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Photochemical Generation of Polymer-Bound CpMn(CO)$_2$(η^2-C=C) Complexes in Polyethylene Film: A Diagnostic Probe for Investigating the Unsaturation of the Polymer

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Abstract: CpMn(CO)$_3$ (Cp = η^5-C_5H_5) is impregnated into polyethylene (PE) film using either supercritical CO_2 (scCO_2) or *n*-heptane. UV photolysis of the impregnated film at 21 K leads to formation of the coordinatively unsaturated intermediate CpMn(CO)$_2$, with ν(C–O) bands similar to those observed in solid CH_4 matrices and frozen hydrocarbon glasses. By contrast, UV irradiation at room temperature leads to the formation of a stable species containing the CpMn(CO)$_2$ moiety. This compound is polymer-bound and is difficult to extract by either scCO_2 or *n*-heptane. On a semiquantitative level, the overall yield of this compound, identified as CpMn(CO)$_2$(η^2-C=C), increases with the degree of unsaturation of the PE sample; larger amounts are formed in low-density PE than in Hostalen GUR 415 PE, which has a very small degree of unsaturation. The formation of the polymer-bound species can be suppressed completely by high pressures of CO. In the presence of other gases, e.g., H_2 or N_2, there is competitive formation of CpMn(CO)$_2$(η^2-C=C) and CpMn(CO)$_2$(X_2) compounds (X = H or N). A more detailed analysis of the IR spectra, obtained with a range of selected samples of PE, shows that the precise wavenumbers of the ν(C–O) bands of CpMn(CO)$_2$(η^2-C=C) depend on the relative amounts of *vinyl* (terminal), *pendant*, and *internal* C=C bonds in the particular PE sample. This assignment has been confirmed by a new technique whereby model CpMn(CO)$_2$(η^2-alkene) complexes are generated *in situ* in Hostalen GUR 415 PE and their ν(C–O) spectra are compared with those of the corresponding polymer-bound species. It is shown that the ν(C–O) bands of CpMn(CO)$_2$(η^2-C=C) provide a convenient diagnostic tool for establishing the unsaturation of different PE polymers. The different CpMn(CO)$_2$(η^2-C=C) complexes studied have significantly different reactivity toward, for example, N_2 (internal > pendant > vinyl), which can be rationalized on the degree of π back-donation. Although PE has considerable promise as a matrix for low-temperature experiments, the unsuspected presence of olefinic C=C groups in a particular sample of PE will give rise to artifacts. Our results provide a simple and rapid means of identifying such samples (and avoiding them) before the start of more complicated low-temperature experiments.

Introduction

The impregnation of organometallics into polymers offers a wide range of opportunities from the preparation of new composites[1] to the activation of the polymers themselves.[2] For the more volatile organometallics, the vapor pressure of the compound has often been sufficient for successful impregnation.[3] Less volatile compounds have usually been impregnated by use of a volatile solvent (e.g., heptane) or by casting films from solutions containing both polymer and organometallic.[4]

The use of supercritical fluids has added a new dimension to the impregnation of polymers. Fluids such as supercritical CO_2 (scCO_2) are relatively good solvents for nonpolar organometallics, and their gaslike properties mean that polymers can be impregnated without leaving *any solvent residues*.[5] We have already exploited this effect for the C–H activation of low- and high-density polyethylene (LDPE and HDPE).[6] More recently, we have used FTIR spectroscopy to monitor the impregnation of CpMn(CO)$_3$ (Cp = η^5-C_5H_5) into polyethylene (PE). This work has shown not only that the impregnation occurs surprisingly rapidly[7] but also that the distribution of CpMn(CO)$_3$ is relatively uniform, even for samples several millimeters thick.[8]

Although scCO_2 is extremely efficient for impregnation, CpMn(CO)$_3$ can also be impregnated quite effectively into PE with more conventional solvents, e.g., *n*-heptane. In this paper, we concentrate on the behavior of CpMn(CO)$_3$ once it is inside the PE. In particular, we explore the effect of the PE environment on the photochemical reactions of the compound. We show that highly consistent results can be obtained with samples of a particular type of PE (e.g., high-density PE) from different sources but that there are substantial differences, both qualitative and quantitative, between the photochemical products in different types of PE (e.g., between high- and low-density PE). These differences are largely the result of the nature and relative concentrations of unsaturated C=C groups in the different types of polyethylene. Our results provide a new, rapid, and relatively simple test for characterizing the unsaturation in PE. Such characterization is important because PE has considerable promise as a matrix for low-temperature experiments,[2] but the presence of olefinic C=C groups in a particular sample of PE can render it unusable for matrix isolation because of unwanted side reactions. The procedure described in this paper should enable others to identify such samples and to avoid matrices which might give rise to unexpected artifacts.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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(2) For a recent example, see: Cooper, A. I.; Kazarian, S. G.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *206*, 175.

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Experimental Section

Preparation of PE Films. The experiments described in this paper were all carried out using polyethylene (PE) film, prepared from powdered samples of the different types of PE listed below. For the preparation of a film, ~1 g of PE powder was typically placed in a constant-thickness melt press (Specac, Model 15620) with either a 250 or a 500 μm spacer. The powder was pressed between sheets of domestic aluminium foil for 5 min at an applied pressure of 5000 kg with the platens of the press heated to a temperature of 150 °C. The film was then quenched for ~4 min in a water-cooled block (Specac). This procedure gave a 50 mm diameter disk of PE film of very uniform thickness. For a typical experiment, two 15 mm diameter disks were cut out, one for impregnation and photolysis and the other as a "blank" for recording reference IR spectra. Before each experiment, the degree and nature of the olefinic bonds in the film was measured[9] from FTIR spectra in the γ(C–H) region (1000–800 cm^{-1}; see Figures 2b and 8). We have found that this hot pressing did not affect the unsaturation of the PE; diffuse reflectance IR (DRIFTS) spectra of raw powders, recorded prior to pressing, show the same degree of unsaturation as did the FTIR spectra of the pressed films. Control measurements showed that our results were unaffected by variations in this pressing procedure, that is, by changing the temperature of the platens or the precise times for pressing and quenching the PE films. Equally acceptable films were obtained by pressing the appropriate weight of 4 mm diameter PE pellets rather than PE powder.

Impregnation of PE Films. Our method for supercritical impregnation of PE has been described in some detail elsewhere.[7] Briefly, for this paper, a disc of PE film (see above) was placed together with solid $CpMn(CO)_3$ (Strem Chemicals) in a modified Nupro TF Series in-line filter, 5 μm pore size, which served as a miniature pressure vessel and was pressurized with SCF grade CO_2 (BOC) at 40 °C and 2000 psi pressure (145 psi ≈ 1 MPa). Alternatively, impregnation was carried out by immersing the PE disk in a solution of $CpMn(CO)_3$ in *n*-heptane (Aldrich, distilled over CaH_2) for at least 1 h. After impregnation, the $CpMn(CO)_3$ content of the film was checked by FTIR, which also indicated whether significant amounts of solid $CpMn(CO)_3$ had been left on the surface (solid and impregnated $CpMn(CO)_3$ have distinct IR spectra in the ν(C-O) region[7]). When solid $CpMn(CO)_3$ was detected in this way, it was removed by careful wiping of the surface of the film and the FTIR spectra were recorded again.

The concentration of $CpMn(CO)_3$ in the impregnated films was estimated spectroscopically (IR and UV); typically, the calculated concentrations were ~0.01 M, based on a uniform distribution within the PE. In practice, impregnation is likely to occur largely or even exclusively in the the amorphous rather than the crystalline regions of the PE; the local concentration of $CpMn(CO)_3$ will therefore be somewhat higher, depending on the crystallinity of the particular sample. For a number of samples, the spectroscopic estimates of Mn content were confirmed by atomic absorption (Perkin-Elmer Model 603). For a particular type of PE, the two methods of impregnation, $scCO_2$ and *n*-heptane, gave the same results in subsequent photolysis experiments. Neither method affected the unsaturation of the PE film.

Doping with Alkenes. All of the alkenes used in this study are liquids at room temperature. Alkenes (hex-1-ene (**1′**), *trans*-hex-2-ene (**2′**), 2-ethylbut-1-ene (**3′**), and 3-methylpent-2-ene (**4′**), all from Aldrich) were used to dope films of Hostalen GUR 415 PE, previously impregnated with $CpMn(CO)_3$, by placing a few drops of the appropriate alkene on the film. Excess alkene was removed by wiping.

UV Photolysis. High-pressure spectroscopic experiments were carried out in miniature stainless steel cells (~0.5 mL volume, 4000 psi pressure rating) with CaF_2 windows (10 mm thick), which have been described previously.[10] (Note that the γ(C–H) region of the IR spectrum cannot be monitored *in situ* in these cells because of the absorptions of the CaF_2 windows.) UV irradiation was carried out in a sealed cell under an inert atmosphere (helium), unless otherwise stated, when N_2, CO, and H_2 (Air Products) were used. The UV photolysis source was a Cermax 300 W Xe arc lamp with a 1 m long Lumatec light guide. This arrangement has the safety advantage of almost totally eliminating stray UV light and permits irradiation to be carried out within the sample compartment of the FTIR interferometer. FTIR spectra were recorded on a Nicolet 730 interferometer with an MCT detector and 680D data station (2 cm^{-1} resolution). Low-temperature and time-resolved IR experiments were carried out with apparatus described elsewhere.[11] Control measurements showed that, under the conditions of our experiments, UV irradiation did not alter the degree of unsaturation of the PE films. **Safety note**: *Some of the experiments described in this paper involve high pressures and should only be carried out with appropriate apparatus.*

Polyethylene Samples. The majority of experiments, described in this paper, involved one of three different types of PE while a few have involved specialist samples. In every case, the degree and nature of the unsaturation has been the most important property of the sample for our experiments. Every sample was carefully characterized at Nottingham by FTIR, see above. Details of the PE samples are as follows:

High-density PE (HDPE): type 6007, manufactured with a Phillips catalyst, CrO_3/SiO_2 (BP Chemicals), unstabilized (i.e., no additives), ρ 0.960 g/cm^3, average MW 135 000; 0.5 ethyl branches per 1000 C atoms. This sample contained almost exclusively terminal $CH{=}CH_2$ bonds, **1**.

Hostalen GUR 415: an ultrahigh molecular weight PE manufactured with a Ziegler-Natta catalyst (Hoechst); average MW 7.3×10^6, ρ 0.93 g/cm^3 (pressed material), ~50% crystallinity; typical impurity content (manufacturer's figures) Ti and Al <40 ppm, Mg <20 ppm, Cl <35 ppm, and Ca <50 ppm. Our results were unaffected by extracting the polymer with $scCO_2$ and CH_2Cl_2, which removed trace amounts of low molecular weight residues (confirmed by GC), prior to preparation of the PE film. This grade is also known as GUR 4150; for further details of the Hostalen range of PE, see ref 12a. Hostalen GUR 415 has very low unsaturation, which is predominantly terminal $CH{=}CH_2$ bonds, **1**.

Low-density PE (LDPE): Aldrich Catalog No. 18189–7; melt index 0.22, T_m 115 °C, ρ 0.915 g/cm^3. We were unable to discover whether this PE, as supplied, contained any additives. Although the concentrations of additives in PE are often lower than those of $CpMn(CO)_3$ used in our experiments, high concentrations could have affected our observations. Therefore, we carried out careful control experiments to eliminate the possibility that our results could be due to unspecified additives in the PE. We obtained identical results after the Aldrich LDPE had been extracted with $scCO_2$ or with CH_2Cl_2, both of which are known to remove common PE antioxidants and stabilizers.[12b] Furthermore,

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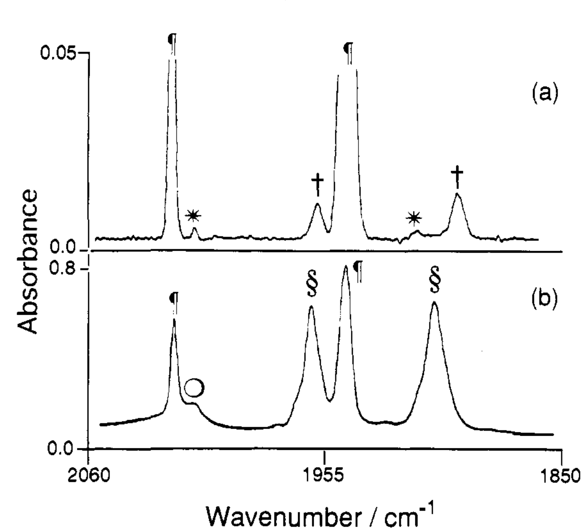

Figure 1. IR absorption spectra in the ν(C–O) region comparing the results of UV photolysis of $CpMn(CO)_3$ impregnated into an LDPE film (250 μm thick) (a) for 50 min at 21 K and (b) 20 min at room temperature. In both spectra, the bands labeled ¶ are due to residual $CpMn(CO)_3$ and the other bands are labeled as follows: (a) †, $CpMn(CO)_2$; *, natural abundance ^{13}CO satellite of $CpMn(CO)_3$. (b) §, the polymer-bound $CpMn(CO)_2(\eta^2\text{-}C{=}C)$; O, absorption of the PE disk itself (the corresponding band of PE has been removed from spectrum (a) by computer subtraction). The experiments at 21 K and room temperature were carried out with different pieces of film, which had been made from the same sample of LDPE and impregnated under identical conditions. Note, however, the considerable difference in the efficiency of the photolysis at the two temperatures.

consistent results were found with a number of other LDPE samples from sources as diverse as UK and Russia, where the impurities are likely to be very different. The Aldrich LDPE contained predominantly pendant $>C{=}CH_2$ bonds, **3**.

Specialist PE samples: Some of the experiments involved special HDPE, prepared at the University of North Carolina (Chapel Hill) by low-pressure polymerization with a Co(III) catalyst. The polymer was cleaved from the metal center with H_2 and characterized by GPZC; MW 21 000, polydispersity 1.14. This sample had a high proportion of trans-internal CH=CH bonds, **2**. We thank Professor J. M. DeSimone and his students for this sample. Samples of LDPE containing *internal* CH=CMe bonds, **4**, were prepared in Nottingham by a novel method, to be described in detail elsewhere,[13] involving UV isomerization of Aldrich LDPE (see above) with use of an organometallic tungsten catalyst.

Results

(a) Photolysis of $CpMn(CO)_3$ in PE Films. When $CpMn(CO)_3$ is impregnated into low-density polyethylene, the ν(C–O) IR bands are similar[7] but slightly broader than those in hydrocarbon solution. There is little change in the spectrum when the polymer is cooled from room temperature to 21 K, apart from a modest broadening of the lower wavenumber band, the *e* mode, probably due to the effect of the frozen polymer or possibly the result of frozen dynamic processes similar to our unpublished observations[14] with (η^4-norbornadiene)$Fe(CO)_3$. There is, however, no evidence for the splitting of either the a_1 or *e* mode, which has been observed[15a] in frozen CH_4 matrices at 20 K.

UV photolysis of $CpMn(CO)_3$ is LDPE at 21 K leads to the appearance of two new IR bands in the ν(C–O) region (Figure 1a). The bands are similar in relative intensity and wavenumber to those assigned to $CpMn(CO)_2$ (eq 1)in cryogenic matrices[15a]

$$\mathrm{CpMn(CO)_3} \xrightarrow{\mathrm{UV}} \mathrm{CpMn(CO)_2} + \mathrm{CO} \tag{1}$$

and frozen hydrocarbon glasses.[15b] The formation of $CpMn(CO)_2$ appears to be rather inefficient in LDPE at these temperatures, possibly because the photoejected CO cannot easily diffuse away through the rigid polymer matrix.

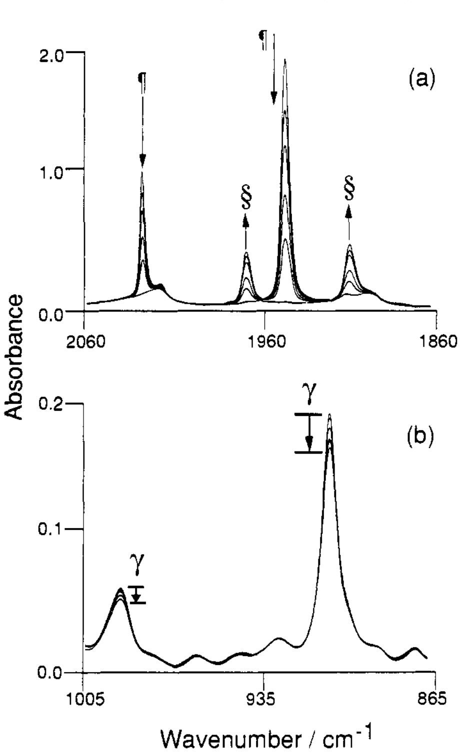

Figure 2. IR spectra obtained during UV irradiation of $CpMn(CO)_3$ impregnated into a film of BP Chemicals HDPE: (a) in the ν(C–O) region, as $CpMn(CO)_3$ is consumed (bands marked ¶) other bands appear (marked §) which are assigned to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$; (b) in the γ(C–H) deformation region, bands assigned to uncoordinated vinyl groups (marked γ) are observed to decrease in intensity at the same time. The spectra were recorded at intervals of 3 min; total irradiation time was 15 min.

The results are quite different when a similar sample of $CpMn(CO)_3$ in LDPE is irradiated at room temperature. The bands of $CpMn(CO)_2$ can only be observed transiently using time-resolved IR (TRIR) techniques,[11b,16] decaying in a period of microseconds with the concomitant appearance of two bands, due to a new stable species which can be observed by conventional FTIR (Figure 1b). This new species is formed even in very lightly impregnated PE and is therefore unlikely to be a dinuclear or polynuclear compound formed by oligomerization of $CpMn(CO)_2$. The wavenumbers and relative intensities of these bands are close to those of $CpMn(CO)_2(\eta^2\text{-alkene})$ complexes (see below). Similar bands are observed on UV irradiation of $CpMn(CO)_3$ in Hostalen PE, but the overall yield is very much smaller than is obtained in LDPE films under the same conditions. The principal difference between LDPE and Hostalen PE lies in the degree of unsaturation of the polymer. LDPE contains a relatively high concentration of C=C bonds while Hostalen PE has an ultrahigh molecular weight (7.3×10^6) and a very low degree of unsaturation.

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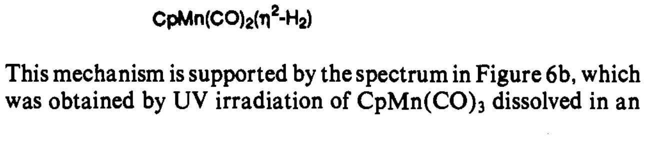
These results suggest that the ν(C–O) bands may be due to polymer-bound $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ species (more detailed discussion of the IR spectra of these species is given below). Hooker and Rest reported effects[17] during the photolysis of $Fe(CO)_5$ in LDPE, which they attributed to a similar reaction of alkene groups with coordinatively unsaturated intermediates. However, those reactions were not investigated in detail. The assignment of the bands to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ is considerably strengthened by the results of irradiating $CpMn(CO)_3$ in HDPE. In this particular type of HDPE (BP Chemicals; see Experimental Section), the overall stoichiometry of $(C_2H_4)_n$ dictates that each PE chain must have a CH_3 group at one end and a vinyl group, $CH{=}CH_2$, at the other. Thus, samples of HDPE with a relatively low average molecular weight (135 000 in this case) have a higher concentration of vinyl groups than does Hostalen GUR. These vinyl groups have characteristic γ(C–H) IR bands[9] in the region 1000–800 cm^{-1} (Figure 2b). UV irradiation of $CpMn(CO)_3$ in this type of HDPE results not only in the appearance of the ν(C–O) bands assigned to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ (Figure 2a) but also in the concomitant *decrease in intensity* of the γ(C–H) IR bands of the uncoordinated vinyl groups (Figure 2b). UV irradiation of a pure PE film (i.e., without impregnation of $CpMn(CO)_3$) causes no changes in the γ(C–H) region of the spectrum.

The implication of the polymer binding of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ is that this species should be much more difficult than $CpMn(CO)_3$ to extract from the polymer, since $CpMn(CO)_3$ is merely impregnated into the polymer and not bound to it. The spectra in Figure 3 show that this is indeed so; $CpMn(CO)_3$ can be extracted from LDPE by means of $scCO_2$, with the ν(C–O) bands reduced by ~80% of their initial intensity. By contrast, the intensities of the bands assigned to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ are reduced by <30%. Extraction with *n*-heptane leads to *complete* extraction of $CpMn(CO)_3$ while leaving $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ within the PE film (Figure 4). Thus, IR spectra indicate that photolysis of $CpMn(CO)_3$ in PE at room temperature leads to the formation of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ bound to the polymer, as shown schematically in Figure 5. We now report the effect of added gases on the formation of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$, before examining the nature of the species in more detail.

(b) Effect of Added Gases. High pressures of CO, >500 psi, largely suppress the formation of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ in LDPE. TRIR measurements show that, although $CpMn(CO)_2$ is still formed,[16a] it reacts more rapidly with CO than it reacts with the C=C bonds (eq 2). There is also a competitive reaction between the C=C groups and other gases. Figure 6a shows the IR spectra obtained after UV irradiation of $CpMn(CO)_3$ in LDPE in the presence of H_2. Photolysis leads to the formation both of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ and of the nonclassical dihydrogen compound $CpMn(CO)_2(\eta^2\text{-}H_2)$, previously characterized in supercritical fluid solution.[18] $CpMn(CO)_2(\eta^2\text{-}H_2)$ appears to be formed within the film directly from $CpMn(CO)_3$ and *not* via $CpMn(CO)_2(\eta^2\text{-}C{=}C)$; the higher the pressure of H_2, the greater is the amount of $CpMn(CO)_2(\eta^2\text{-}H_2)$ compared to that of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$.

$$CpMn(CO)_3 \underset{CO}{\overset{UV}{\rightleftarrows}} CpMn(CO)_2 + CO \xrightarrow{C=C} CpMn(CO)_2(\eta^2\text{-}C{=}C) \quad (2)$$


(3)

$$CpMn(CO)_3 \xrightarrow{UV} CpMn(CO)_2 + CO \xrightarrow{C=C} CpMn(CO)_2(\eta^2\text{-}C{=}C); \quad CpMn(CO)_2 \xrightarrow{+H_2} CpMn(CO)_2(\eta^2\text{-}H_2)$$

This mechanism is supported by the spectrum in Figure 6b, which was obtained by UV irradiation of $CpMn(CO)_3$ dissolved in an $scCO_2/H_2$ mixture within a cell which also contained a piece of LDPE film. When the cell was vented after the irradiation had finished, $CpMn(CO)_2(\eta^2\text{-}H_2)$ was left impregnated in the film together with unreacted $CpMn(CO)_3$ but with little trace of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$.

Figure 3. IR spectra obtained during the extraction with $scCO_2$ (100 atm) of an LDPE film in which $CpMn(CO)_3$ had been photolyzed at room temperature (cf. Figure 1b). Over a period of 2 h, the extraction causes a proportionately much greater drop in intensity of the two bands labeled ¶, due to unreacted $CpMn(CO)_3$, than it does to the bands marked §, due to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$. The band marked O is due to the PE itself and acts as a convenient control.

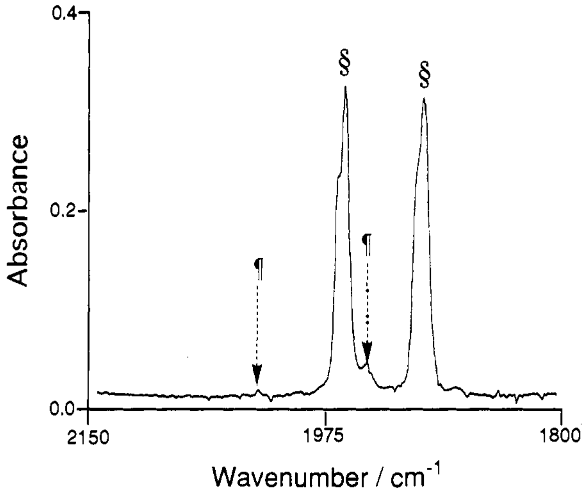


Figure 4. IR spectrum obtained after extraction of an irradiated $CpMn(CO)_3$/LDPE film with *n*-heptane for only 5 min. Before extraction, the IR spectrum of the film was similar to that in Figure 1b. Extraction causes the complete disappearance of the bands of $CpMn(CO)_3$, the former positions of which are indicated by ¶. The bands labeled § are assigned to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$.

$CpMn(CO)_3$ also reacts photochemically with N_2 in PE films. Traces of $CpMn(CO)_2(N_2)$ can even be detected after the irradiation *in air* of a LDPE film impregnated with $CpMn(CO)_3$. In the presence of high pressures of N_2, mixtures of $CpMn(CO)_2(N_2)$ and $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ are formed in LDPE (Figure 7a). Although, as shown below, the formation of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ has considerable potential for the characterization of polymers, there are many occasions when reaction with the PE is unwanted. The spectrum in Figure 7b shows that $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ is *not* formed in Hostalen PE under similar conditions. Hostalen PE has a very much lower level of unsaturation than LDPE yet it still retains a significant permeability to N_2. Thus, the relative rates of reaction are different

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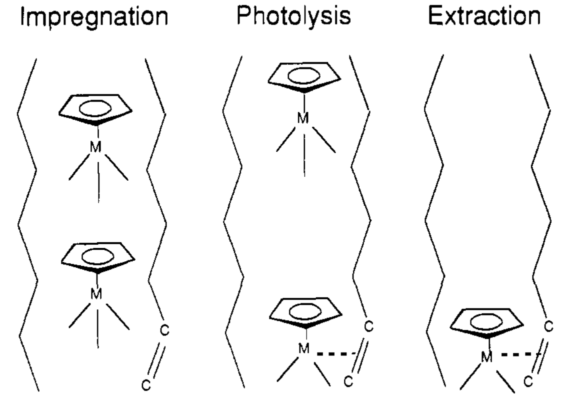


Figure 5. Schematic summary of the three stages of the experiments, which were used to the obtain spectra in Figures 2 and 3. In each stage, the zig-zag lines are a symbolic representation of the PE chains; they are not intended to imply any particular structure or conformation of the PE chains in the actual samples.

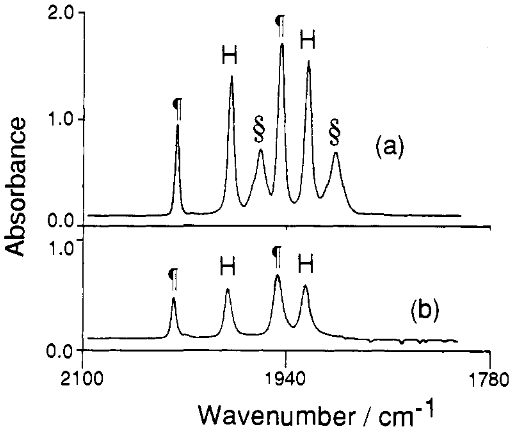
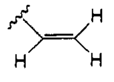


Figure 6. IR spectra to illustrate the difference between UV photolysis of $CpMn(CO)_3$ with H_2 within an LDPE film and in $scCO_2$ solution. In both spectra the bands labeled ¶ are due to $CpMn(CO)_3$; those labeled H are due to $CpMn(CO)_2(\eta^2\text{-}H_2)$ (ν(C–O) bands at 1983.6 and 1922.1 cm^{-1}); those marked § are due to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$. Spectrum (a) was obtained by UV photolysis of an LDPE film, impregnated with $CpMn(CO)_3$, under a pressure of H_2 (100 atm). Spectrum (b) was obtained by a two-stage process: photolysis of $CpMn(CO)_3$ and H_2 (100 atm) in $scCO_2$ solution in a cell which also contained a piece of LDPE film, followed by venting the $scCO_2$, which left the product and unreacted $CpMn(CO)_3$ impregnated in the film. Note that no $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ is present in spectrum (b).

in Hostalen from those in LDPE; in Hostalen, $CpMn(CO)_2(N_2)$ is formed faster relative to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ than in LDPE. The concentration of unsaturated C=C groups, therefore, is sufficiently low in Hostalen PE that photochemistry can be studied essentially free from side reactions with the polymer. Thus, Hostalen PE clearly can be used as an alternative material for matrix isolation experiments and we have already begun to explore the potential of these matrices with the photochemistry of $Fe(CO)_5$ and the thermal reactions of the isoelectronic dinitrogen compound,[19] $Fe(CO)_4(N_2)$.



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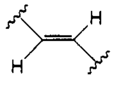

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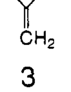

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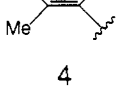

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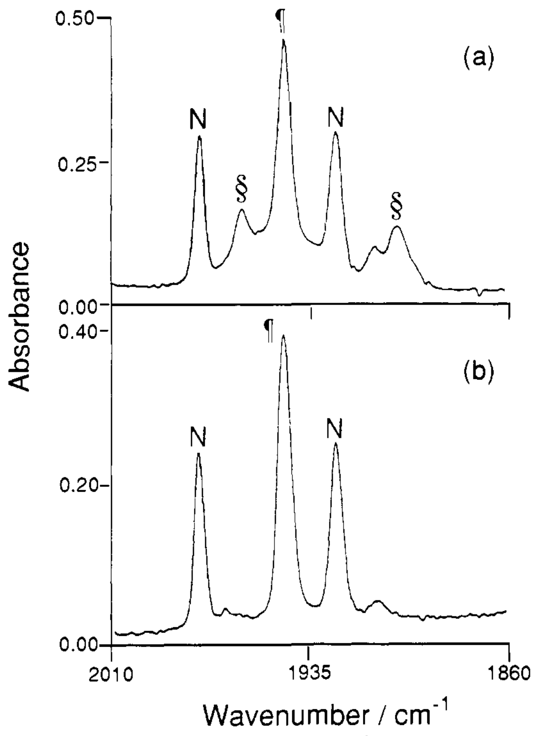

Figure 7. IR spectra comparing the results of 3 min UV photolysis of $CpMn(CO)_3$ and N_2 (600 psi) in (a) LDPE and (b) Hostalen GUR 415 PE. The band labeled ¶ is due to $CpMn(CO)_3$; those labeled N are due to $CpMn(CO)_2(N_2)$ (ν(C–O) bands at 1976.3 and 1924.1; ν(N–N) at 2166.2 cm^{-1}); those marked § are due to $CpMn(CO)_2(\eta^2\text{-}C{=}C)$. Note that almost no $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ is formed in the Hostalen PE under these conditions.

(c) $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ in Different Types of PE. The method of polymerization of C_2H_4 has a profound effect on the degree and the nature of the unsaturation of the resulting sample of PE. For example, radical polymerization gives rise to trans-internal, **2**, pendant, **3**, and *trans*-CMe=CH, **4**, groups as well as the vinyl groups, **1**, found in the BP Chemicals HDPE.

In our experiments, these types of C=C bond are identifiable across the range of polymer samples used. The relative amounts of these different types of alkene group in a polymer sample can be estimated semiquantitatively from IR bands in the region, 1000–850 cm^{-1}, associated with γ(C–H) vibrations.[9] Figure 8 shows such spectra for three of the different PE samples, which we have used. These spectra indicate that the LDPE (Aldrich) has a preponderance of *pendant* C=C bonds while the special sample of LDPE (see Experimental Section) has fewer *pendant* bonds and more trans-internal CMe=CH bonds. The HDPE sample (BP Chemicals; see Figure 2b) has almost exclusively vinyl groups. By contrast, the C=C bonds present in the specialized sample of HDPE (North Carolina) are *trans-internal* HC=CH groups. It is difficult, however, to quantify precisely the relative concentrations of the different types of C=C bonds directly from the relative intensities of the bands; the IR extinction coefficients are significantly different and there is some overlap with unrelated absorption bands of the polymer.[9]

When $CpMn(CO)_3$ is impregnated into these four types of PE (Aldrich and special LDPE and BP Chemicals and North Carolina HDPE), the two ν(C–O) bands due to the a_1 and e vibrations of the $Mn(CO)_3$ moiety have *exactly the same wavenumbers* irrespective of which type of PE is impregnated. In all four types of PE, UV photolysis of $CpMn(CO)_3$ results in the formation of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ but, surprisingly, the ν(C–O) bands in each type of PE are slightly different in wavenumber. For both the *symmetric* (a′) and *antisymmetric* (a″) ν(C–O) vibrations of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$, the IR band in BP Chemicals HDPE is

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[19] Cooper, A. I.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *212*, 611.

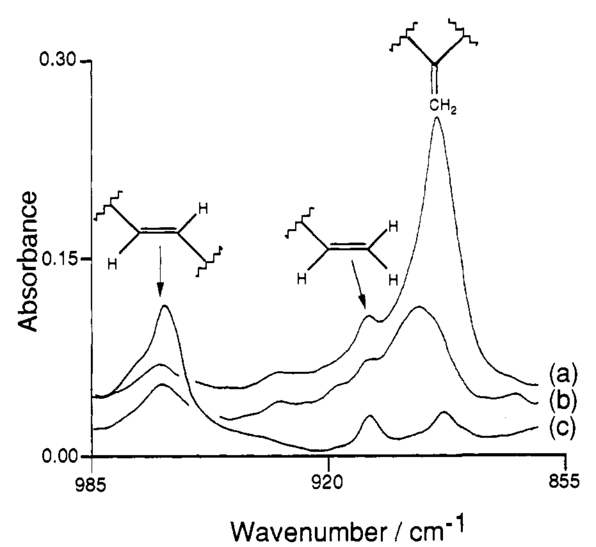


Figure 8. IR spectra in the γ(C–H) region for 500 μm thick samples of (a) Aldrich LDPE, (b) special LDPE[13], which is rich in trans-internal HMeC=CH unsaturated bonds, and (c) North Carolina HDPE, which is rich in trans-internal HC=CH unsaturated bonds. Bands are assigned to trans-internal (HC=CH), vinyl, and pendant C=C bonds as indicated.

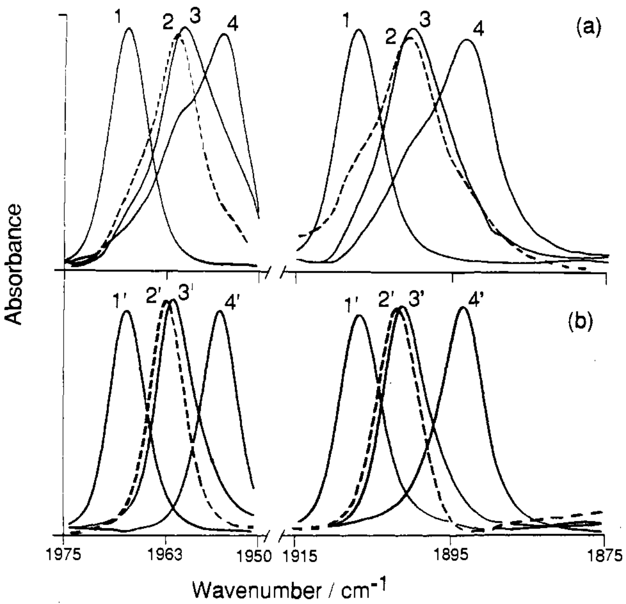
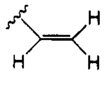


Figure 9. (a) IR spectra illustrating the differences in the positions of ν(C–O) bands of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ generated photochemically in a range of PE samples containing a predominance of different types of C=C group: (**1**) BP Chemicals HDPE (vinyl); (**2**) North Carolina HDPE (trans-internal CH=CH; dashed bands); (**3**) Aldrich LDPE (pendant); (**4**) special LDPE (trans-internal CMe=CH). (b) For comparison, IR spectra illustrating the differences in the positions of ν(C–O) bands of $CpMn(CO)_2(\eta^2\text{-alkene})$ generated by photolysis of $CpMn(CO)_3$ in the presence of a range of different alkenes impregnated into Hostalen GUR 415 polymer films: (**1'**) hex-1-ene; (**2'**) hex-2-ene (dashed bands); (**3'**) 2-ethylbut-1-ene; (**4'**) 3-methylpent-2-ene. Note the close similarity of the band positions of the alkene derivatives with those of the corresponding unsaturated polymer species in (a). The spectra in (a) and (b) are the superimposed bands from different experiments, each carried out with one type of PE or one alkene. All of the bands have been normalized to the same absorbance, and if necessary, any overlapping bands due to residual $CpMn(CO)_3$ have been removed by computer subtraction.

~6 cm^{-1} higher than in the North Carolina HDPE, ~7 cm^{-1} higher than Aldrich LDPE and ~10 cm^{-1} higher than in the specialized LDPE[13] (Figure 9a and Table 1). The fact that the bands of the $CpMn(CO)_3$ starting material do *not* shift between polymer samples shows that the differences in ν(C–O) bands of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ cannot be due to a simple solvent shift. Instead, these differences almost certainly reflect the different type of C=C bonds ligated to the Mn center, predominantly *vinyl* in BP Chemicals HDPE, *trans-internal* CH=CH in the North Carolina HDPE, *pendant* in Aldrich LDPE, and *trans-internal* CMe=CH in the specialized LDPE.

Although a wide range of $CpMn(CO)_2(\eta^2\text{-alkene})$ compounds are known, it is not immediately clear which spectroscopic data would provide the best comparison with the polymer-bound $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ species. We have, therefore, used a new approach to generate a number of $CpMn(CO)_2(\eta^2\text{-alkene})$ complexes *in situ* in Hostalen PE, impregnated with $CpMn(CO)_3$ and then doped with the appropriate low molecular weight alkene (**1'**, **3'**, etc.). The doping of the PE does not appear to affect the



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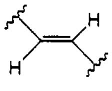

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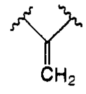

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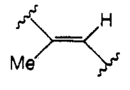

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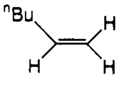

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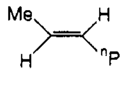

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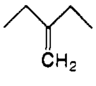

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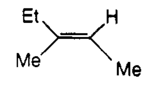

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wavenumbers of the ν(C–O) bands of $CpMn(CO)_3$ itself, but there are significant differences between ν(C–O) bands of the $CpMn(CO)_2(\eta^2\text{-alkene})$ products, generated by UV irradiation of the doped PE films (Figure 9b and Table 1). Several points are clear from the data:

(a) The wavenumbers of the ν(C–O) bands appear to depend on the number of H atoms attached to the C=C group but not on their distribution around the C=C bond. Thus, $CpMn(CO)_2(\eta^2\text{-hex-2-ene})$ (**2'**) and $CpMn(CO)_2(\eta^2\text{-2-ethylbut-1-ene})$ (**3'**) both with *two* =C—H bonds have almost identical ν(C–O) band positions, but these positions differ from those of both $CpMn(CO)_2(\eta^2\text{-3-methylpent-2-ene})$ (**4'**) and $CpMn(CO)_2(\eta^2\text{-hex-1-ene})$ (**1'**), which have *one* and *three* =C—H bonds, respectively.

(b) The wavenumbers of ν(C–O) bands of the different $CpMn(CO)_2(\eta^2\text{-alkene})$ complexes are almost *identical* to those of the corresponding polymer-bound $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ species, cf. Figures 9a and 9b, thus strengthening our identification of the various $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ complexes.

(c) The fact that identical wavenumbers are observed for $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ and $CpMn(CO)_2(\eta^2\text{-alkene})$ compounds suggests that the steric bulk of the polymer chains cannot be significant in determining the position of the ν(C–O) bands. Instead, the important factor is likely to be electronic. The shifts in ν(C–O) bands suggest that a greater degree of substitution around the C=C bond increases the σ donor role of the C=C bond relative to its π acceptor properties.

Lability of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$. The reactivity and thermal stability of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ appears to depend on which type of C=C bond is coordinated to the metal. Figure 10 shows the effect of mild heating of an LDPE film containing $CpMn(CO)_2(\eta^2\text{-}C{=}C)$. After only 10 min at 60 °C, nearly all of the $CpMn(CO)_2(\eta^2\text{-pendant})$ has decayed but there is a small *increase* in intensity of the bands of $CpMn(CO)_2(\eta^2\text{-vinyl})$, indicating a considerably greater thermal stability for the $CpMn(CO)_2(\eta^2\text{-vinyl})$ complex and possibly some exchange of pendant and vinyl groups. Similarly, $CpMn(CO)_2(\eta^2\text{-pendant})$ appears to be significantly more reactive than $CpMn(CO)_2(\eta^2\text{-vinyl})$ towards N_2. When $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ is generated photochemically and the PE film is then left standing under a high pressure of N_2 in the dark, the bands of $CpMn(CO)_2(N_2)$ gradually appear in the IR spectrum. However, $CpMn(CO)_2(N_2)$ is formed largely at the expense of $CpMn(CO)_2(\eta^2\text{-pendant})$; see Figure 11.

The results shown in Figures 10 and 11 indicate that $CpMn(CO)_2(\eta^2\text{-pendant})$ is significantly more labile than is CpMn-

Table 1. Wavenumbers[a] (cm^{-1}) of ν(C–O) Bands of $CpMn(CO)_2L$ Species

$CpMn(CO)_3$ (in LDPE)	2027.0	2026	$CpMn(CO)_3$ in frozen glass[b]
	1943.9	1946	
$CpMn(CO)_2$ (at 21 K in LDPE)	1955.7	1955	$CpMn(CO)_2$ in frozen glass[b,c]
	1888.8	1886	
$CpMn(CO)_2(\eta^2\text{-}C{=}C)$		$CpMn(CO)_2$(alkene) in Hostalen GUR	
$(RHC{=}CH_2)_{(HDPE)}$ (vinyl), **1**	1967.0	1966.9	hex-1-ene (**1′**)
	1907.2	1907.1	
$(RHC{=}CHR')_{(HDPE)}$[d] (trans-internal), **2**	1960.9	1961.4 (1961.8)	*trans*-hex-2-ene (**2′**)
	1900.5	1900.9 (1901.6)	(*trans*-hex-3-ene)
$(RR'C{=}CH_2)_{(LDPE)}$ (pendant), **3**	1959.9	1960.7	2-ethylbut-1-ene (**3′**)
	1901.0	1901.1	
$(RMeC{=}CHR')_{(LDPE)}$[e] (trans-internal), **4**	1955.0	1954.8	3-methylpent-2-ene (**4′**)
	1893.2	1893.2	

[a] Error in band positions, ±0.2 cm^{-1}. [b] Spectra obtained in frozen hydrocarbon matrices.[15b] [c] Compare with spectrum of $CpMn(CO)_2$ obtained in cryogenic methane matrix[15a] with ν(C–O) bands at 1961.4 and 1892.8 cm^{-1}. [d] North Carolina HDPE (see text). [e] Specialist sample of LDPE.[13]

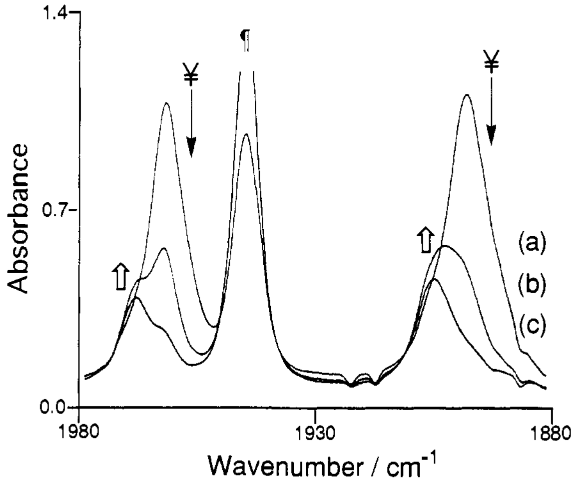

Figure 10. IR spectra illustrating the greater thermal lability of $CpMn(CO)_2(\eta^2$-pendant) compared to $CpMn(CO)_2(\eta^2$-vinyl) in LDPE. Spectrum (a) was recorded immediately after UV photolysis, (b) after 5 min heating to 60 °C, and (c) after a further 5 min heating. The bands are labeled as follows: ¶, $CpMn(CO)_3$; ↑, $CpMn(CO)_2(\eta^2$-vinyl); ¥, $CpMn(CO)_2(\eta^2$-pendant).

$(CO)_2(\eta^2$-vinyl). We have carried out similar experiments using the specialized LDPE sample with a high concentration of internal MeC=CH groups (cf. Figure 8). The results show that $CpMn(CO)_2(\eta^2$-internal MeC=CH) is also more labile than $CpMn(CO)_2(\eta^2$-vinyl) (spectra not illustrated). In addition, $CpMn(CO)_2(\eta^2$-internal MeC=CH) appears to be slightly more labile than $CpMn(CO)_2(\eta^2$-pendant) although the data are less conclusive. Thus, overall we have found the the reactivity of the $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ compounds changes in the order η^2-internal MeC=CH > η^2-pendant > η^2-vinyl.

There have been a number of previous studies of the relative stability of series of compounds, where different alkenes have been coordinated to the same metal center, e.g., nickel species.[20] The question arises whether electronic or steric effects are more important in determining reactivity. In general, these studies have concluded that electronic factors usually predominate. However, the range of alkenes and reactivity was usually much wider than in our experiments, where the difference between η^2-internal MeC=CH and η^2-vinyl is significant but not huge. Nevertheless, the order of reactivity in our experiment correlates inversely with the wavenumbers of the ν(C–O) bands; the most reactive $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ compound has the lowest wavenumber. Since the change in wavenumber can be taken to indicate either a decrease in (M → alkene) π donation or an increase in (alkene → M) σ donation on going from η^2-vinyl to η^2-internal MeC=CH, these trends are consistent with Yamamoto's suggestion[21] that the most electron rich alkenes form the most labile complexes.

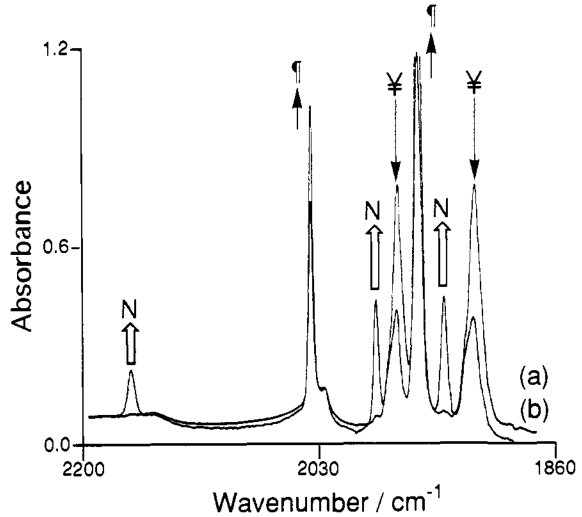

Figure 11. IR spectra illustrating the greater reactivity of $CpMn(CO)_2(\eta^2$-pendant) compared to $CpMn(CO)_2(\eta^2$-vinyl) in the thermal reaction with N_2 in LDPE at room temperature. Spectrum (a) was recorded immediately after N_2 (1000 psi) was admitted to the cell containing the PE film, and spectrum (b) was recorded 2 h later. The film was kept in the dark while the reaction was in progress. The bands are labeled as follows: ¥, $CpMn(CO)_2(\eta^2$-pendant); N, $CpMn(CO)_2(N_2)$; ¶, $CpMn(CO)_3$.

On the other hand, the observed order of reactivity (η^2-internal MeC=CH > η^2-pendant > η^2-vinyl) could be rationalized by a simple stereochemical argument. Coordination of an alkene to a metal center causes a distortion of the geometry around the carbon, from planar sp^2 towards tetrahedral sp^3. Given the three types of C=C bond in PE, it could be argued that the internal, MeC=CH, is sterically the most constrained because of the *three* alkyl groups attached to the C=C bond while the vinyl group, $HC{=}CH_2$, with only *one* alkyl substituent is relatively unconstrained. Therefore, $sp^2 \rightarrow sp^3$ distortion might be hardest and M → alkene bonding the weakest for MeC=CH while $sp^2 \rightarrow sp^3$ distortion should be easiest for $HC{=}CH_2$ and the M → alkene bonding correspondingly stronger.

Conclusions

In this paper, we have shown that UV photolysis of $CpMn(CO)_3$ in PE leads to formation of four different $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ complexes, where the $CpMn(CO)_2$ moiety is bound to vinyl, pendant, or internal C=C bonds in the PE chain. Formation of these species is competitive with other reactions of the $CpMn(CO)_2$ intermediates (e.g., with H_2 or N_2). The *relative* and *absolute* amounts of the four $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ complexes which are formed during photolysis depend on the

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particular type of PE used. Formation of such species is almost negligible in Hostalen GUR 415 PE, which is, therefore, very promising as a material for inert matrices in photochemical experiments.[19] Until now, the development of such low-temperature experiments has been frustrated because the use of more highly unsaturated PE can lead to artifacts.[17]

The four types of $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ complex are easily distinguishable via their ν(C–O) IR bands, and these spectra could be used as a probe to investigate the unsaturation of an unknown sample of PE. The attraction of this approach is that the *extinction coefficients* of the ν(C–O) bands should be largely independent of the type of coordinated C═C bond. The relative intensities of the ν(C–O) bands should, therefore, provide a direct correlation with the relative concentration of three types of C═C groups, potentially a great advantage over the more traditional method[9] using γ(C–H) bands (see Figure 8). There are two problems: first, for some and, perhaps most, samples of PE, the concentration of $CpMn(CO)_3$ within the impregnated polymer may be considerably lower than the concentrations of C═C bonds; second, the different $CpMn(CO)_2(\eta^2\text{-}C{=}C)$ compounds have different thermal stabilities, depending on which type of C═C bond is coordinated to the metal. Nevertheless, the use of $CpMn(CO)_3$ and UV irradiation would clearly be a convenient qualitative test to distinguish between different samples of PE. In particular, the ν(C–O) approach easily differentiates between the two types of internal C═C groups, CH═CH and CMe═CH, which are not easily distinguishable by use of the γ(C–H) region of the spectrum. The advantage is that the technique is robust. The results are not affected by the precise method used for preparing and impregnating the PE sample or by the presence of low levels of additives.

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