

# Photochemical Reactions of Organometallic Complexes Impregnated into Polymers: Speciation, Isomerization, and Hydrogenation of Residual Alkene Moieties in Polyethylene

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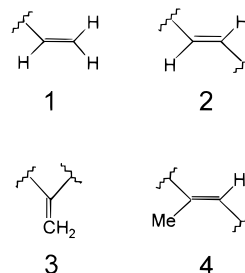
**Abstract:** Tungsten hexacarbonyl,  $W(CO)_6$ , and iron pentacarbonyl,  $Fe(CO)_5$ , were impregnated into four different types of polyethylene (PE) using either supercritical carbon dioxide ( $scCO_2$ ) or conventional solvents (*n*-heptane and carbon tetrachloride). All of the PE samples were known to have some residual alkene unsaturation in the polymer chain, with different relative amounts of *vinyl* (terminal), *pendant*, and *trans-internal* unsaturation.  $W(CO)_6$  was found to react photochemically with residual alkene bonds in the impregnated PE films, and to form polymer-bound species of the type  $W(CO)_5(\eta^2\text{-alkene})_{PE}$ . Extended photolysis led to isomerization of the alkene moieties which was detected by changes in the FTIR spectra of the polymer-bound organometallic. Speciation of the alkene groups both before and after photoisomerization was achieved by use of a probe molecule,  $(\eta^5\text{-C}_5\text{H}_5)\text{Mn(CO)}_3$  (see: Clarke, M. J.; Howdle, S. M.; Jobling, M.; Poliakoff, M. *J. Am. Chem. Soc.* **1994**, *116*, 8621–28). In each case, the isomerization reaction resulted in depletion of *vinyl* unsaturation and a concomitant increase in *trans-internal* unsaturation. This process was scaled-up to allow the photoisomerization and subsequent purification of gram quantities of low-density PE powder.  $Fe(CO)_5$  was shown to act both as a photoisomerization catalyst and as an efficient hydrogenation catalyst leading to significant reduction of unsaturation in the polymers. The degree of hydrogenation was determined by the nature of unsaturation in the PE sample, the reaction conditions, and solvent swelling effects.

## Introduction

Impregnation of organometallic compounds into polymer films provides a novel environment for the study of photochemical and thermal reactions by matrix isolation.<sup>1–7</sup> This technique was pioneered by Rest and co-workers,<sup>8–10</sup> in particular by use of solution-cast host polymers such as PVC and PVA. The method has since been developed by a number of groups including our own, which has concentrated on the use of polyethylene (PE) as a host matrix.

In an earlier publication, we reported that photolysis of metal carbonyl species in PE induced reactions with the polymer substrate. In particular, photolysis of  $(C_5Me_5)Ir(CO)_2$  impregnated into PE led to C–H activation of the polymer and formation of  $(C_5Me_5)Ir(CO)(H)(\eta^1\text{-CH})_{PE}$  for both high and low PE (HDPE and LDPE, respectively).<sup>11</sup> By contrast, other organometallic species, notably  $CpMn(CO)_3$  ( $Cp = C_5H_5$ ),

## Scheme 1



underwent photochemical reaction with residual alkene bonds in PE to form  $CpMn(CO)_2(\eta^2\text{-alkene})_{PE}$ .

PE contains a number of different types of alkene bonds, **1–4**, the relative and absolute concentrations of which depend on the particular type of PE and the method of polymerization. Surprisingly, the precise wavenumbers of the  $\nu(CO)$  bands of the  $CpMn(CO)_2(\eta^2\text{-alkene})_{PE}$  compounds depend on the particular type of alkene bonded to the metal. Indeed, we showed<sup>2</sup> that these  $\nu(CO)$  bands could be used as an analytical tool for speciation of the alkene groups present in a given sample of PE, with a sensitivity significantly higher than the long-established IR method normally used for speciation.<sup>12</sup> In all of these experiments supercritical  $CO_2$  ( $scCO_2$ ) was employed as the medium for impregnation of the  $CpMn(CO)_3$  to ensure that no solvent residues were present to complicate the subsequent

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reactions.<sup>13</sup> UV photolysis of these impregnated samples caused formation of  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  but no isomerization of the C=C bonds in the PE. Molecular weight measurements of PE are difficult to make outside specialist PE laboratories and we were not able to carry out such measurements on our PE samples. However, no gross changes in molecular weight were evident in any of our previous experiments nor in those described in this paper.

Unlike  $\text{CpMn}(\text{CO})_3$ ,  $\text{W}(\text{CO})_6$  is a known isomerization catalyst for carbon-carbon double bonds. Irradiation of  $\text{W}(\text{CO})_6$  in the presence of an alkene can lead to  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})$  complexes, as first reported by Stolz.<sup>14</sup> Subsequently, Wrighton et al. studied the catalytic properties of  $\text{W}(\text{CO})_6$  in the isomerization of pentenes and related branched hexenes.<sup>15,16</sup> In this paper, we demonstrate by FTIR spectroscopy that the photochemical reaction of impregnated  $\text{W}(\text{CO})_6$  leads to isomerization of alkene bonds in PE, and that this process can be scaled up to isomerize gram quantities of PE without any residual traces of metal carbonyl being left in the final polymer. Similar photochemical isomerization behavior was observed for iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ . In the presence of hydrogen gas,  $\text{Fe}(\text{CO})_5$  is also known to mediate photochemical hydrogenation of olefinic species, and we show here that residual olefinic moieties in PE samples can be reduced by in situ photochemical hydrogenation with  $\text{Fe}(\text{CO})_5$  as the catalyst.

The key to the understanding of both isomerization and hydrogenation processes in PE is the use of FTIR spectroscopy. In particular, the interaction of the  $\text{CpMn}(\text{CO})_3$  probe with model alkenes and with the alkene bonds in the various PE samples provides accurate speciation of the products of our isomerization and hydrogenation reactions. PE, and in particular ultrahigh molecular weight polyethylene (UHMWPE), is used extensively in orthopedic medical implants primarily as the acetabulum (socket) in hip implants. The presence of unsaturation in UHMWPE is known to be a factor in the oxidative degradation of such materials in the body, leading to failure and rejection of the implant.<sup>17</sup> The reduction of residual unsaturation in such materials may well contribute to increased implant lifetimes.

## Experimental Section

All materials were used without further purification:  $\text{CpMn}(\text{CO})_3$ ,  $\text{W}(\text{CO})_6$  (Strem), and  $\text{H}_2$  (Air Products), SFC grade  $\text{CO}_2$  (BOC), commercially available LDPE and HDPE (Aldrich and BP Chemicals), and Hostalen GUR 415 PE (Hoechst). PE films were prepared at Nottingham by hot-pressing PE powder at ca. 160 °C with a constant-thickness melt-press<sup>6</sup> [Specac Model 15620]. Supercritical impregnation was carried out as described in detail elsewhere with a modified Nupro TF Series in-line filter, 5  $\mu\text{m}$  pore size, as the pressure vessel.<sup>13</sup> PE films were immersed in a near-saturated solution of  $\text{CpMn}(\text{CO})_3$  in  $\text{scCO}_2$  at 40 °C and 2000 psi of pressure. Alternatively, impregnation was carried out with *n*-heptane (distilled over  $\text{CaH}_2$ ) and  $\text{CCl}_4$  or, in the case of  $\text{Fe}(\text{CO})_5$ , by simple impregnation of the liquid organometallic under reduced pressure. Typical loadings of the PE are <1% organometallic by weight.

Samples of alkenes (2-ethylbut-1-ene, 3-methylpent-2-ene, hex-1-ene, *trans*-hex-2-ene, all from Aldrich) were used to dope films of Hostalen GUR 415 PE which had been previously impregnated with  $\text{CpMn}(\text{CO})_3$ . This was done by placing a few drops of the appropriate

alkene on the film (all of the alkenes used in this study are liquids at room temperature). High-pressure spectroscopic experiments were carried out in miniature cells, described previously.<sup>18,19</sup> The UV photolysis source was a Cermax 300W Xe arc lamp with a 1 m long Lumatec light guide, which has the safety advantage of almost totally eliminating stray UV light. For isomerization reactions, irradiation was carried out in a sealed miniature high-pressure spectroscopic cell with  $\text{CaF}_2$  windows<sup>13</sup> under an inert atmosphere (helium) unless otherwise stated. For hydrogenation, the helium atmosphere was replaced with hydrogen. Irradiation of native PE samples was also performed as a control measure. These experiments showed that, under the conditions of our experiments, UV irradiation in the absence of a metal carbonyl species did not cause any change in the degree of unsaturation, or induce isomerization of olefinic moieties. FTIR spectra were recorded on a Nicolet 730 interferometer with an MCT detector and 680D Data Station (2  $\text{cm}^{-1}$  resolution). Low-temperature IR experiments were carried out with apparatus described elsewhere.<sup>5,7</sup>

In the scale-up experiments,  $\text{scCO}_2$  impregnation was used to exclude any possible contamination from conventional solvents. A gram of LDPE powder was impregnated with  $\text{W}(\text{CO})_6$  in  $\text{scCO}_2$  solution for 12 h at 40 °C. The impregnated powder was then irradiated with UV light for a period of 6 to 12 h, with constant shaking to ensure even photolysis of the whole sample. As in the case of polymer films, the powder developed a pale straw color, indicative of the formation of  $\text{W}(\text{CO})_5(\eta^2\text{-olefin})$  species. **Safety Note:** *Some of the experiments described in this paper involve high pressures and should only be carried out with appropriate apparatus.*

**Polyethylene.** The samples used in this work came from both commercial and academic sources. The samples ranged from low-density to ultrahigh molecular weight polyethylene, and varied significantly in their physical (e.g., density) and chemical (e.g., alkene unsaturation) properties.

**Low-Density Polyethylene (LDPE).** LDPE was obtained in powder form from Aldrich Chemicals (Aldrich Catalog No: [18189-7], density = 0.915  $\text{g cm}^{-3}$ ; melt index = 22 g/10 min;  $T_m$  = 115 °C). We were unable to ascertain whether this LDPE contains any additives such as photochemical stabilizers/free-radical trapping agents. Although the concentration of such additives is usually much lower than the concentration of reagent species in our experiments,<sup>2</sup> it was considered that even low additive concentrations might affect the photochemical studies significantly. Therefore, the LDPE powder was extracted with  $\text{scCO}_2$  modified with 10%  $\text{CH}_2\text{Cl}_2$  or MeOH at 110 °C for 2 h. Extraction of polyethylene under these conditions is known<sup>20</sup> to remove antioxidants and stabilizers. Trace quantities of low molecular weight residues were also extracted and detected by gas chromatography. The results of reactions conducted in LDPE films prepared from extracted powder were identical with those obtained in untreated films, indicating that any additives present in the commercial samples had no effect on the photochemical studies.

**Hostalen GUR 4150 (Hos GUR PE).** Hos GUR PE, an Ultrahigh Molecular Weight Polyethylene (UHMWPE), was supplied in powdered form by Hoechst. Hos GUR PE is manufactured by Ziegler-Natta catalysis (average molecular weight =  $7.3 \times 10^6$   $\text{g mol}^{-1}$ ; density = 0.9300  $\text{g cm}^{-3}$  (of which the amorphous phase is 0.8549  $\text{g cm}^{-3}$  and the crystalline phase is 1.0005  $\text{g cm}^{-3}$ ); percentage crystallinity ~ 52%;  $T_m$  = 130–135 °C). The melt index is not measurable for Hos GUR PE due to its extremely high melt viscosity. Typical impurity content, arising from the polymerization process (manufacturer's figures), was as follows: Ca <50 ppm; Ti and Al <40 ppm; Cl <35 ppm; Mg <20 ppm.<sup>21</sup> Hostalen GUR PE, as supplied, also contains a corrosion stabilizer (but no heat, extrusion, or UV stabilizers or lubricants). A powdered sample of Hos GUR PE was extracted with  $\text{scCO}_2$  modified

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**Table 1.** Wavenumbers ( $\text{cm}^{-1}$ ) of  $\nu(\text{C}-\text{O})$  Bands of  $\text{W}(\text{CO})_5\text{L}$  Species

$\text{W}(\text{CO})_6$ in LDDEL PE	1980.9	1980.9	$\text{W}(\text{CO})_6$ in LDPE
$\text{W}(\text{CO})_4[(\eta^2\text{-RCH}=\text{CH}_2)_2]_{\text{PE}}$	1950.0	1955	$\text{W}(\text{CO})_4(\eta^2\text{-prop-1-ene})_2$ in heptane <sup>14</sup>
$\text{W}(\text{CO})_5$ in LDPE at 21 K	2089 (w)	2090	$\text{W}(\text{CO})_5$ in wax disk <sup>9</sup> at 12 K
	1953 (s)	1956	
	1926 (m)	1929	

with 10%  $\text{CH}_2\text{Cl}_2$  or MeOH at 110 °C for 2 h (cf. LDPE). Trace amounts of residues were extracted but once again no differences were observed between photochemical reactions conducted in extracted and native PE films. Hos GUR PE has a relatively low density, despite the fact that it is largely linear, as determined by FTIR spectroscopy. This is due to the high melt viscosity of the polymer which considerably restricts ordering mechanisms during crystallization. As a result of the method of polymerization, Hostalen GUR PE contains *very* low levels of alkene unsaturation. The small degree of unsaturation is vinyl ( $-\text{CH}=\text{CH}_2$ ) and pendant ( $\text{R}'\text{RC}=\text{CH}_2$ ) in nature (types **1** and **3**, Scheme 1), present in roughly equal concentrations as determined by FTIR spectroscopy. Hos GUR PE possesses remarkable toughness, even at very low temperatures, making it particularly suitable for cryogenic studies [e.g., components made from Hos GUR PE have been employed in nuclear research, at liquid helium temperatures (4 K)].<sup>21</sup>

**High-Density Polyethylene (BPPE).** BPPE was supplied by BP Chemicals (type 6007) and received in pellet form. BPPE is manufactured with a Phillips catalyst ( $\text{CrO}_3/\text{SiO}_2$ ), and has a density of  $0.960 \text{ g cm}^{-3}$  and an average molecular weight of  $135 \times 10^3 \text{ g mol}^{-1}$ . The polymer was essentially linear, with 0.5 ethyl branches per thousand C atoms. This sample of PE was unstabilized and contained no additives. The FTIR spectrum of BPPE revealed a relatively high concentration of alkene unsaturation (ca.  $0.06 \text{ mol dm}^{-3}$ ) which was exclusively vinyl in nature (type **1**, Scheme 1). BPPE had a relatively low average molecular weight (cf. Hos GUR PE) and each polymer chain contained approximately one double bond.

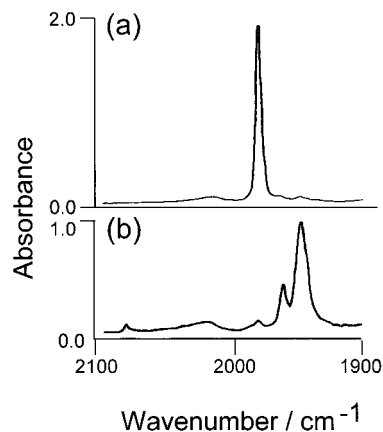
**Specialist Polyethylene Blend (LDDELPE).** A high-density PE (powdered form) was kindly supplied by Prof. Theopold (University of Delaware, USA). This low molecular weight polyethylene (DEL PE) was produced using a homogeneous Cr(III) alkyl catalyst, and was shown spectroscopically to contain *very* high concentrations of vinyl  $-\text{CH}=\text{CH}_2$  unsaturation (type **1**, Scheme 1). DEL PE was found to be very brittle when hot-pressed into a thin film, and was therefore mixed with Aldrich LDPE powder (DEL PE:LDPE ratio of 1:3 by mass) to produce a polymer blend, LDDEL PE, with better physical and spectroscopic properties than pure DEL PE. The FTIR spectrum of LDDEL PE showed that the blend contained a vinyl alkene concentration of ca.  $0.02 \text{ mol dm}^{-3}$ .

The infrared spectrum of polyethylene can be used to estimate the nature and quantity of residual alkene unsaturation<sup>12</sup> present in the sample. The  $\gamma_{\text{w}}(\text{CH}_2)$  region ( $1000\text{--}800 \text{ cm}^{-1}$ ) of the IR spectrum is particularly suitable for alkene determination. Inspection of this region reveals the presence of three types of unsaturation: *vinyl* (**1**); *trans-internal* (**2**); and *pendant* (**3**) (see Scheme 1). The high-pressure radical polymerization process employed in the manufacture of LDPE causes the diversity of unsaturation with *pendant*  $\text{R}'\text{RC}=\text{CH}_2$  groups predominating.

## Results and Discussion

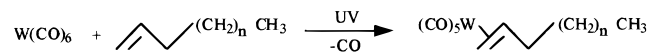
**Photolysis of  $\text{W}(\text{CO})_6$  in LDDEL PE Blend.** The FTIR spectrum of  $\text{W}(\text{CO})_6$ , thermally impregnated into LDDEL PE film (Figure 1a) shows a single  $T_{1u}$   $\nu(\text{CO})$  band that is only slightly broader than that observed in hydrocarbon solution. UV photolysis ( $>300 \text{ nm}$ ) of  $\text{W}(\text{CO})_6$  in LDDEL PE for a few minutes at ambient temperatures generated a single photochemical product (Figure 1b) via reaction of photogenerated transient  $\text{W}(\text{CO})_5$  moieties with residual unsaturation in the polyethylene matrix. The unsaturation in LDDEL PE is mostly vinyl, and the product was therefore assigned to  $\text{W}(\text{CO})_5(\eta^2\text{-RCH}=\text{CH}_2)_{\text{PE}}$  [ $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$ ] (Scheme 2).

The relative intensities of the three  $\nu(\text{CO})$  IR bands of the photoproduct (weak ( $A_{1b}$ ), medium ( $A_{1a}$ ) and strong (E) [Figure



**Figure 1.** IR spectra showing changes in the  $\nu(\text{CO})$  region upon UV photolysis of  $\text{W}(\text{CO})_6$  in LDDEL PE film. The intense  $\text{W}(\text{CO})_6$  band disappears with concomitant generation of a set of three product bands characteristic of  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})$  and assigned to  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$  in the LDDEL PE. Note that the photochemical reaction does not proceed to completion. However, the presence of residual  $\text{W}(\text{CO})_6$  does not affect the subsequent reactions.

## Scheme 2



1b and Table 1]) are characteristic of  $\text{W}(\text{CO})_5(\text{alkene})$  complexes.<sup>14</sup> Organic solutions containing  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})$  complexes have previously been reported to be colorless or pale yellow,<sup>15</sup> in contrast to the strong colors of  $\text{W}(\text{CO})_5(\text{X})$  (X = oxygen- or nitrogen-donating ligand) solutions.<sup>22</sup> After photolysis, the  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$  species gave the polyethylene film a distinct straw color. By contrast, photolysis of a *pure* polyethylene film led to no color change, even over extended periods.

### Isomerization of Alkene Bonds in LDDEL Polyethylene.

Prolonged photolysis of  $\text{W}(\text{CO})_6$  in the LDDEL PE system gave rise to a second set of  $\nu(\text{CO})$  bands, with a concomitant decay of the initial mono-alkene photoproduct and limited regeneration of  $\text{W}(\text{CO})_6$  (Figure 2).  $\text{W}(\text{CO})_6$  is an efficient photocatalyst for alkene isomerization<sup>15,23</sup> and the new product bands were identified by comparison with model alkene compounds [e.g.,  $\text{W}(\text{CO})_5(\eta^2\text{-trans-hex-2-ene})$ , Table 1]. The spectral changes reflect the isomerization of vinyl end groups in the polyethylene chain. Indeed, model experiments described below will demonstrate that the alkene moiety is effectively shifted along the polymer backbone into a *trans-internal* configuration (Scheme 3).




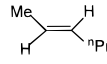


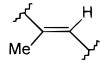
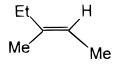
To enhance the isomerization yield, photolysis was performed at elevated temperatures (60 °C). Under these conditions, the initial photoproduct,  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$ , was more rapidly converted ( $t_{1/2} \sim 30 \text{ min}$ ) to the *trans-internal* product,  $\text{W}(\text{CO})_5(\eta^2\text{-RCH}=\text{CHR})_{\text{PE}}$  [ $\text{W}(\text{CO})_5(\eta^2\text{-trans-internal})_{\text{PE}}$ ]. The latter species was more thermally labile than  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$ , and

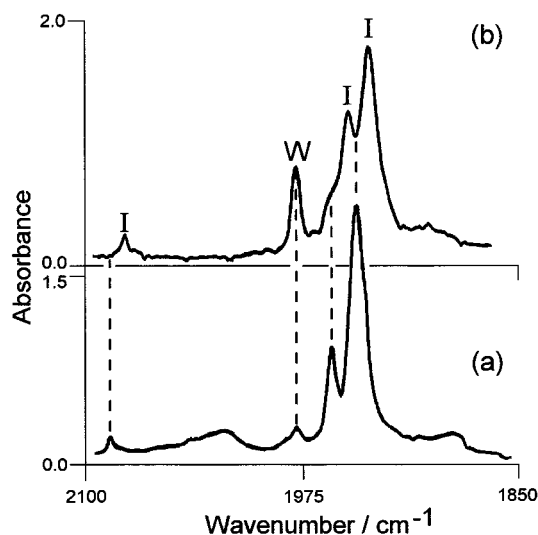
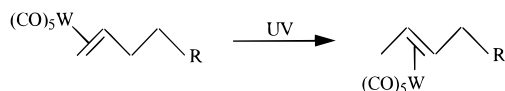
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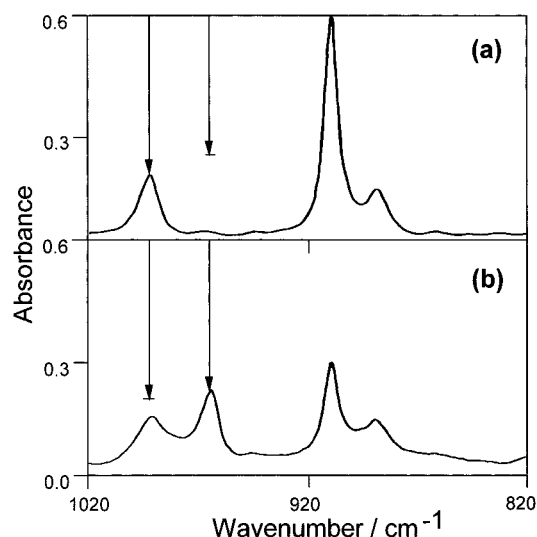
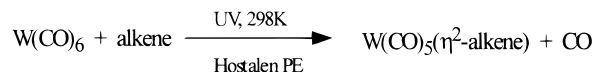
**Table 2.** Comparison of Wavenumbers of  $W(CO)_5(\eta^2\text{-polyethylene})$  Species and  $W(CO)_5(\eta^2\text{-alkene})$  Model Complexes Isolated in Hos GUR

								
	1	1'	2	2'	3	3'	4	4'
$(RCH=CH_2)_{(LDDEL\ PE)}, \mathbf{1}$ ( <i>vinyl</i> )				2080.8 (w)		2080.8 (w)		hex-1-ene, $\mathbf{1}'$
$(RHC=CHR')_{(isom\ LDDEL)}, \mathbf{2}$ ( <i>trans-internal</i> )			1961.7 (m)	1948.0 (s)		1962.3 (m)		<i>trans</i> -hex-2-ene, $\mathbf{2}'$
$(RR'C=CH_2)_{(LDPE)}, \mathbf{3}$ ( <i>pendant</i> )			2078.2 (w)	1958.2 (m)		2078.5 (w)		2-ethylbut-1-ene, $\mathbf{3}'$
$(RMeC=CHR')_{(isom\ LDPE)}, \mathbf{4}$ ( <i>trisubstituted trans-internal</i> )			1944.8 (s)	2076.7 (w)		1944.5 (s)		3-methylpent-2-ene, $\mathbf{4}'$
			1953.4 (m)	1941.8 (s)		1953.9 (m)		
			2075.3 (w)	1951.4 (m)		2075.0 (w)		
			1939.7 (s)	1939.4 (s)		1939.4 (s)		

**Figure 2.** FTIR spectra recorded after photolysis of the  $W(CO)_6$  impregnated into LDDEL PE system. (a) The  $\nu(CO)$  bands of the initial photoproduct  $W(CO)_5(\eta^2\text{-vinyl})_{PE}$ . (b) During extended photolysis, these bands decay with concomitant appearance of a second  $W(CO)_5(\eta^2\text{-alkene})$  type product assigned to  $W(CO)_5(\eta^2\text{-trans-internal})$  (bands labeled I). There is also some regeneration of  $W(CO)_6$  (bands labeled W).**Scheme 3**

was observed to decay completely in a matter of minutes by loss of the  $W(CO)_5$  moiety. This thermal lability is analogous to the behavior observed with the  $CpMn(CO)_2(\eta^2\text{-alkene})_{PE}$ .<sup>2</sup> This photoisomerization process was repeated three times with fresh  $W(CO)_6$  in the *same* polyethylene sample to maximize the yield of the isomerized alkene. The overall change in the unsaturation of the LDDEL PE is shown by the change in relative intensities of the  $\gamma_w(CH_2)$  infrared bands (Figure 3). The concentration of vinyl groups in the irradiated PE was reduced significantly, while *trans-internal* alkene groups, previously undetected in LDDEL PE, were now clearly observed.<sup>24</sup>

**Modeling the Unsaturation in LDDEL PE.** To identify the  $W(CO)_5(\eta^2\text{-alkene})_{PE}$  complexes, a range of  $W(CO)_5(\eta^2\text{-alkene})$  model complexes was generated in situ in Hostalen GUR PE samples. Hostalen GUR PE has a very low degree of unsaturation and is therefore unreactive.<sup>2</sup> The polymer environment

**Figure 3.** FTIR spectra of the  $\gamma_w(CH_2)$  region of LDDEL PE: (a) prior to isomerization, dominant bands are *vinyl* species, and (b) after isomerization, these bands have decreased in intensity and a new band associated with the *trans-internal* alkene bonds is observed.**Scheme 4**(alkene = hex-1-ene, 2-Et-but-1-ene, *trans*-hex-2-ene, 3-Me-pent-2-ene)

in LDDEL PE was modeled by using Hostalen PE impregnated with  $W(CO)_6$  and then doped with the appropriate low molecular weight alkene prior to photolysis. (Scheme 4)

Doping the Hostalen PE with the different alkenes had no measurable effect on the position or line width of the  $\nu(CO)$  band of  $W(CO)_6$ , which was coincident with its position in LDDEL PE. There were significant differences, however, in the  $\nu(CO)$  bands of the various  $W(CO)_5(\eta^2\text{-alkene})$  products, generated by UV irradiation of the doped films (Table 1). It is well-known that the positions of the  $\nu(CO)$  bands of metal

(24) Extended photolysis of such mono-olefin complexes in organic solution leads to *trans* bis-olefin complexes. In LDDEL PE, the alkene bonds are located at the end of very long polymer chains and as such their movement relative to one another is severely restricted. Thus, once a mono-alkene complex,  $W(CO)_5(\eta^2\text{-RCH=CH}_2)$  forms, the opportunity to diffuse through the polymer matrix to a second site of unsaturation is very limited. Surprisingly, a single, weak  $\nu(CO)$  band is observed, which by comparison to known *trans* bis-alkene complexes may be assigned to the bis-polyethylene complex,  $W(CO)_4(RCH=CH_2)_2$ , Table 1. However, the major product of extended photolysis is that of isomerization.

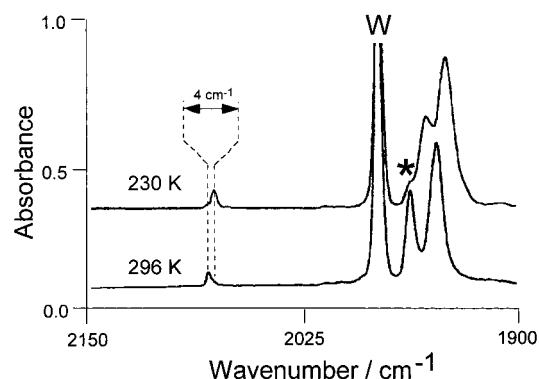
carbonyl species are highly sensitive to the nature and structural features of other ligands bound to the metal center.<sup>2,14,25</sup> The variation in the  $\nu(\text{CO})$  band positions observed for the different model  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})$  complexes in the Hostalen PE matrix reflects the structural differences in the ligated alkenes.

It is clear (Table 1) that the  $\nu(\text{CO})$  band positions for the model complex  $\text{W}(\text{CO})_5(\eta^2\text{-hex-1-ene})$  are in excellent agreement with those of the primary photolysis product of  $\text{W}(\text{CO})_6$  and LDDEL PE, supporting the assignment of this species as  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$ . Similarly, the  $\nu(\text{CO})$  band positions for the  $\text{W}(\text{CO})_5(\eta^2\text{-hex-2-ene})$  complex correspond very closely with those of the secondary (isomerization) photoproduct,  $\text{W}(\text{CO})_5(\eta^2\text{-trans-internal})_{\text{PE}}$ . Our findings are consistent with studies of the  $\text{W}(\text{CO})_6$ -catalyzed photoisomerization of low molecular weight alkenes in alkane solution,<sup>15</sup> although in contrast to this earlier work, no evidence for *trans* to *cis* isomerization was observed in our experiments.

Further independent confirmation was obtained by use of the probe molecule  $\text{CpMn}(\text{CO})_3$  for the photochemical generation of  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  species<sup>2</sup> in LDDEL PE films both *before* and *after* isomerization by  $\text{W}(\text{CO})_6$ . In LDDEL PE before isomerization, a single species was generated which could be assigned to  $\text{CpMn}(\text{CO})_2(\eta^2\text{-vinyl})_{\text{PE}}$  (i.e., the polymer contained predominantly vinyl unsaturation). By contrast, photolysis of  $\text{CpMn}(\text{CO})_3$  in an isomerized sample of LDDEL PE gave rise to  $\nu(\text{CO})$  bands which could be assigned to  $\text{CpMn}(\text{CO})_2(\eta^2\text{-trans-internal})_{\text{PE}}$ . Comparison with two model compounds showed that the FTIR spectrum for this polymer-bound species correlated more closely with the spectrum of  $\text{CpMn}(\text{CO})_2(\eta^2\text{-trans-hex-2-ene})$  than that of  $\text{CpMn}(\text{CO})_2(\eta^2\text{-trans-hex-3-ene})$ . This may suggest that isomerization results in the movement of the site of unsaturation in the polymer by only *one* bond along the polymer backbone. However, the variations in wavenumber for the carbonyl bands of the various  $\text{W}(\text{CO})_5(\eta^2\text{-internal alkene})$  and  $\text{CpMn}(\text{CO})_2(\eta^2\text{-internal alkene})$  model complexes are very small,<sup>2</sup> and we cannot therefore make a firm assignment from these data. It is possible that the double bond is isomerized further along the length of the polymer chain, although verification of this would be extremely difficult.

**Photoisomerization of Commercial Low-Density PE.** We now describe the application of this photoisomerization technique to a commercially available LDPE material and the subsequent scale-up of this process to gram quantities of LDPE powder. The wavenumber of the  $T_{1u}$   $\nu(\text{CO})$  IR band of  $\text{W}(\text{CO})_6$  in the LDPE film was identical with that in LDDEL PE, Table 1. UV photolysis at ambient temperatures again produced a single photochemical product, although the  $\nu(\text{CO})$  band positions were lower in frequency than those seen in LDDEL PE (Table 1). This new product was assigned to the species  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$ , formed by coordination with the predominantly *pendant* alkene bonds found in LDPE. Comparison with the relevant model complex,  $\text{W}(\text{CO})_5(2\text{-ethylbut-1-ene})$  (Table 1) further supported this assignment.

A second set of product IR bands continued to increase in intensity when the UV lamp was switched off, accompanied by depletion of the bands associated with  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$ . The new  $\nu(\text{CO})$  bands were identical with those observed for  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})$  in LDDEL PE (Table 1). This process occurred much faster than the isomerization process observed for LDDEL PE. Moreover, detailed analysis by FTIR and the use of the  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  diagnostic probe showed *no* evidence of any changes in the type of unsaturation in the LDPE (i.e., isomerization had not occurred).

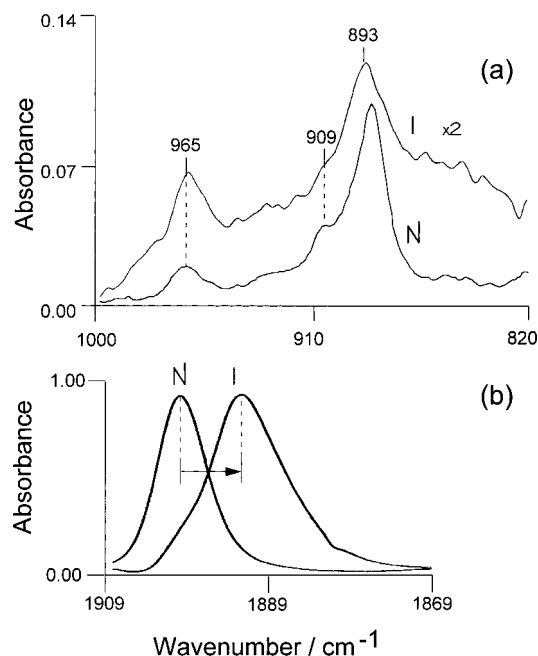


**Figure 4.** FTIR spectra in the  $\nu(\text{CO})$  region of an LDPE film that initially contains predominantly *pendant* unsaturation. The film has been impregnated with  $\text{W}(\text{CO})_6$  and irradiated at low temperatures. Upper spectrum: FTIR bands assigned to the first photoproduct  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$  at 230 K. Lower spectrum: The UV lamp was turned off, and the PE film was then warmed from 230 K to room temperature. A smooth conversion of  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$  to  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$  was observed. The band at  $1980.9\text{ cm}^{-1}$  (labeled W) indicates residual  $\text{W}(\text{CO})_6$ . The band labeled with an asterisk indicates a low initial concentration of  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$  present at 230 K.

LDPE contains mostly *pendant* alkene bonds, and also a smaller but significant concentration of *vinyl* alkene bonds. In solution, the rate of formation of  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})$  complexes is linearly dependent on olefin concentration<sup>25</sup> and so the major *kinetic* photochemical product in LDPE is likely to be  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$ . However, because of steric crowding, the *pendant* complexes are less stable than the corresponding *vinyl* complexes<sup>2</sup> and  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$  was therefore formed as the major *thermodynamic* product. This process would involve the detachment of the  $\text{W}(\text{CO})_5$  fragment from a *pendant* alkene bond, followed by thermal reaction with a neighboring *vinyl* bond.

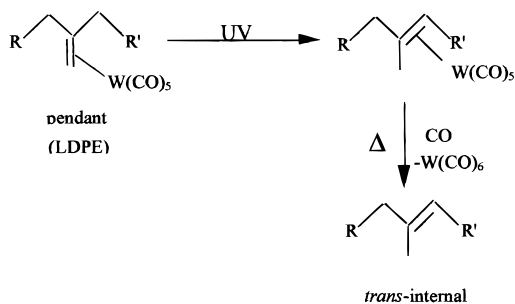
The relationship between the thermodynamic and kinetically favored products was further investigated by low-temperature polymer matrix experiments.<sup>6</sup> A LDPE film was thermally impregnated with  $\text{W}(\text{CO})_6$  and cooled to 21 K. UV irradiation led to depletion of  $\text{W}(\text{CO})_6$  and a set of  $\nu(\text{CO})$  product bands were observed which could be assigned to the 16-electron fragment  $\text{W}(\text{CO})_5$ , isolated in the cryogenic PE matrix (Table 1). Upon warming to 110 K, the  $\text{W}(\text{CO})_5$  fragment re-combined thermally with CO to regenerate  $\text{W}(\text{CO})_6$ ; under these conditions, no reaction of the  $\text{W}(\text{CO})_5$  fragment with alkene bonds was observed. Photolysis of the *same* LDPE film at a higher temperature (230 K) yielded  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$  as the major product (i.e., the same kinetic product that was formed at room temperature). At 230 K, this species was found to be stable indefinitely. On warming the polymer film to 296 K, however, a smooth conversion from  $\text{W}(\text{CO})_5(\eta^2\text{-pendant})_{\text{PE}}$  to the thermodynamic product,  $\text{W}(\text{CO})_5(\eta^2\text{-vinyl})_{\text{PE}}$ , was observed (Figure 4). No change in the relative concentrations of the two alkene species was detected (i.e., no isomerization took place). By way of comparison, the intermolecular migration of  $\text{W}(\text{CO})_5$  from one olefin species to another has been observed in alkane solution at room temperature,<sup>15</sup> where  $\text{W}(\text{CO})_5(\eta^2\text{-pent-1-ene})$ , an  $\eta^2\text{-vinyl}$  species, was reported to be the most stable of a variety of  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})$  complexes.

**Isomerization of Alkene Bonds in a Low-Density Polyethylene Film.** Prolonged photolysis at *ambient* temperature generated a third type of  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})_{\text{PE}}$  species in LDPE, with  $\nu(\text{CO})$  bands at lower wavenumber than those of either the *pendant* or *vinyl* complexes. This species was assigned as  $\text{W}(\text{CO})_5(\text{RMeC}=\text{CHR}')$  by analogy with the model complex



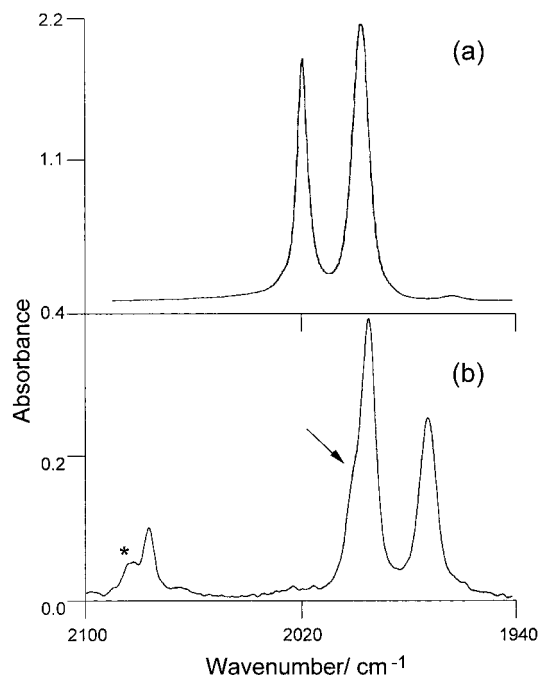
**Figure 5.** (a) DRIFTS spectrum of isomerized LDPE powder (labeled I). After isomerization the butyl branching band<sup>42</sup> at 893  $\text{cm}^{-1}$  is revealed. This band was obscured by the band at 888  $\text{cm}^{-1}$  associated with the *pendant* alkene groups. The dominant alkene at 965  $\text{cm}^{-1}$  is the *trans-internal* isomerization product. The DRIFTS spectrum of Native LDPE (labeled N) is shown for comparison. (b) After melt pressing of these LDPE powders into thin films and impregnation/irradiation with  $\text{CpMn}(\text{CO})_3$ . The FTIR spectra of the  $\nu(\text{CO})$  bands of  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  show a clear difference in the Native and Isomerized species. In Native LDPE, *pendant* groups predominate, in the isomerized LDPE there is a shift in  $\nu(\text{CO})$  band positions indicating the presence of substantial *tris-substituted trans-internal* unsaturation.

#### Scheme 5



$\text{W}(\text{CO})_5(3\text{-methylpent-2-ene})$  (Table 1), indicating that photoisomerization of the disubstituted pendant double bond to the trisubstituted *trans-internal* double bond had occurred (Scheme 5).

**Photoisomerization of Commercial LDPE Powder on a Larger Scale.** Modification of LDPE powder, as opposed to melt-pressed films, enables a greater surface area of the polymer to be exposed to UV irradiation.<sup>13</sup> Moreover, the supercritical fluid extraction of residual  $\text{W}(\text{CO})_6$  from the irradiated powder after photolysis is considerably more efficient. Diffuse Reflectance Infrared Spectroscopy (DRIFTS) is a sensitive probe for the study of modified LDPE powders. The DRIFTS spectrum of the isomerized LDPE powder (Figure 5a) showed a dramatic drop in the intensity of pendant alkene bands after UV photolysis, accompanied by the growth of an IR band associated with *trans-internal* alkene bonds at 965  $\text{cm}^{-1}$ . These results are in excellent agreement with the isomerization observed in the polymer films. After  $\text{scCO}_2$  extraction<sup>13,26,27</sup> of the  $\text{W}(\text{CO})_6$



**Figure 6.** (a) FTIR spectrum of  $\text{Fe}(\text{CO})_5$  in an LDPE film showing the expected  $\nu(\text{CO})$  bands {2021.3 ( $A_2''$ ), 1997.7 ( $E'$ )  $\text{cm}^{-1}$ }. (b) After UV photolysis, four new  $\nu(\text{CO})$  bands can be seen which indicate the conversion to  $\text{Fe}(\text{CO})_4(\eta^2\text{-pendant})$ . One of these bands is present as a shoulder on the intense band at 1994.0  $\text{cm}^{-1}$  (arrowed).<sup>46,47</sup> The band labeled with an asterisk is tentatively assigned to formation of a low concentration of a trimeric species.

photocatalyst, the isomerized LDPE powder was then melt-pressed into a film. Careful comparison of the relative intensities of the  $\gamma_{\text{w}}(\text{CH}_2)$  bands for powder and for film showed that melt-pressing had no effect on the extent or nature of the unsaturation present in the LDPE films.

To corroborate further the isomerization process, probe complexes of the type  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  were generated photochemically in both native and isomerized LDPE films. In native LDPE, the  $\nu(\text{CO})$  bands of the  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  probe complex indicated predominantly *pendant* unsaturation, with a smaller concentration of *vinyl* groups, in agreement with the absorbance pattern in the  $\gamma_{\text{w}}(\text{CH}_2)$  region of the IR spectrum. By contrast, the major type of unsaturation in the isomerized PE film (Figure 5b) arose from the trisubstituted *trans-internal* species.<sup>2</sup> These results demonstrate that our methods can be extended to the efficient photoisomerization of gram quantities of commercial LDPE.

**The  $\text{Fe}(\text{CO})_5$ -Catalyzed Photoisomerization and Hydrogenation of PE.** Iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , is a volatile, orange liquid under ambient conditions, and is known to be an efficient isomerization and hydrogenation agent for alkenes.  $\text{Fe}(\text{CO})_5$  was impregnated into two different types of PE film at room temperature under reduced pressure. The infrared spectra of  $\text{Fe}(\text{CO})_5$ -doped LDPE and BPPE were identical, and similar to spectra of  $\text{Fe}(\text{CO})_5$  in cyclohexane solution,<sup>28</sup> with two  $\nu(\text{CO})$  bands occurring at 2021.3 ( $A_2''$ ) and 1997.7  $\text{cm}^{-1}$  ( $E'$ ) [Figure 6a].

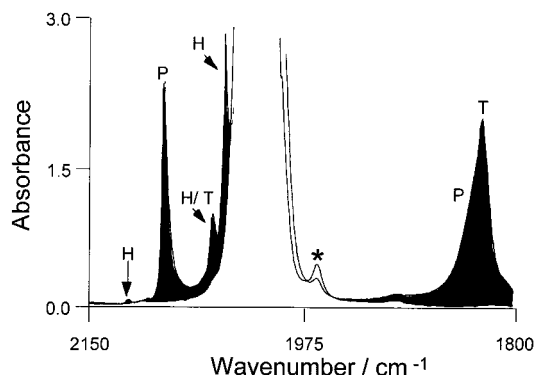
**The Photochemistry of  $\text{Fe}(\text{CO})_5$  in Commercial LDPE.** A 250  $\mu\text{m}$  film of LDPE, doped with  $\text{Fe}(\text{CO})_5$ , was irradiated

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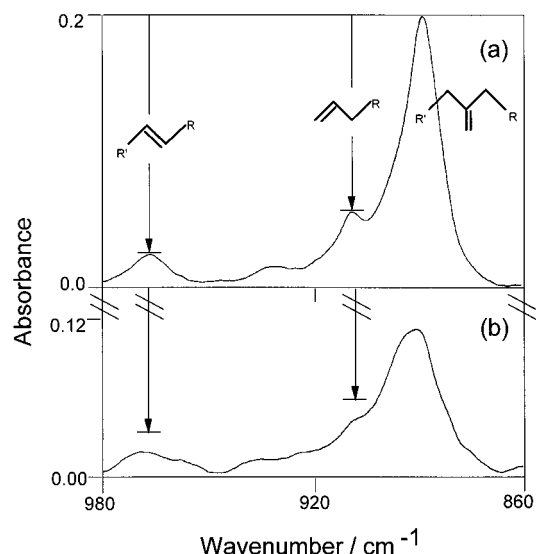


**Figure 7.** The FTIR spectrum of  $\text{Fe}(\text{CO})_5$  in LDPE at much higher concentration [ $\nu(\text{CO})$  bands off scale,  $^{13}\text{C}$  satellite denoted by an asterisk]. Following extended photolysis (2 h) under  $\text{H}_2$  (1000 psi) at 25 °C new bands appear (colored black) in the  $\nu(\text{CO})$  region. Bands labeled “H” correspond to  $\text{H}_2\text{Fe}(\text{CO})_4$ , those labeled “T” are assigned to  $\text{Fe}_3(\text{CO})_{12}$ , and “P” denotes bands assigned to the proposed  $\text{Fe}_3(\text{CO})_{11}(\eta^2\text{-alkene})_{\text{PE}}$  species. The consumption of  $\text{Fe}(\text{CO})_5$  during photolysis is clearly demonstrated by the fall in the  $^{13}\text{C}$  band intensity.

with UV light under an inert atmosphere of He (1000 psi) to replicate the high-pressure conditions encountered in the hydrogenation experiments. The parent  $\nu(\text{CO})$  bands decreased over a period of a few minutes, accompanied by formation of a set of product bands in the carbonyl stretching region (Figure 6b). The product bands (2075.6, 1994.0, and 1971.7  $\text{cm}^{-1}$ ) corresponded closely with those reported in a previous study of the UV photolysis of  $\text{Fe}(\text{CO})_5$  in polyethylene (2074, 1993, and 1973  $\text{cm}^{-1}$ ).<sup>9</sup> In that work, the product was tentatively assigned to a complex of  $\text{Fe}(\text{CO})_4$  with sites of unsaturation in the polymer. In view of our own work<sup>2</sup> with  $\text{CpMn}(\text{CO})_3$  and  $\text{W}(\text{CO})_6$ , we now confidently assign this product as  $\text{Fe}(\text{CO})_4(\eta^2\text{-alkene})_{\text{PE}}$ . Since *pendant* alkene bonds predominate in LDPE, the photoproduct was most likely  $\text{Fe}(\text{CO})_4(\eta^2\text{-pendant})_{\text{PE}}$ .

After UV photolysis, the  $\text{Fe}(\text{CO})_4(\eta^2\text{-pendant})_{\text{PE}}$  species decayed in the dark over a period of several hours. During this time, changes in the  $\gamma_{\text{w}}(\text{CH}_2)$  region of the IR spectrum (not illustrated) were observed which were analogous to the changes observed during the  $\text{W}(\text{CO})_6$ -catalyzed isomerization of *pendant* and *vinyl* double bonds to the internal alkenes (Figure 5).  $\text{Fe}(\text{CO})_5$  is well-known as an efficient alkene-isomerization photocatalyst,<sup>29</sup> and similar results were shown for the  $\text{Fe}(\text{CO})_5$ -catalyzed isomerization of short chain terminal alkenes to their internal isomers.<sup>30,31</sup> This isomerization occurs readily and has even been reported at temperatures as low as 77 K.<sup>29</sup>

**The Hydrogenation of Commercial LDPE Films.**  $\text{Fe}(\text{CO})_5$  is known to be an efficient photocatalyst for alkene hydrogenation.<sup>15,32</sup> To test for hydrogenation of residual alkenes in PE, thin films of  $\text{Fe}(\text{CO})_5$ -doped PE were exposed to high pressures of  $\text{H}_2$  and irradiated with UV light ( $>300$  nm) at temperatures in the range 25–60 °C. Several new bands were seen to grow almost immediately in the  $\nu(\text{CO})$  region of the IR spectrum (Figure 7). Three bands (2117.1, 2046.6, and 2036.3  $\text{cm}^{-1}$ ) can be assigned to  $\text{H}_2\text{Fe}(\text{CO})_4$  (cf. 2117, 2047, and 2036  $\text{cm}^{-1}$  for  $\text{H}_2\text{Fe}(\text{CO})_4$  in HDPE at 210 K<sup>6</sup>). The  $\nu(\text{CO})$  absorbance at 1824  $\text{cm}^{-1}$  lies in the region normally associated with *bridging* CO groups, and its broad, unsymmetrical nature suggests the



**Figure 8.** FTIR spectrum in the  $\gamma_{\text{w}}(\text{CH}_2)$  region of (a) native LDPE, showing the three types of unsaturation present in this polymer, predominantly *pendant* alkene bonds, and (b) after hydrogenation with  $\text{Fe}(\text{CO})_5$ . The FTIR bands of all of the alkene species have decreased in intensity. A broad feature at 891  $\text{cm}^{-1}$  assigned to the butyl branches in LDPE is revealed after hydrogenation.

presence of multiple  $\nu(\text{CO})$  bands in an unresolved envelope. The band at 1824  $\text{cm}^{-1}$  is very close to that reported<sup>33</sup> (1828  $\text{cm}^{-1}$ ) for triiron dodecacarbonyl ( $\text{Fe}_3(\text{CO})_{12}$ ). A terminal CO stretching band was also reported for this species<sup>30</sup> which would be obscured by the  $\text{H}_2\text{Fe}(\text{CO})_4$  band at 2046  $\text{cm}^{-1}$  in our experiments. The remaining terminal  $\nu(\text{CO})$  bands for  $\text{Fe}_3(\text{CO})_{12}$  would be similarly obscured by other absorptions. Furthermore, the irradiated LDPE film showed a deep green coloration and a pronounced maximum in the UV/visible spectrum at 603 nm, in good agreement with data for  $\text{Fe}_3(\text{CO})_{12}$  in hexane solution ( $\lambda_{\text{max}} = 605$  nm).<sup>30</sup> The formation of  $\text{Fe}_3(\text{CO})_{12}$  is perhaps unsurprising, since high concentrations of  $\text{Fe}(\text{CO})_5$  are known to favor trimer formation.<sup>34</sup>

An intense high-frequency band (2087.0  $\text{cm}^{-1}$ ) was also observed that followed exactly the growth and decay of the absorbance envelope centered at 1824  $\text{cm}^{-1}$ . This probably arises from a bridged, polynuclear complex. However, no corresponding band is reported for  $\text{Fe}_3(\text{CO})_{12}$  in heptane solution<sup>30</sup> or in cryogenic matrices,<sup>33</sup> nor does this band correlate with those reported for the dinuclear cluster,  $\text{Fe}_2(\text{CO})_9$ , in PE (2055, 2030  $\text{cm}^{-1}$ )<sup>9</sup> or with a simple  $\text{Fe}(\text{CO})_4(\eta^2\text{-alkene})$  complex with the polymer. UV photolysis (313 nm) of  $\text{Fe}_3(\text{CO})_{12}$  is known to lead to loss of CO and to generate a complex of the form  $\text{Fe}_3(\text{CO})_{11}\text{L}$  in the presence of a suitable ligand, L.<sup>35</sup> Hence, we tentatively assign the band at 2087.0  $\text{cm}^{-1}$  to coordination of the trimer species with residual unsaturation in the LDPE [i.e.,  $\text{Fe}_3(\text{CO})_{11}(\eta^2\text{-alkene})_{\text{PE}}$ ]. A weak band was in fact observed at 2087.0  $\text{cm}^{-1}$  in the previous control experiment where  $\text{Fe}(\text{CO})_5$  was irradiated under a high-pressure atmosphere of helium. The low intensity of this band was presumably a result of the much lower  $\text{Fe}(\text{CO})_5$  concentration in that experiment.

The effect of hydrogenation on the unsaturation in LDPE can be seen clearly by examining the relevant  $\gamma_{\text{w}}(\text{CH}_2)$  IR bending modes (Figure 8). The native LDPE contained a significant concentration of residual *pendant* alkene bonds. However,

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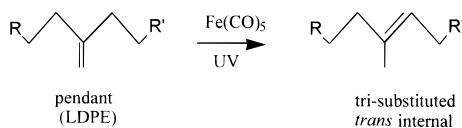
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## Scheme 6



photolysis led to a large decrease in this concentration via hydrogenation. The hydrogenated LDPE film was subsequently re-impregnated with fresh  $\text{Fe}(\text{CO})_5$  and the hydrogenation process repeated. No further reduction in unsaturation was observed. To probe the extent and nature of hydrogenation, the reduced film was impregnated with  $\text{CpMn}(\text{CO})_3$  from heptane solution. UV photolysis yielded bands at 1955 and 1894  $\text{cm}^{-1}$  as the major product, characteristic of a  $\text{CpMn}(\text{CO})_2$  complex of trisubstituted *trans*-internal alkenes. This type of alkene was not detected in native LDPE and must therefore have arisen from isomerization of *pendant* groups. Scheme 6

As described above,  $\text{Fe}(\text{CO})_5$  can cause isomerization of *pendant* alkenes to the trisubstituted *trans*-internal isomer. It is likely that this isomerization process will still occur in the presence of  $\text{H}_2$ , in competition with hydrogenation. This is a reasonable supposition since the same precursor,  $\text{Fe}(\text{CO})_4(\eta^2\text{-alkene})_{\text{PE}}$ , is common to *both* processes.<sup>36</sup> Indeed, when  $\text{CpMn}(\text{CO})_3$  was used to characterize the residual unsaturation after the PE had been treated with  $\text{Fe}(\text{CO})_5/\text{H}_2$ , the IR spectra (not illustrated) showed bands of  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  complexes of both *vinyl* and *pendant* alkenes, but at much lower intensities than were formed in native LDPE. This indicates that much of the *vinyl* and *pendant* unsaturation had therefore been removed by a combination of isomerization and hydrogenation. After hydrogenation, the trisubstituted *trans*-internal alkene moieties were present in relatively higher concentration than *vinyl* or *pendant* because they are the favored products of isomerization. It is also possible that *trans*-internal alkene bonds were less readily hydrogenated, since trisubstituted moieties are sterically more hindered and their heat of hydrogenation is smaller than for *vinyl* and *pendant* isomers.<sup>37</sup>

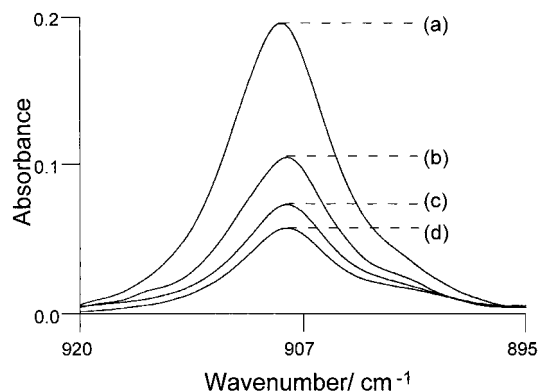
The efficiency of the hydrogenation process was estimated by comparison of the integrated absorbances of the  $\nu(\text{CO})$  product bands of all  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  complexes in LDPE before and after photolysis. Assuming that the extinction coefficients of the  $\nu(\text{CO})$  bands are roughly equal for all  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  complexes, it was possible to calculate a hydrogenation efficiency of approximately 45%. Three factors which may limit hydrogenation of LDPE are the formation of catalytically inactive polynuclear compounds (e.g.,  $\text{Fe}_3(\text{CO})_{12}$ ),<sup>38</sup> the isomerization of the predominant *pendant* groups to less readily hydrogenated trisubstituted *trans*-internal alkenes, or simply the inaccessibility of some of the olefinic moieties within the crystalline regions of the PE structure. In an attempt to raise the hydrogenation efficiency, the hydrogenation of BPPE was explored.

**The Hydrogenation of High-Density Polyethylene (BPPE).** The IR spectrum of BPPE revealed almost exclusively *vinyl* alkene unsaturation, with an approximate concentration of 0.06  $\text{mol dm}^{-3}$ . Isomerization of the vinyl groups by  $\text{Fe}(\text{CO})_5$  should therefore lead only to disubstituted *trans*-internal alkenes, which are more susceptible to hydrogenation than the trisubstituted counterparts formed in LDPE. Thus, under equivalent conditions, the hydrogenation efficiency might be expected to

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(37) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn & Bacon: Boston, 1983.

(38) Laine, R. M. *J. Mol. Catal.* **1982**, *14*, 137.



**Figure 9.** Effect of different impregnation methods on efficiency of hydrogenation. FTIR spectra of the  $\gamma_w(\text{CH}_2)$  mode of *vinyl* groups in BPPE film: (a) untreated BPPE, (b) liquid  $\text{Fe}(\text{CO})_5$  impregnation (54% hydrogenation efficiency), (c) *n*-heptane assisted impregnation (75%), and (d)  $\text{CCl}_4$  assisted impregnation (82%).

increase. Since the inactive  $\text{Fe}_3(\text{CO})_{12}$  trimer is known to decompose thermally to transient  $\text{Fe}(\text{CO})_4$  species at elevated temperatures,<sup>30</sup> the hydrogenation of BPPE was carried out at 60 °C to inhibit trimer formation. Note that this temperature increase should have a relatively small effect on the polymer itself, since no phase transitions occur in low-density polyethylene in the temperature range 0–100 °C.<sup>39</sup>

BPPE film (250  $\mu\text{m}$ ) was thermally impregnated with  $\text{Fe}(\text{CO})_5$  under reduced pressure and irradiated with UV light under an atmosphere of  $\text{H}_2$  (1000 psi) at 60 °C. The IR bands in the  $\nu(\text{CO})$  region were again totally absorbing; however, at this higher temperature no modes due to polynuclear clusters were detected on photolysis. Spectral changes in the  $\gamma_w(\text{CH}_2)$  region (Figure 9) demonstrated that hydrogenation was indeed occurring. Since native BPPE contains almost exclusively *vinyl* unsaturation, the extent of hydrogenation could be estimated simply by comparison of the vinyl rocking mode at 909  $\text{cm}^{-1}$  before and after hydrogenation. The calculated hydrogenation efficiency (54%) represented only a very modest improvement over that achieved in LDPE (45%). Repetition of the hydrogenation process did not increase the efficiency beyond 54%.<sup>40</sup> This yield was still somewhat disappointing in comparison with the excellent hydrogenation efficiency of  $\text{Fe}(\text{CO})_5$  reported in both gas<sup>41</sup> and liquid<sup>29</sup> phases.

Photolysis of the  $\text{CpMn}(\text{CO})_3$  probe in the hydrogenated BPPE film confirmed the presence of a significant concentration of residual *vinyl* unsaturation. Clearly, the  $\text{CpMn}(\text{CO})_3$  was able to access and complex with alkene groups in BPPE, even after exhaustive hydrogenation, suggesting that these alkene groups were accessible to  $\text{CpMn}(\text{CO})_3$  but not to  $\text{Fe}(\text{CO})_5$ . These residual alkene species are unlikely to reside in the *crystalline* phase of the polymer since these would tend to be inaccessible to *all* dopant species.

The difference in accessibility of these sites was probably a result of the impregnation method. Neat  $\text{Fe}(\text{CO})_5$  (a *liquid* under ambient conditions) was perhaps not such an effective swelling

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(40) To investigate any detrimental effects to the hydrogenation process caused by film thickness, a thinner, 100  $\mu\text{m}$  film of BPPE was prepared and impregnated with  $\text{Fe}(\text{CO})_5$  at reduced pressure. If the 250  $\mu\text{m}$  polymer film was in some way preventing penetration of UV photons to its core and hence lowering hydrogenation efficiency, the use of a thinner film should improve the extent of olefinic reduction. Hydrogenation was effected as described above, with a reduction of 52% of the vinyl concentration. This corresponded exactly (within experimental error) with the efficiency achieved in the thicker films, indicating that the UV light was able to completely penetrate the 250  $\mu\text{m}$  films, even when saturated with  $\text{Fe}(\text{CO})_5$ .

(41) Miller, M. E.; Grant, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 4635.



agent as the heptane solution used to impregnate  $\text{CpMn}(\text{CO})_3$  (which is a crystalline solid). The extent to which a liquid can swell PE is dependent upon the chemical nature of that liquid: <sup>42,43</sup> heptane, being chemically similar to polyethylene, causes significant swelling of the polymer matrix whereas  $\text{Fe}(\text{CO})_5$  appears to be less efficient in this respect. Hence, we carried out the impregnation of  $\text{Fe}(\text{CO})_5$  in the presence of a swelling solvent (heptane or carbon tetrachloride) followed by hydrogenation of BPPE to increase the efficiency of the hydrogenation process.

**Hydrogenation in Solvent-Swollen BPPE Films.** A BPPE film (250  $\mu\text{m}$ ) was initially swollen in *n*-heptane for 1 h, followed by impregnation from a 1:1 (v/v) solution of  $\text{Fe}(\text{CO})_5$  in *n*-heptane. After evaporation of residual heptane from the film, the hydrogenation process was repeated under  $\text{H}_2$  (1000 psi) at 60 °C. This procedure led to a significant improvement (Figure 9) in efficiency (75% hydrogenation). When the procedure was repeated using carbon tetrachloride (a particularly effective solvent for swelling PE), a maximum hydrogenation efficiency of 82% was observed. The polymers were further characterized by impregnation and speciation with the  $\text{CpMn}(\text{CO})_3$  probe. In complete contrast to previous experiments, no FTIR bands associated with  $\text{CpMn}(\text{CO})_2(\eta^2\text{-alkene})_{\text{PE}}$  species were detectable, even after prolonged photolysis. By comparison, a film of native BPPE irradiated in the presence of  $\text{CpMn}(\text{CO})_3$  showed rapid growth of  $\nu(\text{CO})$  bands associated with the species  $\text{CpMn}(\text{CO})_2(\eta^2\text{-vinyl})_{\text{PE}}$ , which became very intense after only 20 min of photolysis.

The use of swelling agents would not be expected to affect the degree of crystallinity in the polyethylene sample<sup>44</sup> but it does increase the flexibility of the polymer chains by occupying and expanding the free volume between them.<sup>43</sup> This in turn aids the diffusion of dopant species (such as  $\text{Fe}(\text{CO})_5$ ) through the polyethylene matrix, which requires extraordinary chain motions by the host polymer.<sup>45</sup> It is likely that the increase in hydrogenation efficiency was caused by increased diffusion during reaction and/or increased catalyst loading prior to reaction.

## Conclusions

In this paper, we have demonstrated that both  $\text{W}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$  can be employed as efficient photoisomerization catalysts in a range of different PE samples. As outlined previously,<sup>2</sup>  $\text{CpMn}(\text{CO})_3$  was employed as a sensitive probe molecule for the analytical speciation of unsaturation in PE films, in conjunction with low molecular weight substituted alkene model compounds.  $\text{W}(\text{CO})_6$  was found to isomerize

alkene bonds in PE, and the process was found to follow established literature precedent for the photoisomerization of substituted alkenes. The thermal stability of the  $\text{W}(\text{CO})_5(\eta^2\text{-alkene})_{\text{PE}}$  complexes was strongly influenced by the substitution pattern on the coordinate alkene bond. Gram quantities of LDPE powder were photoisomerized by this method, and subsequently purified by removal of organometallic catalyst using supercritical fluid extraction.  $\text{Fe}(\text{CO})_5$  was found to be an active catalyst for both the photoisomerization and hydrogenation of PE samples. The maximum extent of hydrogenation was dependent on the type of unsaturation in the sample and the reaction conditions (e.g., temperature). Moreover, it was found that the degree of hydrogenation could be strongly influenced by the choice of impregnation solvent, presumably due to an increase in loading and/or mobility of the catalytic species. Supercritical  $\text{CO}_2$  was used to extract solvent and organometallic catalyst residues from the polyethylene samples. Future work will involve the extension of these methods to the modification and subsequent purification of polymeric materials for specialized applications.

The major motivation for these studies of PE has been to remove unsaturation which would otherwise interfere with the use of PE as a matrix for studying the photochemistry of organometallic compounds.<sup>3</sup> In this context, our failure to reduce all of the olefinic C=C bonds in the PE is probably not a serious limitation. The use of PE as a matrix involves the impregnation of organometallic compounds into a PE disk. Almost certainly, this impregnation only occurs in the noncrystalline (interlamellar) regions of the PE, the same regions where most of the C=C bonds are to be found. However, not all of these noncrystalline regions will necessarily be accessible to impregnation in a particular sample. Our results have shown that it is possible to reduce PE to such an extent that subsequent impregnation of  $\text{CpMn}(\text{CO})_3$  leads to almost no detectable reaction between  $\text{CpMn}(\text{CO})_3$  and residual C=C bonds in the PE. *Therefore, we have shown that it is possible to reduce all of the accessible C=C bonds and to prepare a PE matrix that is effectively inert.* This is important because it opens up a potentially wide range of mechanistic and photochemical experiments. The fact that we can process intact PE disks, after they have been melt-pressed, means that we have the ability to treat and isomerize small quantities of speciality polymers for specific experiments rather than needing to process large quantities of material.

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