBD.* As the photolysis proceeds, the bands of **2** decay and bands due to Mo(CO)$_6$ (**2P**) and (η^2-olefin)Mo(CO)$_5$ (**2X**) grow in (see Figure 9a). However, when the UV irradiation is stopped, the spectra continue to change and the bands due to **2X** species disappear completely over a period of ca. 5 min, with a corresponding growth in the absorption bands of **2P**. An even more dramatic difference becomes apparent when the products are extracted and analyzed using GC-MS, see Figure 10. In the absence of free NBD, NBA is transformed from a trace product to the major product. At the same time, the formation of NTC is also increased. Thus, (NBD)Mo(CO)$_4$ is quite different from its Cr analogue because the product distribution it totally changed by removal of excess NBD from the reaction mixture. Most importantly, the fact that NBA is the major product provides a new opportunity to investigate the formation of this fully hydrogenated product, which has been largely ignored in previous mechanistic studies.

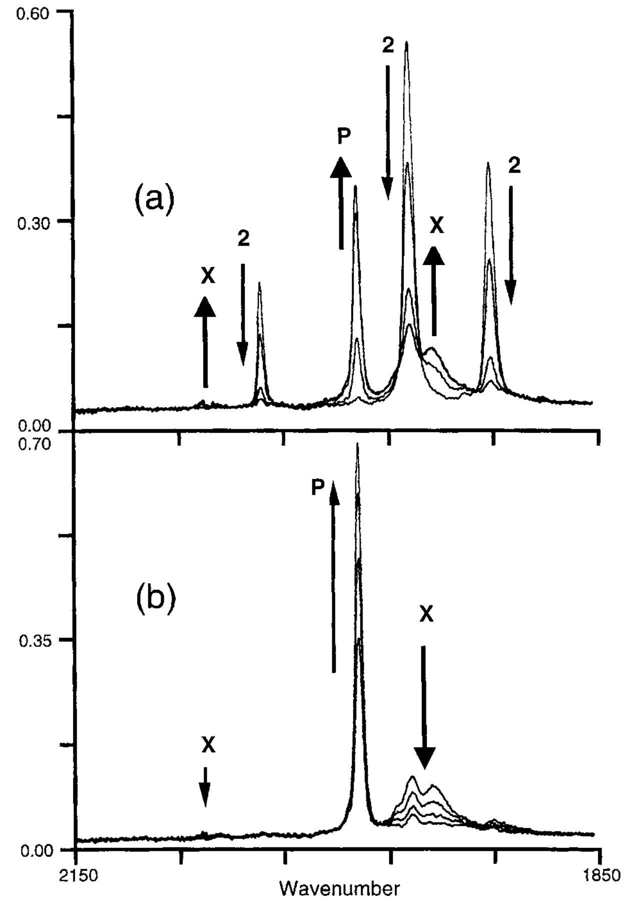


Figure 9. (a) FTIR spectra obtained following irradiation of **2** under H_2 in PE at room temperature *in the absence of excess NBD.* As the bands due to **2** decay, the growth of absorptions due to Mo(CO)$_6$ (**2P**) and (η^2-C=C)Mo(CO)$_5$ (**2X**) is observed. (b) When the UV irradiation is halted, the growth of the band due to **2P** continues at the expense of the bands due to **2X**.

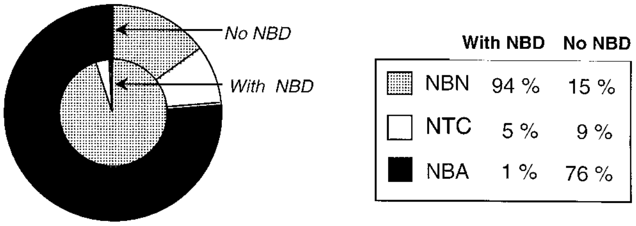


Figure 10. Relative distribution of the hydrogenated products following UV irradiation of (NBD)Mo(CO)$_4$ (**2**) under H_2 in PE at room temperature in both the absence and presence of excess NBD.

The initial stage of our investigation was to exploit the ease with which the gas around the PE film can be changed. We have used H_2 and D_2, either individually or mixed, to generate various isotopomers of NBA via the photolysis of (NBD)Mo(CO)$_4$. The different isotopomers are quantified by GC-MS using SIM over the mass range 96 (NBA) to 100 (d_4-NBA) (see Experimental Section). Three experiments were performed and the results are summarized in Figure 11. In the first experiment, **2** was irradiated under a mixture of H_2 and D_2 (ca. 60:40) *in the absence of NBD.* As expected, the products were a mixture of the three isotopomers, NBA, d_2-NBA, and d_4-NBA, in approximately the correct statistical ratio (see Figure 11a). d_2-NBA was clearly the major product.[47]

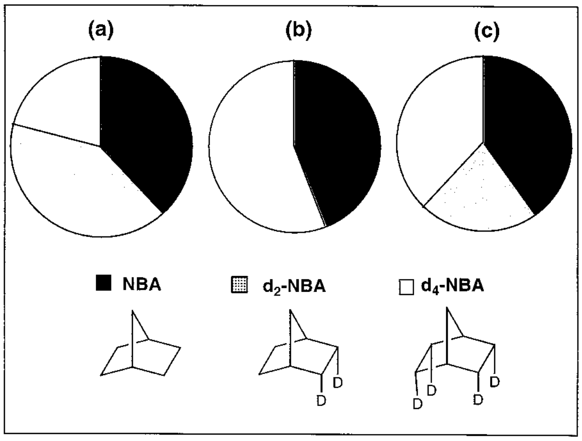


Figure 11. Distribution of the isotopomers of NBA following irradiation of (NBD)Mo(CO)$_4$ (**2**) in PE at room temperature under (a) a mixture of H_2/D_2 (60:40) *in the absence of excess NBD,* (b) alternate pulses of H_2 and D_2 *in the absence of excess NBD,* and (c) alternate pulses of H_2 and D_2 *in the presence of excess NBD.*

In the second experiment, the photolysis was repeated, but this time with a series of irradiation periods, each of 20 or 30 min. Between each photolysis period the gas surrounding the PE was changed, using alternately H_2 and D_2. The gases were changed repeatedly to give a total irradiation time similar to that used in the first part of the experiment. Thus **2** was irradiated for 70 min under H_2 and also 70 min under D_2, but H_2 and D_2 were never present in the cell together, apart from any residual gases which may have been trapped within the PE matrix. Figure 11b shows the relative amounts of the isotopomers. *It is immediately clear that no d_2-NBA was formed when H_2 and D_2 were used alternately.* This experiment shows that any intermediates involved in the formation of NBA at room temperature are short-lived compared to the time needed to exchange the gases (ca. 10 min). This is consistent with the rapid decay of the bands shown in Figure 9b.

In the final stage of the investigation, the experiment with alternate pulse of H_2 and D_2 was repeated, but this time with **2** *in the presence of excess NBD.* Figure 11c shows that this time, the three isotopomers were formed in approximately a 1:1:1 ratio. Thus, unlike the experiment with **2** alone, the presence of NBD gave rise to a longer lived intermediate that could "store" H_2 or D_2 while the gases were being exchanged. We believe that the most likely candidate for this intermediate is free NBN.

The reason for identifying NBN as the long-lived intermediate is shown in Figure 12. In this experiment, **2** was irradiated under a pressure of D_2 and in the presence of excess NBN. After 40 min of UV irradiation, two major products could be identified, namely Mo(CO)$_6$ (**2P**) and (NBN)Mo(CO)$_5$ (**2X**), the spectra of which could be established by a separate experiment involving the photolysis of Mo(CO)$_6$ in the presence of NBN. GC-MS analysis indicated d_2-NBA as the major product. There were also traces of d_2-NBN, d_2-NTC, and d_4-NBA, presumably generated through deuteration of the NBD ligand in **2**. Given the fact that NBD was initially coordinated to the metal center, one would expect the deuteration of the NBD to be the kinetically preferred product, even though the NBN was in considerable excess. Thus, we propose that the principal pathway for the formation of NBA in a catalytic reaction (i.e. in the presence of excess NBD) is as shown in Scheme 3.

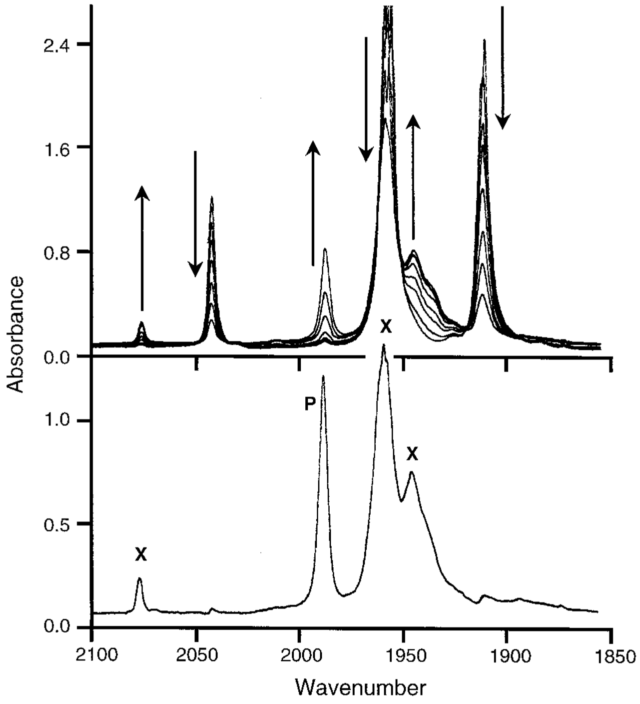
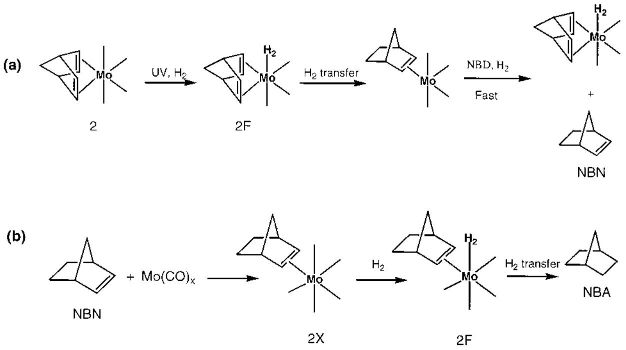


Figure 12. (a, top) IR spectra and (b, bottom) IR subtraction spectrum obtained following irradiation of PE containing **2**, excess NBN, and D_2 at room temperature. The bands due to **2** decrease in intensity, concurrent with the growth of new bands assignable to both Mo(CO)$_6$ (**2P**) and (η^2-NBN)Mo(CO)$_5$ (**2X**).

Scheme 3. Reaction Scheme Showing the Mechanism for the Formation of NBA in the Presence of Excess NBD (i.e. a catalytic reaction)[a]



[a] Part a: Irradiation of (NBD)Mo(CO)$_4$ under H_2 results in the formation of the singly hydrogenated product NBN, which is released from the metal center. Part b: Further photolysis leads to recoordination of NBN to the metal center, along with another molecule of H_2. This results in the hydrogenation of the second double bond to form NBA.

As demonstrated above, the formation of NBA from **2** in the absence of excess NBD must involve relatively short-lived intermediates. Indeed the TRIR studies[37] by Hodges et al. implicated short-lived dihydrogen complexes in the initial stage of this reaction. To investigate the formation of NBN further, we carried out reactions in PE film at low temperature, exploiting the cryogenic capability of our high-pressure cell. Figure 13 shows the relatively complicated spectra that are obtained when **2** is irradiated under H_2 at 180 K. Apart from one weak band at 1973 cm^{-1} (possibly due to a polymeric species), all of the bands in these spectra can be assigned with reasonable certainty to different Mo(CO)$_x$ species, previously identified from experiments in fluid solution. Most significantly, there are bands due to both the *fac* and *mer* isomers of (NBD)-

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(47) Since the gas is in great excess it is not feasible, in this study, to detect HD, which is a possible byproduct of reactions involving mixtures of H_2 and D_2.

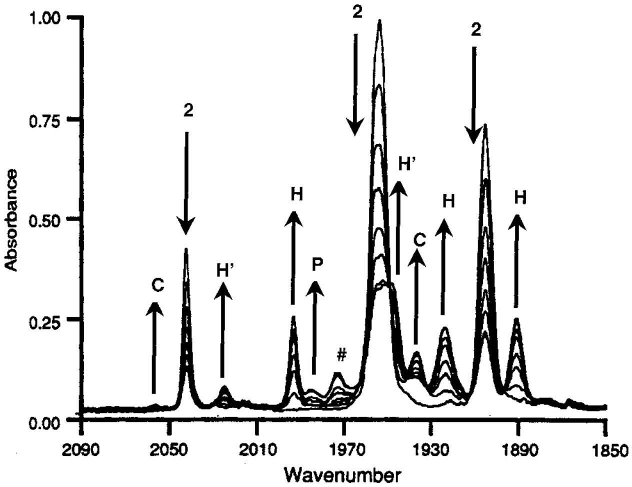


Figure 13. IR spectra recorded after UV photolysis of **2** under H_2 in PE at 180 K in the absence of excess NBD. The bands due to **2** decrease in intensity, with concomitant growth of new bands assignable to *fac* (marked **H**) and *mer* (marked **H′**) isomers of $(NBD)Mo(CO)_4(H_2)$ and to *cis*-$(\eta^2\text{-}NBD)Mo(CO)_4(H_2)$ (**2C**), where C=C is either NBD or NBN. The band marked # is due to an unidentified dimer.

$Mo(CO)_4(H_2)$ (**2H** and **2H′**, respectively) and to *cis*-$(\eta^2\text{-}C{=}C)\text{-}Mo(CO)_4(H_2)$ (**2C**), where C=C is either NBD or NBN. When the PE is warmed to 230 K, the major changes in the spectrum were the almost complete decay of *fac*-$(NBD)Mo(CO)_4(H_2)$ isomer and the formation of a $(\eta^2\text{-}C{=}C)Mo(CO)_5$ complex, where C=C is either NBD or NBN. This η^2-complex was only observed upon annealing, and was not observed immediately following the UV photolysis. GC-MS analysis of the products formed in this reaction indicated a distribution between NBA, NBN, and NTC, very similar to that observed at room temperature.

These experiments suggest that low temperature can be used to arrest the hydrogenation of NBD, at least partly. The effect is even more striking at 80 K. Figure 14a shows a simple subtraction spectrum obtained after photolysis of **2** in PE without addition of H_2 or other additives. The three peaks formed can be assigned to the coordinatively unsaturated intermediate, *fac*-$(NBD)Mo(CO)_3$ (**2U**). This intermediate has also been observed in frozen argon matrices and by TRIR experiments in *n*-heptane at room temperature. Identical spectra were obtained when **2** was irradiated at this temperature in the presence of H_2. This is not surprising because previous work[23] with $Mo(CO)_6$ and H_2 has shown that low-temperature photolysis results in the formation of $Mo(CO)_5$ rather than $Mo(CO)_5(H_2)$, even though this dihydrogen compound is formed at higher temperatures. When PE containing **2U** was heated from 80 to 160 K in the absence of H_2, there was near quantitative recombination with photoejected CO and regeneration of **2** (see Figure 14b). On the other hand, when **2U** was heated to 160 K under H_2, new bands were observed to grow in at the same rate as the regeneration of **2** (Figure 14c). These new bands could be assigned, on the basis of published data, to the dihydrogen complexes *fac*-$(NBD)Mo(CO)_3(H_2)$ and *cis*-$(\eta^2\text{-}C{=}C)Mo(CO)_4\text{-}(H_2)$, where C=C is either NBN or NBD.

GC-MS analysis of the products, following the warming of the PE from 160 K to room temperature, showed a ratio of NBN:NTC:NBA almost identical to that observed a room temperature (see Figure 15). The similarity of the product distributions obtained in the experiments at 80 K, 180 K, and room temperature strongly suggests that the mechanism of the reaction in low temperature and room temperature experiments must be very similar, if not identical. The difference between the experiments is that, at low temperature, the experiment can be halted at key stages.

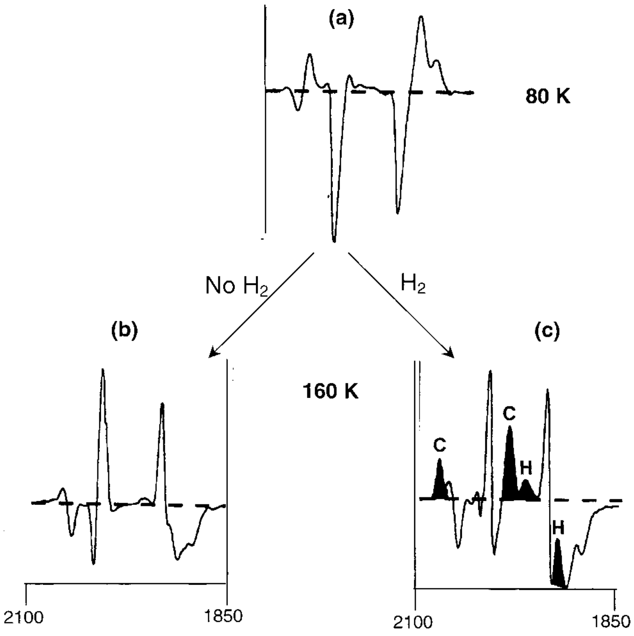
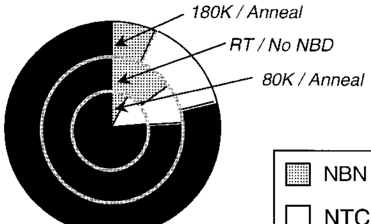


Figure 14. (a) FTIR subtraction spectrum obtained following UV irradiation of **2** in PE in the absence of a reactive gas at 80 K. The positive peaks can be assigned to the coordinatively unsaturated intermediate *fac*-$(NBD)Mo(CO)_3$ (**2U**), with the negative peaks due to depletion of **2**. Warming the PE containing **2U** from 80 to 160 K (b) in the absence of a reactive gas results in regeneration of **2**. However, warming in the presence of H_2 (c) leads to regeneration of **2** and formation of the dihydrogen complexes *fac*-$(NBD)Mo(CO)_3(H_2)$ (**2H**) and *cis*-$(\eta^2\text{-}C{=}C)Mo(CO)_4(H_2)$ (**2C**), where C=C is either NBN or NBD.



	80 K	180 K	RT
▨ NBN	7 %	7 %	15 %
☐ NTC	17 %	14 %	9 %
■ NBA	76 %	79 %	76 %

Figure 15. Product distributions of the hydrogenated products (NBN, NTC, and NBA) obtained following irradiation of **2** under H_2 in the absence of excess NBD at 80, 180, and 298 K.

The final part of our investigation involved combining two of the experimental strategies described above, namely exchange of H_2 and D_2 gases around the PE film and the use of low temperatures.[48] The purpose of the experiments, as before, was to look at the distribution of H_2 and D_2 in the NBA extracted from the PE at the end of the reaction. **2** was irradiated in PE under a pressure of D_2 at 80 K. The PE was then warmed to 160 K, and formation of *fac*-$(NBD)Mo(CO)_3(D_2)$ and *cis*-$(\eta^2\text{-}C{=}C)Mo(CO)_4(D_2)$ was observed. The pressure of D_2 was released, and the cell evacuated for a period of 1 h. The cell was then repressurized with H_2 and warmed slowly in the dark

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(48) The use of D_2 rather than H_2 produces small changes in the wavenumbers of IR bands of compounds which contain coordinated H_2/D_2, but otherwise the spectra in the ν(C−O) regions are almost indistinguishable and are not illustrated.

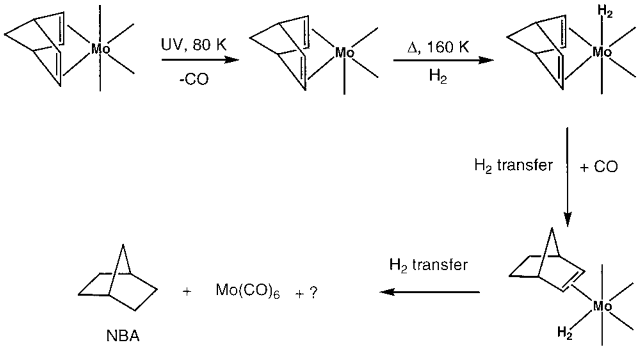
to room temperature. The products were extracted and analyzed by GC-MS to give the distribution NBA (33%), d_2-NBA (22%), and d_4-NBA (45%). This experiment shows that (i) once the sample has been irradiated at 80 K, no further UV irradiation is needed to generate NBA, (ii) the majority of hydrogenation occurred after the H_2 and D_2 were exchanged (the formation of d_4-NBA may well be due to residual D_2 trapped in the PE matrix), and (iii) intermediates exist at 160 K which are sufficiently stable to survive the change of gases and yet are reactive enough to exchange fully with H_2 to form unlabeled NBA.[49]

As in any mechanistic study, the experiments described above are indicative rather than totally conclusive. Nevertheless, they strongly suggest that the formation of NBA, in the absence of added NBD, follows a pathway similar to that shown in Scheme 4. All the intermediates and transformations shown in Scheme 4 have been detected here, and most were also observed in TRIR studies in fluid solution at room temperature. In addition we have detected the product NBA. However, the direct transformation from (NBD)Mo(CO)$_3$H$_2$ to *cis*-(NBN)Mo(CO)$_4$(H$_2$) has not been observed directly, possibly because the conversion involves addition of not only H_2 but also CO, which can only come from the photoejected CO in the PE.

Conclusions

In this paper we have shown how the combination of PE matrices and high pressure−low temperature experiments can provide new insights into the mechanism of even very well studied reactions. As far as we are aware, our experiments are among the first to link matrix isolation and product analysis in homogeneous catalytic reactions. The highly unusual nature of these experiments has enabled us to carry out an isotopic labeling experiment, which would have been difficult, if not impossible, to carry out by more conventional means. For the first time it has been possible to compare the products of reactions performed stoichimetrically and catalytically usually literally microgram quantities of the compounds. The experiments have also come closer than most previous studies to capturing the key steps in a complicated multistep catalytic reaction. Currently we are extending this concept to the study of immobilized homogeneous catalysts in continuous flow reactors.

Scheme 4. Reaction Mechanism for the Formation of NBA in the Absence of Excess NBD[a]



[a] Notice that in this reaction scheme the singly hydrogenated product is not released from the metal center, but rearranges to allow the addition of a second molecule of H_2.

Acknowledgment. We are grateful to Prof. F. W. Grevels for the gift of samples of (NBD)M(CO)$_4$ and Fe(CO)$_4$(DF). We thank Dr. K. Dost for helpful discussions, Mr. M. Guyler and Mr. K. Stanley for their technical support, and the EPSRC, Nicolet Instruments Ltd, and the University of Nottingham for financial support.

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(49) Any investigation of this complexity obviously needs control experiments, and a considerable variety of controls were performed. For example, cooling **2** in PE under H_2 and warming to room temperature did not result in the formation of NBA. More importantly, some of our results could be explained if photolysis of the carbonyl precursors were to generate metal nanoparticles which could subsequently act as highly active heterogeneous catalysts. This explanation seems highly unlikely because photolysis of **2** in the absence of H_2, followed by subsequent pressurization with H_2, did not result in the formation of NBA or other hydrogenation products.

(50) Hooker, R. H. Ph.D. Thesis, University of Southampton, 1987.