

# Chemistry of Reactive Organometallic Compounds at Low Temperatures and High Pressures: Reactions of $M(\text{CO})_6$ ( $M = \text{Cr}, \text{Mo}, \text{W}$ ), $(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{M}(\text{CO})_3$ ( $M = \text{Cr}$ and $\text{Mo}$ ), and $\text{W}(\text{CO})_5\text{CS}$ with $\text{H}_2$ and $\text{N}_2$ in Polyethylene Matrices

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An unusual high-pressure (<5000 psi) and low-temperature (>30 K) cell is used to study the photochemistry of  $d^6$  metal carbonyl complexes and related compounds in a polyethylene (PE) matrix. This approach combines some of the advantages of traditional matrix isolation with those of low temperature solvents (e.g. liquid Xe). UV photolysis of  $M(\text{CO})_6$  under pressures of  $\text{N}_2$  lead initially to the formation of  $M(\text{CO})_5\text{N}_2$  and, on longer photolysis, to more highly substituted  $M(\text{CO})_{6-n}(\text{N}_2)_n$  ( $n \leq 4$ ) species. Photolysis under a pressure of  $\text{H}_2$  leads to  $M(\text{CO})_5(\eta^2\text{-H}_2)$  and *cis*- $M(\text{CO})_4(\eta^2\text{-H}_2)_2$ , disubstituted compounds which were previously unknown for Mo and W. The thermal reactivities of all of these compounds were qualitatively established by raising the temperature of the PE matrix and monitoring the reaction with CO. The UV photolysis of  $\text{W}(\text{CO})_5\text{CS}$  and  $(\eta^6\text{-C}_6\text{H}_3(\text{CH}_3)_3)\text{M}(\text{CO})_3$  ( $M = \text{Cr}$  and  $\text{Mo}$ ) also leads to previously uncharacterized  $\text{H}_2$  and  $\text{N}_2$  complexes. The low-temperature, high-pressure (LT-HP) cell allows gases to be exchanged during the course of a single experiment. The conditions needed for  $\text{H}_2$  and  $\text{N}_2$  to penetrate the PE and to be removed from it have been investigated, and this information has been used to study thermal exchange reactions between coordinated  $\text{N}_2$  and  $\eta^2\text{-H}_2$  ligands in  $M(\text{CO})_5\text{L}$  compounds. It was found that the reactivity followed the order  $\text{Mo} > \text{Cr} > \text{W}$ .

## Introduction

Spectroscopic techniques have played a major role in expanding our understanding of the chemistry of unstable organometallic compounds and reaction intermediates.<sup>1</sup> A whole variety of techniques have been developed: matrix isolation,<sup>2</sup> low-temperature glasses,<sup>3</sup> liquefied noble gases,<sup>4</sup> polymer matrices,<sup>5</sup> and time-resolved infrared spectroscopy.<sup>6</sup> Each of these techniques has wide applicability and specific advantages, but none of them is easily applied to reactions involving organometallic compounds and permanent gases, for example  $\text{H}_2$  and  $\text{N}_2$ . Such reactions are important in a wide range of catalytic<sup>7</sup> and biological<sup>8</sup> processes. Of

course, one can generate unstable compounds by the reaction of the organometallic with these gases, either in matrices<sup>2</sup> or in low-temperature media,<sup>4</sup> but it is difficult if not impossible to study the subsequent chemistry of the products.

Recently we reported a new technique involving high pressures and low temperatures which is designed both to complement existing methods and to overcome some of their limitations in reactions involving permanent gases.<sup>9</sup> The technique is a development of Rest's pioneering work on polymer matrices.<sup>10</sup> The key advance is a miniature high-pressure cell which can be attached to a slightly modified matrix isolation apparatus and then be cooled to cryogenic temperatures (see Experimental Section). The organometallic compound is impregnated into a polymer film and surrounded by a high pressure of gas, a situation which provides an extremely large interfacial area between gas and "solvent", Figure 1. This arrangement allows unstable organometallic compounds to be generated under the pressure of the reactant gas. Our first demonstration of this technique<sup>9</sup> involved the photochemical generation of  $\text{Fe}(\text{CO})_4\text{N}_2$  in a polyethylene (PE) matrix at 190 K and then monitoring its thermal reaction with  $\text{H}_2$ ; see Scheme 1. This experiment was

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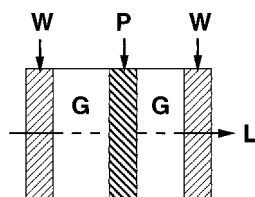
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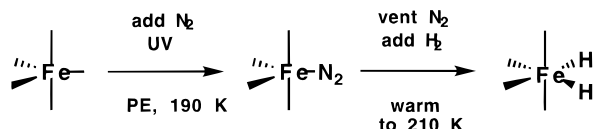
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**Figure 1.** Schematic view of the low-temperature/high-pressure (LT-HP) cell containing a high pressure of gas (G) and a polymer film (P) impregnated with an organometallic compound. UV and IR sources provide light (L) for photolysis and spectroscopic analysis through windows (W).

### Scheme 1



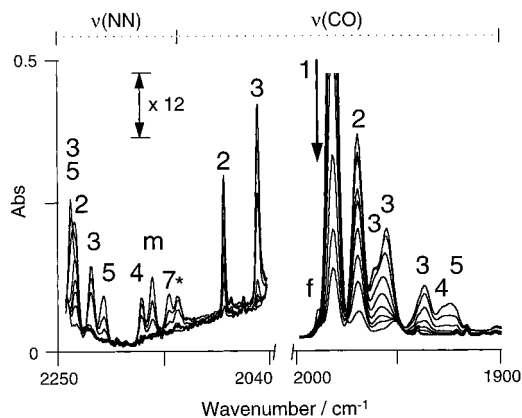
significant because  $\text{Fe}(\text{CO})_4\text{N}_2$  had previously only been observed in solid  $\text{N}_2$  matrices at 20 K, without any indication of its thermal stability or reactivity.

It is now important to establish whether the use of a polymer matrix influences the course of a particular reaction. This paper is the first of a series aimed at examining the strengths and limitations of our new technique on a more systematic basis. We study the reactions of group 6 metal compounds  $\text{M}(\text{CO})_6$  and related compounds with  $\text{H}_2$  and  $\text{N}_2$  and compare the use of PE films with cryogenic matrices and liquid noble gas solvents. In particular, we investigate how the PE environment affects multiple substitution of CO by  $\text{N}_2$  and  $\text{H}_2$  and then use these reactions to quantify how easily gases within the PE can be vented and replaced.

## Results and Discussion

**Photolysis of  $\text{Cr}(\text{CO})_6$  under  $\text{N}_2$ .** PE is considerably more rigid than liquid solvents. The photolysis of  $\text{Cr}(\text{CO})_6$  under  $\text{N}_2$  provides a convenient test of how much this rigidity affects photochemical substitution. The reaction has already been studied in liquid Xe (IXe) by Turner *et al.*<sup>11</sup> IR analysis of the products indicated that up to five of the six CO ligands could be substituted successively with  $\text{N}_2$  groups in IXe solution.

Figure 2 shows the  $\nu(\text{N}-\text{N})$  and  $\nu(\text{C}-\text{O})$  regions of IR spectra collected as  $\text{Cr}(\text{CO})_6$  (**1**) was being photolyzed. Initially the single  $\nu(\text{C}-\text{O})$  band ( $t_{1u}$ ) of  $\text{Cr}(\text{CO})_6$  is observed.<sup>12</sup> As the PE film is irradiated,  $\text{Cr}(\text{CO})_6$  is destroyed. The primary photoproduct  $\text{Cr}(\text{CO})_5\text{N}_2$  (**2**) is easily identified by comparison with IXe data (see Table 1). The single  $\nu(\text{N}-\text{N})$  and three  $\nu(\text{C}-\text{O})$  bands are consistent with  $C_{4v}$  symmetry.  $\text{Cr}(\text{CO})_5\text{N}_2$  is itself photoreactive and begins to decay on further irradiation, producing bands that can be assigned to *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$  (**3**) and *fac*- $\text{Cr}(\text{CO})_3(\text{N}_2)_3$  (**5**). The *trans* (**4**) and *mer* (**6**) substituted isomers are also formed, but they can only be observed in the  $\nu(\text{N}-\text{N})$  region because their  $\nu(\text{C}-\text{O})$  bands are expected to be obscured by bands of other species, a consequence of the broadening of IR



**Figure 2.** IR spectra in the  $\nu(\text{N}-\text{N})$  and  $\nu(\text{C}-\text{O})$  regions showing the effects of 3 h of UV photolysis of  $\text{Cr}(\text{CO})_6$  (**1**) impregnated into Hostalen PE under  $\text{N}_2$  (1500 psi) at 190 K. The band of **1** decays with the concomitant growth of several product bands, which can be assigned to photoproducts  $\text{Cr}(\text{CO})_5\text{N}_2$  (**2**), *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$  (**3**), *trans*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$  (**4**), *fac*- $\text{Cr}(\text{CO})_3(\text{N}_2)_3$  (**5**), *mer*- $\text{Cr}(\text{CO})_3(\text{N}_2)_3$  (**6**), *trans*- $\text{Cr}(\text{CO})_2(\text{N}_2)_4$  (**7**), and trapped CO (\*). Some bands of products **3**, **5**, and **6** are predicted to be obscured by other species; see Table 1. Note that, in this and all subsequent figures, the spectra are recorded at equal time intervals over the total irradiation time; i.e., in this case, eight spectra recorded at ca. 25 min intervals over a period of 3 h.

bands in PE relative to those in IXe or noble gas matrices. There is even evidence in our spectra for the replacement of a fourth carbonyl group giving *trans*- $\text{Cr}(\text{CO})_2(\text{N}_2)_4$  (**7**). An additional band at  $2130\text{ cm}^{-1}$  is assigned to molecular CO "trapped" within the PE; see below.

The results are summarized in Scheme 2, and the band positions are compared with IXe data in Table 1. The following points are clear: (1) Multiple substitution of the CO groups is possible in PE, comparing well with IXe experiments.<sup>12</sup> (2) IR data from IXe experiments are useful for assigning the bands in PE. Band positions are downshifted by  $\leq 7\text{ cm}^{-1}$  relative to those in IXe with lower wavenumber bands shifted more than higher wavenumber bands. However, the relative band intensities for a particular compound are broadly similar in the two media.

**Photolysis of  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  under  $\text{N}_2$ .** The photochemical reactions of  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  with  $\text{N}_2$  in IXe have been investigated much less thoroughly than that of  $\text{Cr}(\text{CO})_6$ . UV photolysis of  $\text{Mo}(\text{CO})_6$  under  $\text{N}_2$  in PE at 190 K results in depletion of  $\text{Mo}(\text{CO})_6$  with the concomitant growth of IR bands assigned<sup>13</sup> to the compound  $\text{Mo}(\text{CO})_5\text{N}_2$  (see Table 1). Further irradiation leads to formation of the previously unknown complex *cis*- $\text{Mo}(\text{CO})_4(\text{N}_2)_2$ . However prolonged irradiation caused the IR bands of all these species to decrease in intensity without the appearance of further product bands.

Figure 3 shows the changes in the  $\nu(\text{N}-\text{N})$  and  $\nu(\text{C}-\text{O})$  regions of the IR spectrum as  $\text{W}(\text{CO})_6$  (**8**) is irradiated under similar conditions.  $\text{W}(\text{CO})_5\text{N}_2$  (**9**) is the primary photoproduct,<sup>13</sup> and this reacts further to form the previously unreported and highly unstable, *cis*- $\text{W}(\text{CO})_4(\text{N}_2)_2$  (**10**), Scheme 3.

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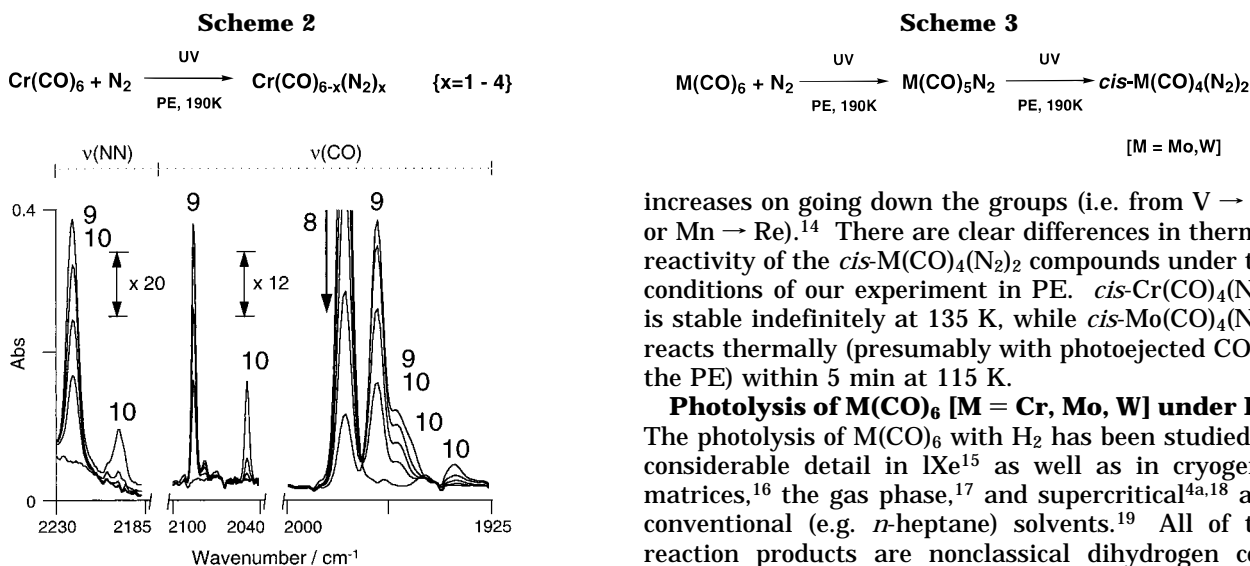
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**Table 1.** IR Data for  $M(\text{CO})_x(\text{N}_2)_y$  and  $M(\text{CO})_x(\eta^2\text{-H}_2)_y$  ( $M = \text{Cr, Mo, W}$ ) in PE at 190 K ( $y = 0-2$ ;  $x = 6 - y$ )

compd	Cr	Mo	W	assign of $\nu(\text{CO})$
$\text{M}(\text{CO})_6$	1984.1	1985.8	1980.3	$t_{1u}$
$\text{M}(\text{CO})_5(\text{N}_2)^a$	2236.0	2243.0 (2253.3)	2222.3 (2226.9)	$a_1 \nu(\text{NN})$
	2084.9	2088.9 (2092.8)	2086.4 (2089.2)	$a_1$
<i>cis</i> - $\text{M}(\text{CO})_4(\text{N}_2)_2^b$	1971.9	1973.8 (1978.2)	1967.3 (inactive)	$e$
	1959.8	1959.2 (1964.4)	1959.0 (1961.1)	$a_1$
	2241.0	2244.9	2224.5	$a_1 \nu(\text{NN})$
	2220.2	2226.5	2197.4	$b_2 \nu(\text{NN})$
	2050.3	2052.9	2049.2	$a_1$
	1963.3	1961.0	1961.2	$a_1$
	1957.5	1959.9	1953.4	$b_1$
	1938.8	1936.4	1937.7	$b_2$
<i>trans</i> - $\text{M}(\text{CO})_4(\text{N}_2)_2$	2169.0 (2170.6)			$a_{2u} \nu(\text{NN})$
<i>fac</i> - $\text{Cr}(\text{CO})_3(\text{N}_2)_3$	$c$ (1961.3)			$e_u$
	2241.0 (2241.3)			$a_1 \nu(\text{NN})$
	2207.8 (2207.2)			$e \nu(\text{NN})$
	1991.3 (1994.6)			$a_1$
<i>mer</i> - $\text{Cr}(\text{CO})_3(\text{N}_2)_3$	1926.1 (1931.8)			$e$
	$c$ (2233.5)			$a_1 \nu(\text{NN})$
	$c$ (2186.3)			$a_1 \nu(\text{NN})$
	2157.9 (2159.3)			$b_1 \nu(\text{NN})$
	$c$ (2023.0)			$a_1$
	$c$ (1947.2)			$b_2$
<i>trans</i> - $\text{Cr}(\text{CO})_2(\text{N}_2)_4$	$c$ (1939.6)			$a_1$
	2141.0 (2142.4)			$e_u \nu(\text{NN})$
$\text{M}(\text{CO})_5(\text{H}_2)^c$	1929.0 (1935.7) <sup>e</sup>			$a_{2u}$
	2093.0 (2094.0)	2096.1 (2097.7)	2096.1 (2098.2)	$a_1$
<i>cis</i> - $\text{M}(\text{CO})_4(\text{H}_2)_2^e$	1971.0 (1974.3)	1974.4 (1978.7)	1967.6 (1972.2)	$e$
	obs (1971.9)	1965.0 (1971.5)	obs (obs)	$a_1$
	2063.7 (2065.9)	2068.1	2068.1 (2078.5)	$a_1$
	1955.6 (1961.1)	1961.1	1957.9 (obs)	$a_1$
	obs (1958.9)	obs	obs (obs)	$b_1$
	1938.6 (1943.7)	1942.2	1931.1 (1940.9)	$b_2$

<sup>a</sup> In parentheses, IR bands for  $\text{Mo}(\text{CO})_5\text{N}_2$  and Raman bands for  $\text{W}(\text{CO})_5\text{N}_2$ , both species isolated in an argon matrix.<sup>17</sup> <sup>b</sup> A band for  $\text{W}(\text{CO})_4(\text{N}_2)_2$  in the gas phase was reported<sup>20a</sup> at 1973  $\text{cm}^{-1}$ . <sup>c</sup> Predicted to be obscured by other bands (obs). <sup>d</sup> Calculated and not observed. <sup>e</sup> In parentheses, IR bands in IXe.



**Figure 3.** IR spectra obtained during 1 h of UV photolysis of  $\text{W}(\text{CO})_6$  (**8**) impregnated into Hostalen PE under  $\text{N}_2$  (2800 psi) at 190 K. The band of **8** decays with photolysis time with growth of bands assigned to  $\text{W}(\text{CO})_5\text{N}_2$  (**9**), which under further irradiation reacts with  $\text{N}_2$  to form *cis*- $\text{W}(\text{CO})_4(\text{N}_2)_2$  (**10**); see Table 1.

Thus irradiation of  $\text{Cr}(\text{CO})_6$  and  $\text{N}_2$  in PE leads to a considerably greater degree of substitution (up to 4 CO groups) than is observed with  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  under similar conditions. This contrasts quite strongly with the behavior of the group 5 metal  $\text{CpM}(\text{CO})_4$  and group 7 metal  $\text{CpM}(\text{CO})_3$  complexes where, in fluid solution at least, the degree of substitution of CO by  $\text{N}_2$

increases on going down the groups (i.e. from  $\text{V} \rightarrow \text{Ta}$  or  $\text{Mn} \rightarrow \text{Re}$ ).<sup>14</sup> There are clear differences in thermal reactivity of the *cis*- $\text{M}(\text{CO})_4(\text{N}_2)_2$  compounds under the conditions of our experiment in PE. *cis*- $\text{Cr}(\text{CO})_4(\text{N}_2)_2$  is stable indefinitely at 135 K, while *cis*- $\text{Mo}(\text{CO})_4(\text{N}_2)_2$  reacts thermally (presumably with photoejected CO in the PE) within 5 min at 115 K.

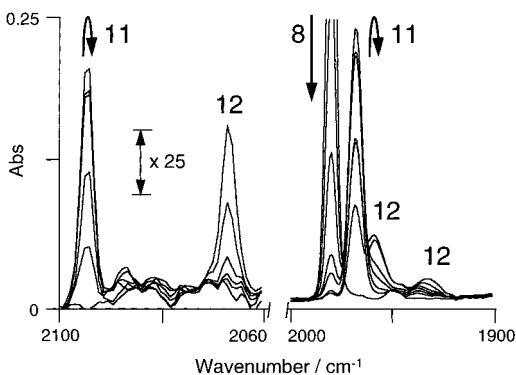
**Photolysis of  $\text{M}(\text{CO})_6$  [M = Cr, Mo, W] under  $\text{H}_2$ .** The photolysis of  $\text{M}(\text{CO})_6$  with  $\text{H}_2$  has been studied in considerable detail in IXe<sup>15</sup> as well as in cryogenic matrices,<sup>16</sup> the gas phase,<sup>17</sup> and supercritical<sup>4a,18</sup> and conventional (e.g. *n*-heptane) solvents.<sup>19</sup> All of the reaction products are nonclassical dihydrogen complexes, containing  $\eta^2\text{-H}_2$  ligands. In IXe, the reactivity of  $\text{M}(\text{CO})_5(\eta^2\text{-H}_2)$  varies in the order  $\text{Cr} < \text{Mo} \gg \text{W}$ . In the case of  $\text{Cr}(\text{CO})_6$ , a secondary product *cis*- $\text{Cr}(\text{CO})_4$ -

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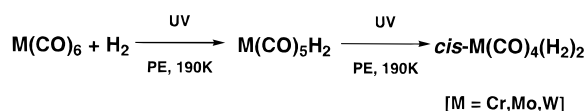
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**Figure 4.** IR spectra recorded during continuous UV photolysis (30 min) of  $W(CO)_6$  (**8**) impregnated into Hostalen PE under  $H_2$  (2000 psi) at 190 K. The product bands are assigned to  $W(CO)_5(\eta^2-H_2)$  (**11**) and *cis*- $W(CO)_4(\eta^2-H_2)_2$  (**12**); see Table 1.

#### Scheme 4



$(\eta^2-H_2)_2$  was also observed,<sup>15</sup> which had the intriguing property of catalyzing isotopic exchange  $H_2 + D_2 \rightarrow 2HD$ . We now extend our investigations to probe these reactions in PE using the LT-HP cell.

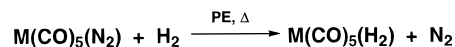
In three separate experiments, the hexacarbonyl of each metal was impregnated into a Hostalen PE disk and pressurized with  $H_2$ . Essentially, identical results were obtained; changing the metal center neither affects the degree nor the geometry of the resultant substitution. For example, Figure 4 shows the changing  $\nu(C-O)$  region as  $W(CO)_6$  is photolyzed under  $H_2$ . As the  $W(CO)_6$  decays, bands due to  $W(CO)_5(\eta^2-H_2)$  (**11**) grow in. When the concentration of  $W(CO)_6$  approaches zero, the secondary reaction of  $W(CO)_5(\eta^2-H_2)$  (**11**) with  $H_2$  predominates. The bands of **11** decrease in intensity, and three new bands appear, assigned to the previously unknown compound *cis*- $W(CO)_4(\eta^2-H_2)_2$  (**12**), see Scheme 4 and Table 1.

There are interesting differences from IXe; in particular, there was only incomplete evidence for  $W(CO)_4(\eta^2-H_2)_2$  in IXe and  $Mo(CO)_4(\eta^2-H_2)_2$  was not observed at all in IXe. The reason these compounds were not observed in IXe may be different for W and Mo. It can be seen from Figure 4 that  $W(CO)_4(\eta^2-H_2)_2$  (**12**) is only formed in PE after the  $W(CO)_6$  (**8**) has been almost totally destroyed, possibly because the UV/vis bands of  $W(CO)_6$  are relatively more intense than those of  $W(CO)_5(\eta^2-H_2)$  and so prevent the secondary photolysis of  $W(CO)_5(\eta^2-H_2)$ .  $W(CO)_6$  has a very low solubility in IXe at these temperatures, and therefore, most of the reported IXe experiments have been carried out in the presence of excess solid  $W(CO)_6$ . Consequently, the dissolved  $W(CO)_6$  in solution would have been constantly replenished as fast as it was converted to  $W(CO)_5(\eta^2-H_2)$ . This constant concentration of  $W(CO)_6$  may, therefore, have prevented the secondary photolysis

of  $W(CO)_5(\eta^2-H_2)$  from occurring.  $W(CO)_5(\eta^2-H_2)$  is a relatively stable compound which has even been observed by FTIR at room temperature in supercritical Xe solution.<sup>18</sup> By contrast,  $Mo(CO)_5(\eta^2-H_2)$  is extremely labile even in IXe at low temperatures where its decomposition appears to be hastened by trace impurities in the solution. Clearly this short lifetime of  $Mo(CO)_5(\eta^2-H_2)$  reduces the probability of secondary photolysis in IXe and, hence, the formation of  $Mo(CO)_4(\eta^2-H_2)_2$ . The problems of trace impurities are considerably smaller in PE matrices because the rigid nature of the polymer at low temperatures renders bimolecular reactions with these impurities highly unlikely. Thus,  $Mo(CO)_5(\eta^2-H_2)$  appears to be thermally more unstable in IXe than in PE. Nevertheless, within the PE matrix,  $Mo(CO)_5(\eta^2-H_2)$  is still markedly more reactive than  $Cr(CO)_5(\eta^2-H_2)$  or  $W(CO)_5(\eta^2-H_2)$ ; see the section on exchange processes (next).

#### Low-Temperature Exchange Processes between Group 6 $M(CO)_5(\eta^2-H_2)$ and $M(CO)_5N_2$ Compounds.

The thermal exchange of dinitrogen by dihydrogen is of interest because it offers a new synthetic route to nonclassical dihydrogen complexes.<sup>20</sup> Experiments in IXe have shown that  $M(CO)_5(\eta^2-H_2)$  compounds react thermally with  $N_2$  to form the corresponding  $M(CO)_5N_2$  complex.<sup>15</sup> Such experiments were possible because the enormous difference in vapor pressure of  $H_2$  and Xe makes it relatively easy to vent  $H_2$  from IXe solution. Recent high-pressure photoacoustic measurements of  $Cr-N_2$  and  $Cr-H_2$  bond dissociation energies<sup>21</sup> suggest that the reverse exchange



should be observable in the presence of a great excess of  $H_2$ . Such experiments are not usually possible in IXe because, once  $N_2$  has been added to IXe solution, it is extremely difficult to remove again. Indeed, many of the published spectra of organometallic species in IXe show bands due to dinitrogen species generated through the presence of trace impurities of  $N_2$ . By contrast, these inverse exchange experiments are quite straightforward in PE matrices.

$M(CO)_5N_2$  is generated from  $M(CO)_6$  under a pressure of  $N_2$  as described above. The PE is then warmed, the  $N_2$  is vented, and the LT-HP cell is repressurized with  $H_2$ . The subsequent thermal exchange reaction is then monitored by FTIR. There is one important difference, however, between experiments in PE and in dilute fluid solution. In PE, the CO which is photoejected from  $M(CO)_6$  during the formation of  $M(CO)_5(\eta^2-H_2)$  or  $M(CO)_5N_2$  may remain trapped nearby in the PE. Therefore, there is the possibility of irreversible reaction with CO as well as the desired exchange reaction. In dilute fluid solution, photoejected CO will diffuse away and recombination reactions are much less likely than in PE.

The results of the  $H_2/N_2$  exchange reactions for group 6 metals are summarized in Table 2. All reactions occurred within the temperature range 180–220 K. As

(18) See Figure 2 in: Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804.

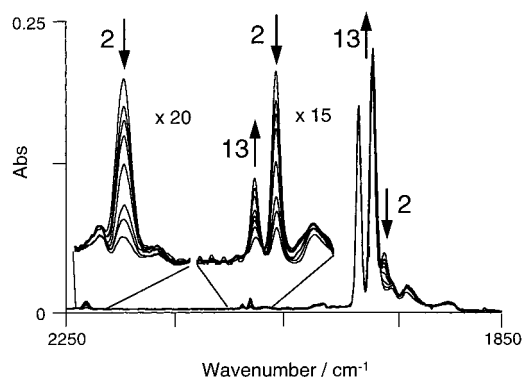
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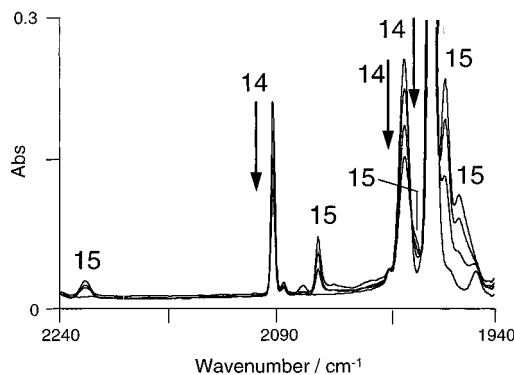
**Table 2. Summary of the Thermal Exchange Experiments of  $M(\text{CO})_5(\eta^2\text{-H}_2)$  and  $M(\text{CO})_5\text{N}_2$  ( $M = \text{Cr, Mo, W}$ ) under Pressures (ca. 1000 psi) of  $\text{N}_2$  or  $\text{H}_2$ , Respectively, over a Range of Temperatures**

$\text{Cr}(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow \text{Cr}(\text{CO})_5\text{N}_2$		$\text{Cr}(\text{CO})_5\text{N}_2 \rightarrow \text{Cr}(\text{CO})_5(\eta^2\text{-H}_2)$	
200 K	no reaction	190 K	no reaction
210 K	some parent regeneration	200 K	partial exchange
220 K	full exchange occurs (1 h)	210 K	full exchange occurs (34 h)
230 K	parent regeneration	220 K	parent regeneration
$\text{Mo}(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow \text{Mo}(\text{CO})_5\text{N}_2$		$\text{Mo}(\text{CO})_5\text{N} \rightarrow \text{Mo}(\text{CO})_5(\eta^2\text{-H}_2)$	
180 K	full exchange occurs (23 h)	180 K	partial exchange (5 h)
190 K	parent regeneration	190 K	parent regeneration
$\text{W}(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow \text{W}(\text{CO})_5\text{N}_2$		$\text{W}(\text{CO})_5\text{N}_2 \rightarrow \text{W}(\text{CO})_5(\eta^2\text{-H}_2)$	
200 K	no reaction	200 K	no reaction
210 K	full exchange occurs (41.5 h)	210 K	full exchange occurs (156 h)
220 K	parent regeneration	220 K	parent regeneration

**Figure 5.** IR spectra showing  $\text{N}_2 \rightarrow \text{H}_2$  ligand exchange. The bands of  $\text{Cr}(\text{CO})_5\text{N}_2$ , labeled **2**, diminish as the bands of  $\text{Cr}(\text{CO})_5(\eta^2\text{-H}_2)$ , **13**, grow in. The unlabeled peak is due to  $\text{Cr}(\text{CO})_6$ . This reaction is purely thermal. It occurs within the PE matrix over a period of 34 h at 210 K under approximately 1200 psi  $\text{H}_2$ ; see Table 2.

expected, the thermodynamically more favorable  $M(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow M(\text{CO})_5\text{N}_2$  exchange proceeded faster than the  $M(\text{CO})_5\text{N}_2 \rightarrow M(\text{CO})_5(\eta^2\text{-H}_2)$  reactions, but all three  $M(\text{CO})_5\text{N}_2$  complexes could be forced to undergo, at least to some extent, the thermodynamically less favorable reaction with  $\text{H}_2$  by the presence of a high pressure of  $\text{H}_2$  gas. Thus,  $\text{Cr}(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow \text{Cr}(\text{CO})_5\text{N}_2$  exchange occurring cleanly at 220 K, taking 1 h to react fully, while  $\text{Cr}(\text{CO})_5\text{N}_2$  took 34 h to react with  $\text{H}_2$  at 210 K, Figure 5. Reaction times at 210 K were substantially longer for W, 41.5 h for  $\text{W}(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow \text{W}(\text{CO})_5\text{N}_2$  and nearly 1 week for  $\text{N}_2 \rightarrow \text{H}_2$ , reflecting the greater thermal stabilities of  $\text{W}(\text{CO})_5\text{N}_2$  and  $\text{W}(\text{CO})_5(\eta^2\text{-H}_2)$ . These reactions emphasize the length of time that conditions can be stabilized in the LT-HP apparatus. However, there is a significant difference between Cr and W if we consider the ratio for the reaction times of the following reactions:  $M(\text{CO})_5(\eta^2\text{-H}_2) \rightarrow M(\text{CO})_5\text{N}_2$ :  $M(\text{CO})_5\text{N}_2 \rightarrow M(\text{CO})_5(\eta^2\text{-H}_2)$ . We find a value of 1:34 for Cr compared with 1:4 for W, suggesting that the energy difference between  $M\text{-N}_2$  and  $M\text{-H}_2$  bonds is smaller for W than for Cr.

Thus PE matrices provide the first confirmation that  $\text{H}_2$  can displace coordinated  $\text{N}_2$  from  $M(\text{CO})_5\text{N}_2$  complexes. The experiments, however, will clearly be influenced by the amount of  $\text{N}_2$  remaining within the PE after venting of the gas from the LT-HP cell. The Experimental Section describe a series of experiments

**Figure 6.** IR spectra recorded during 30 min of UV photolysis of  $\text{W}(\text{CO})_5\text{CS}$ , **14**, impregnated into Hostalen PE under  $\text{N}_2$  (1400 psi) at 190 K. The bands of **14** decay as *cis*- $\text{W}(\text{CO})_4\text{CS}(\text{N}_2)$ , **15**, is formed. The band in the  $\nu(\text{C-S})$  region (not illustrated) was too broad to provide any information beyond the fact that the CS group was retained during photolysis; see Table 3.

aimed at establishing how effectively CO,  $\text{N}_2$ , and  $\text{H}_2$  can be removed from the PE matrix.

**Photolysis of  $\text{W}(\text{CO})_5\text{CS}$  under  $\text{N}_2$  and  $\text{H}_2$ .** In this section we examine the effect on the resultant photochemistry of changing one CO group for an electronically similar ligand. Photolysis of  $\text{W}(\text{CO})_5\text{CS}$  in matrices<sup>22</sup> at 20 K leads to photoejection of CO but no apparent loss of CS.  $\text{W}(\text{CO})_4\text{CS}$  was generated as a mixture the  $C_{4v}$  and  $C_s$  square-pyramidal isomers, the relative amounts of which depend on the material of the matrix and on the wavelength of the UV irradiation.

Figure 6 shows IR spectral changes in the  $\nu(\text{N-N})$  and  $\nu(\text{C-O})$  regions as  $\text{W}(\text{CO})_5\text{CS}$  (**14**) was irradiated under  $\text{N}_2$  in PE at 190 K. As the concentration of  $\text{W}(\text{CO})_5\text{CS}$  fell, five product bands grew in, including one  $\nu(\text{N-N})$  band. This is consistent with the formation of previously unreported *cis*- $\text{W}(\text{CO})_4\text{CS}(\text{N}_2)$  (**15**). The relative band intensities and positions compare well with the analogous matrix-isolated  $C_s$  species<sup>22</sup>  $\text{W}(\text{CO})_4\text{CS}$ , which has a vacant site instead of an  $\text{N}_2$  ligand in the *cis* position. Visible photolysis ( $\lambda > 400$  nm) of *cis*- $\text{W}(\text{CO})_4\text{CS}(\text{N}_2)$  provided evidence for *cis*  $\rightarrow$  *trans* isomerization.

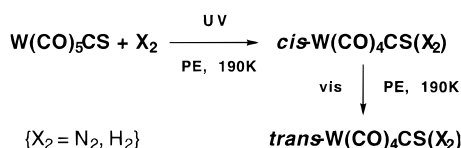
Photolysis of  $\text{W}(\text{CO})_5\text{CS}$  in the presence of  $\text{H}_2$  resulted in the growth of bands assigned to a *cis*-substituted product,  $\text{W}(\text{CO})_4\text{CS}(\eta^2\text{-H}_2)$ . Such a product should have

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**Table 3. IR Data for W(CO)<sub>5</sub>CS, W(CO)<sub>4</sub>(N<sub>2</sub>)CS, and W(CO)<sub>4</sub>(η<sup>2</sup>-H<sub>2</sub>)CS in PE at 190 K**

compd	band posn/cm <sup>-1</sup>	assgnt		
		ν(NN)	ν(CO)	
W(CO) <sub>5</sub> CS	2096.2		a <sub>1</sub>	
	2004.5		a <sub>1</sub>	
	1984.9		e	
<i>cis</i> -W(CO) <sub>4</sub> (H <sub>2</sub> )CS	2071.3		a'	
	1998.0		a'	
	1975.4		a' + a''	
	2226.4		a <sub>1</sub>	
<i>cis</i> -W(CO) <sub>4</sub> (N <sub>2</sub> )CS	2064.5		a'	
	1996.0		a'	
	1974.9		a''	
	1965.3		a'	
	<i>trans</i> -W(CO) <sub>4</sub> (H <sub>2</sub> )CS	<i>a</i>		a <sub>1</sub>
	1977.0		e	
<i>trans</i> -W(CO) <sub>4</sub> (N <sub>2</sub> )CS	2227.5		a <sub>1</sub>	
	<i>a</i>		a <sub>1</sub>	
	1975.7		e	

<sup>a</sup> Predicted to be obscured by other bands.

**Scheme 5**

4 distinct ν(C–O) bands, but only 3 are observed; presumably, the two lowest frequency ν(C–O) bands overlap. Such overlap is not unusual and occurs for both W(CO)<sub>5</sub>(η<sup>2</sup>-H<sub>2</sub>) and *cis*-W(CO)<sub>4</sub>(η<sup>2</sup>-H<sub>2</sub>)<sub>2</sub> but not for the dinitrogen compound, **15**. Again *cis* → *trans* isomerization was observed during visible photolysis. The IR data are collected in Table 3, and the reactions are summarized in Scheme 5.

Broad-band UV photolysis (300 < λ < 400 nm) favors formation of the *cis*-compounds, possibly due to photoisomerization of the *trans*-isomer at these wavelengths. Both W(CO)<sub>4</sub>CS(η<sup>2</sup>-H<sub>2</sub>) and W(CO)<sub>4</sub>CS(N<sub>2</sub>) react with CO above 190 K to re-form W(CO)<sub>5</sub>CS.

**Photolysis of (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>)M(CO)<sub>3</sub> (M = Cr and Mo) under N<sub>2</sub> and H<sub>2</sub>.** Although substitution by N<sub>2</sub> or H<sub>2</sub> of two CO groups occurs in W(CO)<sub>6</sub> (see above), we did not observe substitution of more than one CO group in W(CO)<sub>5</sub>CS in PE. By contrast, multiple substitution has been observed for (arene)Cr(CO)<sub>3</sub> complexes in supercritical fluid solution.<sup>18,23</sup> Therefore, we have investigated the photochemistry of (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)M(CO)<sub>3</sub> (M = Cr and Mo) in PE. UV irradiation of (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)Cr(CO)<sub>3</sub> in PE the presence of N<sub>2</sub> (2000 psi) generated the mono-, bis-, and tris-N<sub>2</sub> complexes, (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>)Cr(CO)<sub>3-x</sub>(N<sub>2</sub>)<sub>x</sub>, at room temperature. Similar results were obtained for (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>)Mo(CO)<sub>3</sub>, although none of these dinitrogen compounds had been observed previously. By contrast, irradiation of these (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)M(CO)<sub>3</sub> compounds in PE in the presence of H<sub>2</sub> only generated the mono-H<sub>2</sub> complexes (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>)M(CO)<sub>2</sub>(H<sub>2</sub>). All IR data are collected in Table 4. The fact that these compounds can be generated in PE at room-temperature underlines the stabilizing

**Table 4. IR Data for mesM(CO)<sub>3</sub>, mesM(CO)<sub>2</sub>(N<sub>2</sub>), and mesM(CO)<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>) (mes = η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>); M = Cr or Mo)**

compd	Cr	Mo	assgnt	
			ν(NN)	ν(CO)
mesM(CO) <sub>3</sub>	1968.2	1971.3		a <sub>1</sub>
	1898.0	1898.0		e
mesM(CO) <sub>2</sub> (N <sub>2</sub> )	2128.1	2131.2	a'	
	1925.0	1927.5		a'
	1882.7	1882.6		a''
	2128.6 <sup>a</sup>	2129	a'	
mesM(CO)(N <sub>2</sub> ) <sub>2</sub>	2081.0	2088.5	a''	
	1888 <sup>b</sup>	obs <sup>c</sup>		a'
	obs <sup>c</sup>	obs <sup>c</sup>	a <sub>1</sub>	
mesM(N <sub>2</sub> ) <sub>3</sub>	2060	2064	e	
	1924.5	1930.5		a'
mesM(CO) <sub>2</sub> (η <sup>2</sup> -H <sub>2</sub> )	1873.5	1879.5		a''
	1985.1	1986.4		t <sub>1u</sub>

<sup>a</sup> Revealed by computer subtraction. <sup>b</sup> Observed as shoulder on another band. <sup>c</sup> Obs = predicted to be obscured by other bands.

effects of the (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>) group on dinitrogen and dihydrogen compounds.

**Conclusions**

In this paper, we have described how low-temperature/high-pressure techniques can be used to generate a series of unstable organometallic compounds in polyethylene (PE) films and to investigate their reactions. These experiments have not only reproduced inexpensively the results of much more costly experiments previously carried out in liquid Xe but also have opened up a whole range of experiments (e.g. the displacement of coordinated N<sub>2</sub> by H<sub>2</sub> in unstable compounds) which would be difficult if not impossible to study by other methods. We have identified the key experimental parameters which influence the penetration of gases into PE films and their subsequent removal from the films so that the effect of the matrix on the reactions can be understood. The high-pressure/low-temperature technique has wide applications. In future papers, we will describe how these techniques can be extended to the reactions of MeM(CO)<sub>5</sub> (M = Mn and Re), to the formation of ionic compounds in a neutral matrix by protonation with gaseous HCl, and to investigate the detailed mechanism of photocatalytic hydrogenation.

**Experimental Section**

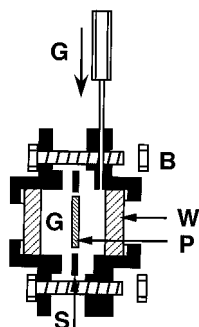
**Preparation and Impregnation of PE Disks.** Two types of polyethylene were used, either Hostalen GUR-415 PE (Hoechst), a very high molecular weight polymer, or low-density PE (Aldrich). In both cases powdered PE was heated (150 °C) for 5 min under pressure (5 tons) in a constant thickness melt press (Specac model 15620) to form a film (10–500 μm thick) from which disks (6 or 10 mm diameter) were cut. Disks were then impregnated with the reactant organometallic compound, either a group 6 metal M(CO)<sub>6</sub> (Aldrich), (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>)M(CO)<sub>3</sub> (synthesized using standard literature procedures), or W(CO)<sub>5</sub>CS (a gift from Professor R. J. Angelici), using supercritical fluids,<sup>25</sup> liquid organic solvents, or vapor diffusion. Organic solvent impregnation involved immersing the disk in

(23) (η<sup>6</sup>-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>)Cr(CO)<sub>2</sub>(N<sub>2</sub>) was isolated 25 years ago: Sellmann, D. Z. Naturforsch., B **1972**, 27, 718.

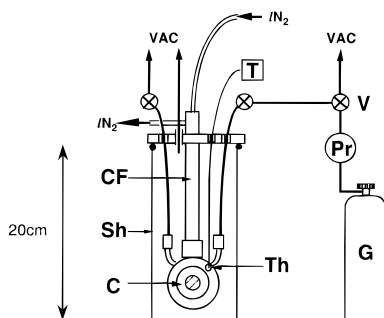
(24) (η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>2</sub>(H<sub>2</sub>) has been characterized following photolysis of (η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub> in supercritical CO<sub>2</sub>.

(25) (a) Howdle, S. M.; Ramsay, J.; Cooper, A. I. J. Polym. Sci., Part B: Polym. Phys. **1994**, 32, 541. (b) Clarke, M. J.; Howdle, S. M.; Jobling, M.; Poliakov, M. J. Am. Chem. Soc. **1994**, 116, 8621.

(26) Maier, W. B., II; Freund, S. M.; Holland, R. F.; Beattie, W. H. J. Chem. Phys. **1978**, 69, 1961.



**Figure 7.** Cross-section of the LT-HP cell, with stainless steel tubing for introducing the gas (G). Tightening the four bolts (B) compresses a thin lead gasket (S) between the two halves of the copper cell body thus sealing it. Indium-sealed  $\text{CaF}_2$  windows (W) permit UV photolysis and IR monitoring of the polymer disk (P).

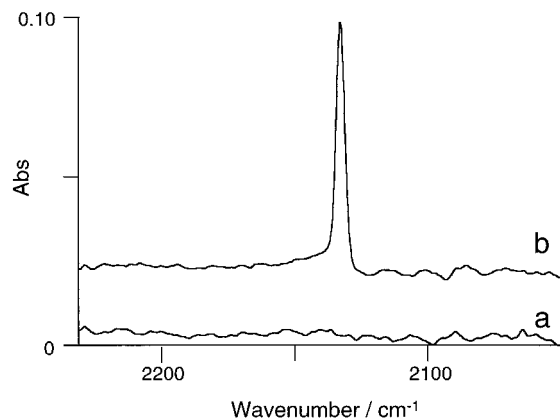


**Figure 8.** Schematic of the LT-HP apparatus cooled by liquid  $\text{N}_2$  (not drawn to scale). Gas from the cylinder (G) can be filled into or evacuated from the LT-HP cell (C) through a network of stainless steel tubing ( $1/16$  in. o.d.) and high-pressure valves (V) with a pressure transducer indicator (Pr). Cooling of the cell is achieved by pulsing<sup>4a,26</sup> liquid  $\text{N}_2$  through the cold finger (CF), at a rate controlled by a digital gauge (T) and Fe/constantan thermocouple (Th). An evacuated shroud (Sh) prevents icing of the windows during cool-down. The gas system was built from steel tubing ( $1/16$  in. o.d.) and miniature valves (HIP). Gas pressure was monitored by a transducer (RDP Electronics), and a rotary pump was used to evacuate the lines and cell.

a saturated solution of the compound in *n*-heptane or dichloromethane until a suitable concentration of organometallic was achieved within the PE, warming the solution if necessary. If the compound had a sufficiently high vapor pressure (i.e.  $> 10^{-1}$  mbar), the preferred technique was to place the PE disk together with the pure compound under vacuum in a Schlenk tube. Vapor impregnation eliminates the possibility of solvent residues interfering with any subsequent reactions.

Degassed *n*-heptane, distilled over  $\text{CaH}_2$ , was used for solvent impregnation of Hostalen PE disks (250  $\mu\text{m}$  thick). Each experiment required *extremely small amounts* of chemicals, gases and PE. The total internal volume of cell and gas-handling system was only 4 mL. Each PE disk weighs 5–20 mg. The concentration of the organometallic compound impregnated in the PE disk is  $< 0.01$  M, which is equivalent to a loading of  $< 20$   $\mu\text{g}$  of complex in each disk. Gases,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{N}_2$  (Air Products, 99.999% pure) were used without further purification.

**Cell Design and Use.** The PE disk was mounted inside the low-temperature, high-pressure (LT-HP) cell, Figure 7, a modification of a design<sup>4b</sup> originally used for working with IXe. The cell was fixed to a *cold finger* of a cryogenic cooling system. In this study two similar experimental rigs were used. The first set of apparatus, shown schematically in Figure 8, was capable of temperature stabilization of  $\pm 1$  K, with a



**Figure 9.** IR spectra showing the effect of temperature on the  $\nu(\text{C}-\text{O})$  band of  $\text{CO}$  "trapped" in Hostalen PE. At 298 K (a) the band is too broad to be detected above the background. However, on cooling to 30 K (b), the band sharpens sufficiently to be observed easily. The behavior is completely reversible.

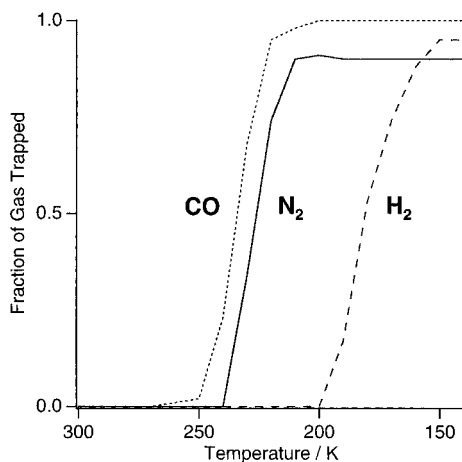
minimum temperature of 77 K. The second set of equipment,<sup>27</sup> used in the  $\text{H}_2/\text{N}_2$  exchange and probe experiments, has improved temperature stabilization ( $\pm 0.1$  K) and a lower minimum temperature (30 K) which are obtained by attaching the LT-HP cell to an Air Products Displex HC-2 closed-cycle cooler with a Scientific Instruments Inc. 9600-1 silicon diode temperature controller.

**Spectroscopy and Photolysis.** IR spectra were recorded at 2  $\text{cm}^{-1}$  resolution using either a Nicolet 60SX interferometer connected to a 680 DSP spectral workstation or with a Nicolet 730 interferometer linked to a PC running Nicolet OMNIC software. Polyethylene (PE) has very weak, temperature- and sample-dependent IR absorptions in the  $\nu(\text{C}-\text{O})$  region due to a variety of combination and overtone bands. Therefore, background spectra were recorded with clean PE disks over the range of temperatures required for each experiment. A Xenon high-intensity light source (ILC 302UV) provided broadband UV ( $300 < \lambda < 400$  nm) or visible ( $\lambda > 400$  nm) radiation. In the exchange experiments, a Philips HPK 125W medium-pressure Hg arc was the photolysis source.

**Investigating the Behavior of  $\text{CO}$  in the PE Matrix.** A simple experiment was used to investigate the trapping of  $\text{CO}$  in PE. A PE disk was pressurized with  $\text{CO}$  (1500 psi for 10 min) in the LT-HP cell at 298 K. The system was then evacuated, and the  $\nu(\text{C}-\text{O})$  region of the IR spectrum was monitored as the cell was cooled to 30 K, see Figure 9. Cooling is necessary because  $\text{CO}$  bands which are undetectable at room temperature due to broadening become sharp and easily detectable at low temperatures. With 250  $\mu\text{m}$  thick Hostalen PE disks,  $\text{CO}$  remained trapped within the PE matrix even at room temperature and remains there even after repeated attempts to remove it. Thus, once  $\text{CO}$  is introduced into the 250  $\mu\text{m}$  PE disk, it cannot easily be removed from the film by our evacuation methods (see later section), so that there will always be  $\text{CO}$  available within the PE in photochemical experiments with metal carbonyl compounds.

By contrast, it was found that, using a series of  $5 \times 50$   $\mu\text{m}$  thick PE disks rather than a single 250  $\mu\text{m}$  disk, not only was it possible to remove the  $\text{CO}$  completely from the PE matrix at room temperature but also the  $\text{CO}$  did not become trapped within the matrix until a temperature of 260 K. Even then, only a small amount of  $\text{CO}$  was retained. It was possible to quantify the amount of  $\text{CO}$  trapped within the 50  $\mu\text{m}$  disks at different temperatures by measuring the area of the IR band of trapped  $\text{CO}$ , when subsequently cooled to 30 K. Hence, a trapping profile was produced that shows that the 50  $\mu\text{m}$  PE

(27) Cooper, A. I. Ph.D. Thesis, University of Nottingham, 1994.



**Figure 10.** Summary of the results for the trapping in PE (50  $\mu\text{m}$  thick) of CO (dotted),  $\text{N}_2$  (solid), and  $\text{H}_2$  (dashed) at various temperatures. The values for  $\text{H}_2$  and  $\text{N}_2$  were obtained by a series of experiments using  $\text{Mo}(\text{CO})_6$  as a probe and by comparing the ratios of the integrated areas of the bands  $\text{Mo}(\text{CO})_5(\eta^2\text{-H}_2):\text{Mo}(\text{CO})_5$  or  $\text{Mo}(\text{CO})_5\text{N}_2:\text{Mo}(\text{CO})_5$  and assuming that  $\text{Mo}(\text{CO})_5(\eta^2\text{-H}_2)/\text{Mo}(\text{CO})_5$  and  $\text{Mo}(\text{CO})_5$  have comparable IR extinction coefficients.

disks do not become saturated with trapped CO until the temperature is lowered to 210 K; see Figure 10.

**Investigating the Behavior of  $\text{N}_2$  and  $\text{H}_2$  in the PE Matrix with a  $\text{M}(\text{CO})_6$  Probe.** Our LT-HP cell opens up a range of new experiments which were previously very difficult to perform. Thus, by evacuating gases from the cell and replacing them with others, one can carry out sequential reactions involving a series of gases. However, it has been reported that PE tends to trap gases at low temperatures leading to a hysteresis in the gas transport properties of PE at low temperatures,<sup>28</sup> and we have already found that  $\text{CO}_2$  takes a considerable time to diffuse out of PE at room temperature.<sup>29</sup> We now have established the temperatures at which PE becomes impermeable to  $\text{H}_2$  and  $\text{N}_2$ , trapping them within the polymer or preventing them from penetrating the matrix at all. Since  $\text{H}_2$  and  $\text{N}_2$  cannot be detected using FTIR spectroscopy, it was necessary to impregnate  $\text{Mo}(\text{CO})_6$  as a probe compound into the PE to react with these gases. If the gas were present in the PE, photolysis of  $\text{Mo}(\text{CO})_6$  would produce  $\text{Mo}(\text{CO})_5(\eta^2\text{-H}_2)$  or  $\text{Mo}(\text{CO})_5\text{N}_2$ , while irradiation, in the absence of gas, would merely result in fragmentation and formation of "naked"  $\text{Mo}(\text{CO})_5$ , as seen in matrices.<sup>13</sup>

These experiments were performed for both  $\text{H}_2$  and  $\text{N}_2$  (ca. 1000 psi), varying the temperatures and reaction conditions. It was found that, in the case of standard 250  $\mu\text{m}$  thick PE disks,  $\text{H}_2$  entered the cold PE at 180 K or above and was suddenly trapped within it at 220 K or below. For  $\text{N}_2$ , the limits were found to be 220 K for entry and 260 K for trapping. These temperatures quoted above are for disks where the

vapor impregnation method was used. When a  $\text{CH}_2\text{Cl}_2$  solution had been used, the trapping temperatures were lowered to 200 K for  $\text{H}_2$  and 250 K for  $\text{N}_2$ .

When  $5 \times 50 \mu\text{m}$  disks were used instead of  $1 \times 250 \mu\text{m}$  disk, the temperature at which  $\text{H}_2$  entered the cold PE was lowered to 160 K and, similarly, the corresponding limit for  $\text{N}_2$  was lowered to 200 K. An even greater change occurred in the gas trapping figures. It was found that  $\text{H}_2$  was able to escape from the PE matrix above 200 K but that, as with the trapping of CO, full saturation of the PE with trapped  $\text{H}_2$  did not occur above 150 K. Hence, a trapping profile became apparent for  $\text{H}_2$  in 50  $\mu\text{m}$  PE, in contrast to the sudden change that occurred for  $\text{H}_2$  in 250  $\mu\text{m}$  PE; see Figure 10.  $\text{H}_2$  and  $\text{D}_2$  behaved identically. These changes also occurred when  $\text{N}_2$  was tested in 50  $\mu\text{m}$  PE disks. The trapping limit was lowered to 240 K, and a trapping profile was observed such that full saturation of the PE with trapped  $\text{N}_2$  did not occur until 210 K; see Figure 10.

Neither the type of polyethylene (either Hostalen PE or Aldrich LDPE), the evacuation method (pumping or flushing with He gas), nor moderate changes in the initial pressure of  $\text{H}_2$  or  $\text{N}_2$  in the cell were found to have much effect on gas behavior in the polymer. However, the substantial effect of varying the disk thickness means that it should be possible to use the thickness of a PE matrix to tailor the gas transport properties to the needs of a particular experiment.<sup>30</sup>

The effect of changing impregnation method from vapor impregnation to  $\text{CH}_2\text{Cl}_2$  solution is also interesting, because it shows that the treatment of the PE sample influences the final experimental results. Our observation is consistent with the reported lowering of the glass transition temperature,  $T_g$ , of PE by organic solvents.<sup>31</sup> Less readily explained is the fact that gases penetrate the cold PE more easily than they can escape from it. It might have been expected that the penetration and trapping temperatures for a given gas would be similar. Although the processes involved are superficially similar, a high pressure of gas entering "empty" PE from a large reservoir is not the reverse of pumping a finite amount of gas at low pressure from "full" PE. It is therefore not unreasonable that the temperature limits of the two processes should be different.

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(30) The PE films were all hot-pressed. Thus, it is possible that the crystallinity of the 50 and 250  $\mu\text{m}$  films may have been different since the thinner film would cool somewhat faster after pressing. However, the effect is probably not significant, given that, for a given thickness, we found no difference in our results between different types of PE.

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