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Complexes in polymers III:* Addition reactions of *trans*-$Ir(PPh_3)_2(CO)Cl$ embedded in polystyrene with hydrogen, oxygen, sulfur dioxide, carbon monoxide and gaseous iodine and of $(\eta\text{-}C_5H_5)Ru(\eta^4\text{-}1,5\text{-cyclooctadiene})Cl$ in polystyrene with carbon monoxide

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The addition reactions of *trans*-$Ir(PPh_3)_2(CO)Cl$ embedded in films of polystyrene (PS) with hydrogen, oxygen, sulfur dioxide, carbon monoxide and gaseous iodine were monitored by infrared spectroscopy and found to be similar to those occurring in toluene. While the reaction with iodine was rapid at the surface of the film as determined by attenuated-total-reflectance infrared spectroscopy, the reaction was much slower in the body of the film, as shown by transmission infrared spectroscopy. No such difference was observed for oxygen. The complex CpRu(COD)Cl (Cp = $\eta\text{-}C_5H_5$, COD = 1,5-cyclooctadiene) in PS readily undergoes ligand substitution by carbon monoxide (CO and ^{13}CO) to give $CpRu(CO)_2Cl$ and $CpRu(^{13}CO)_2Cl$ embedded in PS, respectively.

Keywords: Iridium complex, ruthenium complex, polystyrene film, addition reactions

INTRODUCTION

Chemical reactions between gases and metal complexes in rigid or semi-rigid environments are of practical[2] and theoretical[3] interest. Respiration in animals and photosynthesis in plants are two important examples. An analogy between the environment surrounding a metal complex in a metal–protein and that of a complex embedded in a polymer has long been recognized.[3a,4] Thus, heme and 1-(2-phenylethyl) imidazole embedded in polystyrene (PS) reversibly binds oxygen (O_2) in the presence of water.[4] More recently a material consisting of copper complexes covalently attached, via ligands, to the polymer backbone of cross-linked polystyrene beads was shown[2a] to bind carbon monoxide (CO) gas reversibly. This ability is potentially applicable in membrane or pressure-swing recovery of CO from gas streams. It has also been reported[5] that certain iron-complex-containing conjugated polymers become much better electrical conductors when exposed to iodine (I_2). Finally, polymer-trapped microparticles of lead sulfide (PbS) possessing unusual band gaps have been prepared[6] by treatment of lead acetate embedded in ethylene–15% methacrylic acid with hydrogen sulfide (H_2S). These results exploit the high reactivity and selectivity of isolated, homogeneously dispersed metal complexes, while the polymer matrices impart an environment with mechanical advantages inherent in heterogeneous-phase reaction systems.

We have developed a facile method of embedding soluble metal complexes in various polymers.[7] The absence of a covalent link between the complex and the polymer greatly simplifies the preparation of such materials. Since the polymers exhibit a low absorbtivity window in the 2100–1750 cm^{-1} region of the infrared spectrum, it is possible to characterize the environment of metal carbonyl complexes in the polymer by examining the metal carbonyl stretching bands.[7] The photochemistry of such complexes can also be monitored. Recently, we reported the effect of different

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polymer environments on the rate of gaseous iodine oxidation of $[CpFe(CO)_2]_2$ (Cp = η-C_5H_5) and other organometallic dimers.[1]

There is great interest in facilitated transport membranes for gas separation wherein a metal complex acts as a carrier.[8] Since Vaska's complex, *trans*-$Ir(PPh_3)_2(CO)Cl$, in solution reacts easily and often reversibly with commercially important gases such as hydrogen, oxygen, sulphur dioxide and carbon monoxide, we decided to study these reactions with the complex embedded in PS.

EXPERIMENTAL

Homogeneously dispersed solid-solutions of the complexes in PS were prepared as previously reported[1,7] and contained 5% by weight of each complex. The pressed films were 0.06–0.08 mm in thickness. All the films were stored under nitrogen gas (N_2). The polystyrene (Polysciences) had a molecular weight in the range 125 000–250 000 Da. The complex *trans*-$Ir(PPh_3)_2(CO)Cl$ (Strem) was used without further purification whilst CpRu(COD)Cl (COD = cyclooctadiene) (kindly provided by Dr Eric Singleton) was recrystallized from dichloromethane/hexanes. The gases sulfur dioxide (99.98%, Matheson), and hydrogen, oxygen, CO (Linde) and ^{13}CO (ILON) were used as received. Infrared spectra were recorded on a Bomem Michelson 100 spectrometer operating at 4 cm^{-1} resolution and using a deuterium triglycine sulfate (DTGS) detector. The spectrum of each film was taken before and after treatment with a particular gas. The relative intensities of individual reactant and product carbonyl stretching bands as well as nearby polystyrene bands were used to monitor the reactions. The infrared spectra of surfaces of films were measured by means of an attenuated-total-reflectance (ATR) attachment. The film was placed snugly against the surface of a multireflection KRS-5 crystal (10 mm × 5 mm × 1 mm, 45° entrance angle) through which the spectrometer radiation was directed by a beam condenser accessory (Spectra-Tech). The penetration depth (dp) was of the order of one wavelength (6×10^{-4} mm, i.e. 1% of film thickness) calculated according to the equation[9]

$$dp = \lambda/2\pi\ n_p(\sin^2 \theta\text{-}n_{sp}{}^2)^{1/2}$$

where $\lambda = 5 \times 10^{-3}$ mm, $\theta = 45°$, $n_s = 1.6$ (PS) and $n_p = 2.4$ (KRS-5). The transmission infrared spectra of films examined with the ATR device were measured at the same time.

The iodine reactions were performed at ambient temperature in glass jars (5 cm in diameter, 2.5 cm high) containing pulverized iodine (10 g). The films were suspended 1 cm above the iodine. The reactions were monitored over several months. Reactions with hydrogen, oxygen and sulfur dioxide were conducted at ambient temperature in a Carius tube fitted with a wide-bore, high-vacuum stopcock (Teflon plug, FETFE O-rings, Ace glass). A film was placed into the tube containing nitrogen gas and the tube was evacuated. The appropriate gas was introduced to a pressure of about two atmospheres (2×10^5 Pa) and the tube was sealed and stored in the dark. The procedure was repeated each time after the film had been removed to record a spectrum. Films treated for some time were subjected to vacuum to test the reversibility of the reaction. Faster reactions with carbon monoxide were conducted in a demountable flow-through gas cell. This consisted of a short stainless-steel tube equipped with two stainless-steel valves on its side and two sodium chloride optical windows sealed to the ends by means of rubber gaskets. The film was introduced and the cell was evacuated, then filled with the appropriate gas to a pressure of about one atmosphere (10^5 Pa) and the infrared spectrum was monitored continuously.

RESULTS AND DISCUSSION

Vaska's complex reacts in solution with gaseous reactants such as oxygen, hydrogen, carbon monoxide and sulfur dioxide to give adducts whose structures have been well characterized.[10] In many cases the reactions are reversible. Vaska's complex in polystyrene (Ir/PS) exhibits one strong infrared band in the CO stretching region at 1964 cm^{-1} (Table 1) which is quite similar to that for the complex in toluene.[11]

Reaction with hydrogen

The yellow colour of Ir/PS became quite faint upon treatment with hydrogen in a Carius tube for 1 h but did not fade further over a period of five days. Three new infrared bands appeared at 2204(w), 2092(vs) and 1990(s) cm^{-1} consistent[12] with the two metal hydride bands and CO band, respectively, of the *cis*-dihydride

Table 1 The carbonyl stretching frequencies of *trans*-$Ir(PPh_3)_2(CO)Cl$ and selected adducts and of $CpRu(CO)_2Cl$ in PS and other media (cm^{-1})

Complex	Medium	ν(CO)
$Ir(PPh_3)_2(CO)Cl$	PS	1964
	Toluene	1967
	Nujol	1952
$Ir(PPh_3)_2(^{13}CO)Cl$	PS	1917
$Ir(PPh_3)_2(CO)_2Cl$	PS	1964, 1928
$Ir(PPh_3)_2(^{13}CO)_2Cl$	PS	1917, 1884
$Ir(PPh_3)_2(CO)(^{13}CO)Cl$	PS	1950, 1905
$Ir(PPh_3)_2(CO)(H)_2Cl$	PS[a]	1990
	Benzene[b]	1983
	Nujol[c]	1970
$Ir(PPh_3)_2(CO)(O_2)Cl$	PS	2006
$Ir(PPh_3)_2(CO)(SO_2)Cl$	PS	2022
$Ir(PPh_3)_2(CO)(SO_4)Cl$	PS	2050
$Ir(PPh_3)_2(CO)(I)_2Cl$	PS	2066
$CpRu(CO)_2Cl$	PS	2050, 1998
$CpRu(^{13}CO)_2Cl$	PS	2003, 1955

[a] ν(Ir—H): 2202, 2092. [b] ν(Ir—H): 2220, 2095; Ref. 12.
[c] ν(Ir—H): 2190, 2100; Ref. 12.

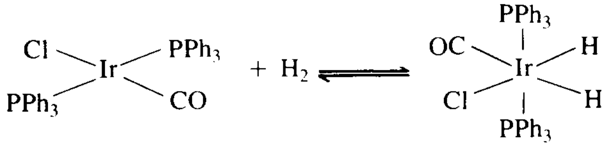
adduct (Eqn [1]). Concomitantly, the intensity of the CO band of the starting complex decreased. The peak positions of the adduct in PS ($Ir \cdot H_2$/PS) are closer to those in benzene than of the solid complex in Nujol (Table 1), consistent with the postulate that PS provides a solvent-like environment. Whilst adduct formation is reversible in solution the solid dihydride is stable to loss of hydrogen (H_2) *in vacuo*. When $Ir \cdot H_2$/PS was pumped (three days), the bands due to the dihydride significantly decreased in intensity while that of Vaska's complex recovered appropriately. The same changes happened upon exposure of $Ir \cdot H_2$/PS to air except that quite intense carbonyl bands due to the oxygen (O_2) adduct of Vaska's complex appeared, thus reducing the relative intensity of the CO band of Vaska's complex.

Reaction with oxygen

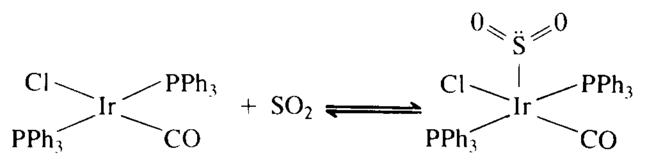
Treatment of Ir/PS with oxygen (O_2) for five days gave a film displaying a strong new band in the infrared at 2006 cm^{-1} and a weak band due to the starting complex. The new band is consistent[12c,13] with the formation of the oxygen (O_2) adduct of Vaska's complex whose structure is similar to that of the H_2 adduct. The band due to $Ir \cdot O_2$/PS decreased in intensity gradually upon standing in air but rapidly *in vacuo* with the appropriate recovery of the band of Ir/PS in each case.

Reaction with sulfur dioxide

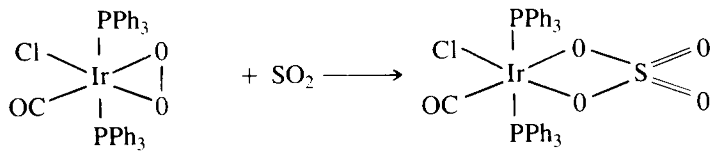
Exposure of Ir/PS to sulfur dioxide resulted in a rapid color change from yellow to green and the appearance of only one band in the infrared at 2022 cm^{-1} assigned to the presence[14] of the SO_2 adduct of Vaska's complex (Eqn [2]). At room temperature in air, this band gradually diminished in intensity accompanied by the recovery of the band due to Vaska's complex and the appearance of the band due to $Ir \cdot O_2$/PS. The pure crystalline sulfur dioxide adduct is reported to lose sulfur dioxide above 150°C whilst in benzene sulfur dioxide is lost at reflux. The



[1]



[2]



[3]

formation of some $Ir \cdot O_2/PS$ suggested an experiment whereby $Ir \cdot O_2/PS$ was exposed to sulfur dioxide at two atmospheres (2×10^5 Pa) pressure. This gave a film with a strong band at 2050 cm^{-1} consistent[15] with formation of $Ir(PPh_3)_2(CO)(Cl)(SO_4)$ (Eqn [3]). The band due to $Ir \cdot SO_4/PS$ was invariant in air over the period of a month.

Reaction with carbon monoxide

Films of Ir/PS react rapidly with carbon monoxide (CO or ^{13}CO) to give strong peaks at 1964, 1929 cm^{-1} and 1916, 1884 cm^{-1}, respectively, consistent with the formation of $Ir(PPh_3)_2(CO)_2Cl$ and the ^{13}CO analog as is observed in solution.[11,16,17] *In vacuo*, one carbonyl ligand is rapidly lost and a band due to starting Ir/PS (1964 cm^{-1}) and its ^{13}CO analog (1917 cm^{-1}), respectively, were observed. Treatment of the latter with carbon monoxide (CO) in a flow-through cell gave several new peaks (Fig. 1) consistent with the presence of five different complexes: $Ir(PPh_3)_2(^{13}CO)Cl$ (1917 cm^{-1}), $Ir(PPh_3)_2(CO)(^{13}CO)Cl$ (1954, 1905 cm^{-1}), $Ir(PPh_3)_2(CO)Cl$ (1966 cm^{-1}), $Ir(PPh_3)_2(CO)_2Cl$ (1966, 1929 cm^{-1}), $Ir(PPh_3)_2(^{13}CO)_2Cl$ (1917, 1887 cm^{-1}) (Scheme 1).

The complex CpRu(COD)Cl is known to undergo facile ligand substitution in solution by carbon monoxide to give $CpRu(CO)_2Cl$.[18] Treatment of CpRu(COD)Cl embedded in PS with carbon monoxide resulted in the appearance of two strong bands (2050, 1998 cm^{-1}) in the infrared spectrum consistent with the formation of $CpRu(CO)_2Cl$. Use of ^{13}CO gave bands at 2003 and 1955 cm^{-1} due to the formation of $CpRu(^{13}CO)_2Cl$. The bands of both samples were invariant with time (months) when stored in air.

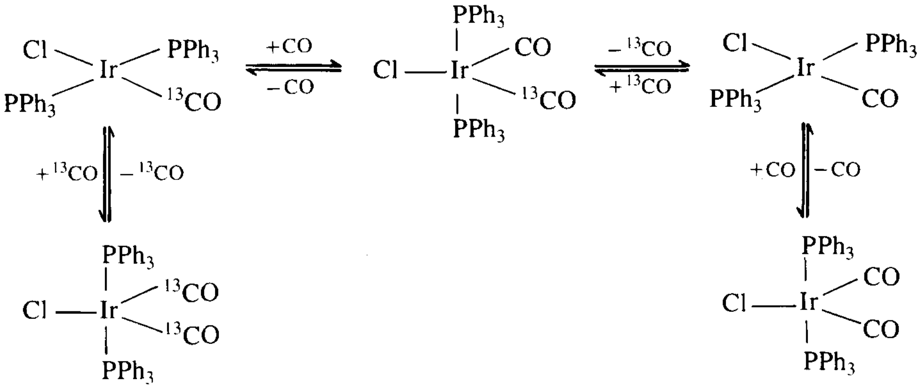
Reaction with iodine

The film Ir/PS reacted slowly (20 days) with iodine and a strong band at 2066 cm^{-1} due[19] to the iodine adduct $Ir \cdot I_2/PS$ gradually appeared together with a very strong band due to $Ir \cdot O_2/PS$ while the band due to the starting Ir/PS was still present. After two months' exposure, only the band due to the iodine adduct was present. Clearly the reaction of Ir/PS with iodine is much slower than that with oxygen. However, because the latter reaction is reversible, the final product is $Ir \cdot I_2/PS$.

A film of Ir/PS was exposed to iodine for only 3 h and its transmission and ATR infrared spectra were examined. The former spectrum had a very weak peak due to $Ir \cdot I_2/PS$, suggestive of less than 5% reaction. However the ATR infrared spectrum revealed a very strong band due to $Ir \cdot I_2/PS$, a weak band due to $Ir \cdot O_2/PS$, and no band due to the starting Ir/PS. After one month's exposure there was no difference between the transmission and ATR infrared spectra. Similarly there was no difference between the transmission and ATR infrared spectra of a Ir/PS film briefly treated with oxygen so that a low percentage of $Ir \cdot O_2/PS$ was formed. The results are consistent with a low rate of diffusion of iodine in PS relative to oxygen.

CONCLUSIONS

The environment surrounding complexes embedded in PS is very similar to that in toluene solution. This is illustrated by the similarity of the infrared peak positions of the CO stretching bands of complexes in



Scheme 1

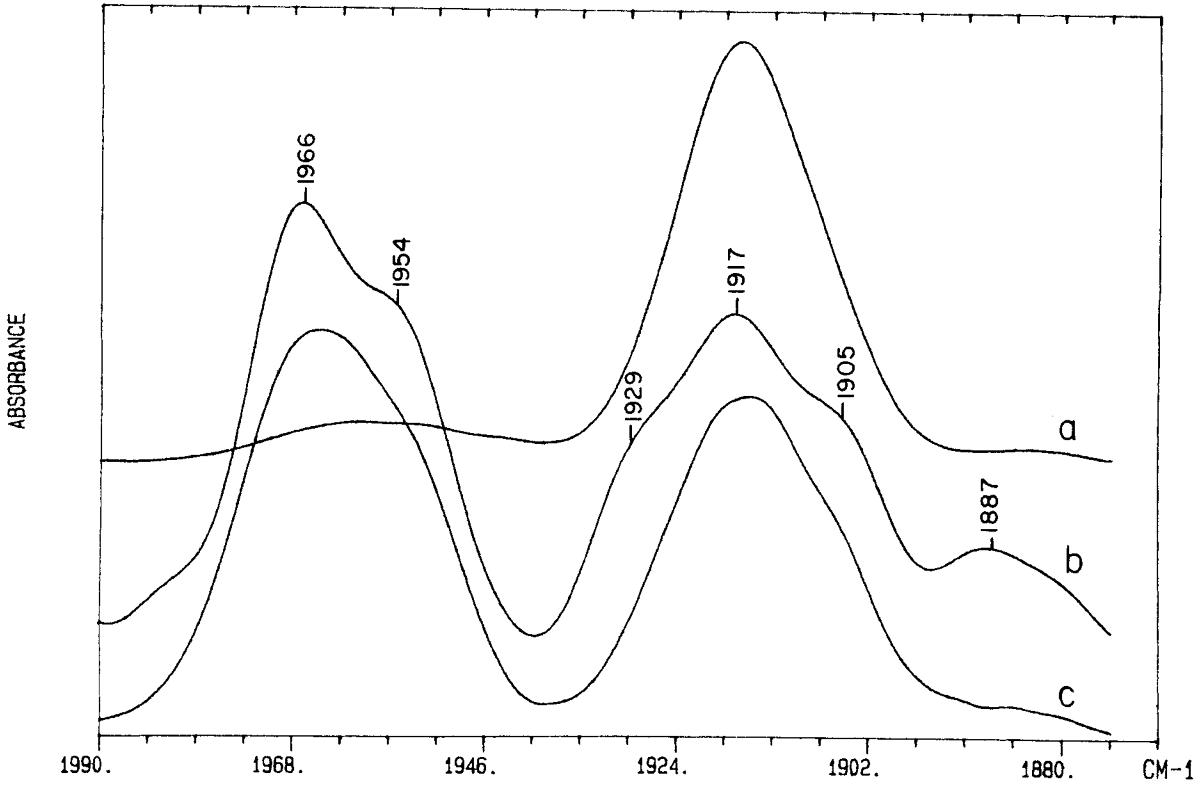


Figure 1 Infrared spectra in the carbonyl stretching region of Ir·^{13}CO/PS upon treatment with CO: (a) before treatment; (b) after treatment for 20 min; (c) followed by exposure to vacuum for 30 min.

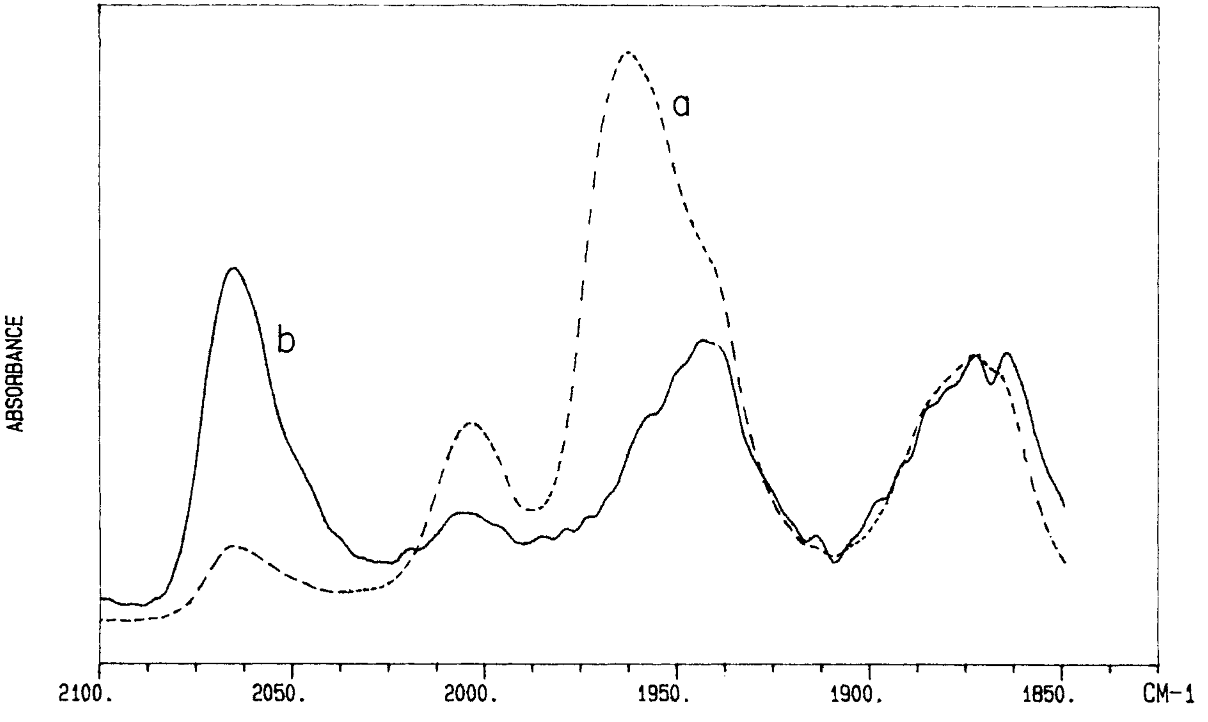


Figure 2 (a) Transmission and (b) ATR infrared spectra in the carbonyl region of Ir·I_2/PS.

PS and toluene. In addition, the reactivity of Vaska's complex in PS with gaseous reagents is similar to that in benzene. However, our results suggest that the PS matrix may modify the relative rates of reactions by hindering the diffusion of large gaseous molecules in the plastic. This provides an extra element of selectivity not possible with normal solvents. The preparation of the films is very easy since it is not necessary to anchor the complex to the polymer by covalent bonds. Materials of this kind are potentially useful in gas separation and as gas sensors.

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