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Preliminary communication

Photochemistry of trichloro(carbonyl)-tris(dimethylphenylphosphine)rhenium(III) in low temperature media *

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Abstract

Infrared and ultraviolet–visible spectroscopic evidence is presented to show that photolysis of $ReCl_3(CO)(PMe_2Ph)_3$ in poly(vinyl chloride) films and caesium iodide discs at ca. 12 K affords, irreversibly, free CO and presumably the *fac*-$ReCl_3(PMe_2Ph)_3$ isomer; i.e. CO ejection rather than PMe_2Ph ejection is the primary photoprocess.

Transition metal carbonyl complexes have been employed for many years as homogeneous catalysts in a variety of processes in the petrochemicals industry, e.g. the hydroformylation of olefins [1]. In such processes it has been assumed that the facile loss of a CO ligand from the metal complexes affords a site at the metal for the incoming substrate ligand which is involved in subsequent reactions. Improved product selectivity and yields are often achieved with phosphine-substituted metal carbonyl catalysts. In such complexes it is a matter of debate whether the loss of CO or loss of phosphine is the key step.

Matrix isolation studies [2] employing Ar, N_2, CH_4 and CO gas matrices at ca. 10 to 20 K have provided a wealth of information about unstable transition metal carbonyl species related to catalysis cycles, e.g. $HCo(CO)_3$ and $Co(CO)_4^{\cdot}$ [3]. Unfortunately gas matrices are inappropriate for studying metal carbonyl phosphine and metal phosphine complexes as catalyst precursors because phosphine-containing complexes are either involatile or decompose on attempted volatilisation. It turns out, however, that species of this type can be dispersed in organic glasses,

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* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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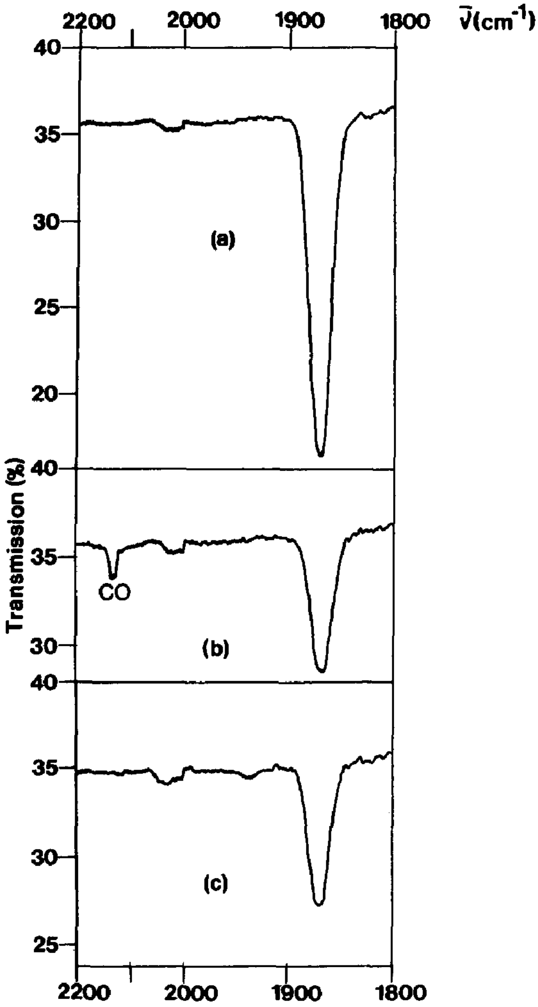
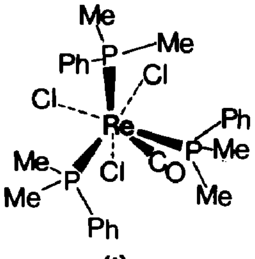


Fig. 1. Infrared spectra (Perkin-Elmer 983G; ca. 3 cm^{-1} resolution) from an experiment with a PVC film (cast from THF) containing $ReCl_3(CO)(PMe_2Ph)_3$: (a) before irradiation at 12 K; (b) after 5 hours irradiation with UV light ($310 < \lambda < 350$ nm); (c) after warming the film to 298 K and then recooling to 12 K before recording the spectrum.

polymer films, paraffin waxes, alkali halide discs and Nujol mulls. These media have been found to behave analogously to gas matrices at ca. 12 K [4]. We report here briefly the results of a study of the photochemistry of $ReCl_3(CO)(PMe_2Ph)_3$ (I) * in poly(vinyl chloride) films and caesium iodide discs at ca. 12 K aimed at determining whether ejection of CO or PMe_2Ph is the preferred primary process.

The complex I, which adopts a staggered structure with a CO capping ligand like that found for $TcCl_3(CO)(PMe_2Ph)_3$ by X-ray crystallography [6], in a poly(vinyl chloride) (PVC) ** film cast from tetrahydrofuran (THF) at ca. 12 K affords a single terminal IR CO stretching band at 1870 cm^{-1} (Fig. 1(a)) analogous to that for solutions in halocarbon solvents (ν(CO) at 1862 cm^{-1} for $CHCl_3$ [5]). Irradiation of the film (2 mg of I to 250 mg of PVC) for 5 hours with ultraviolet light corresponding to the prominent electric transition at $\lambda_{max} = 340$ nm ($310 < \lambda < 350$



(I)

nm; Pyrex glass disc + bromine gas filters) resulted in a decrease of the CO band for I and the formation of free CO (Fig. 1(b)). Attempted reversal using longer wavelength light ($\lambda > 410$ nm; pyrex glass disc + chlorine gas filters) corresponding to the new electronic band at $\lambda_{max} = 417$ nm or warming the film to 298 K and recooling to ca. 12 K in order to record the spectra were unsuccessful (Fig. 1(c)).

The ejection of CO and the non-reversibility point to a highly stable photoproduct, i.e. $ReCl_3(PMe_2Ph)_3$. This species seems likely to adopt a *fac* configuration given the staggered conformation of I and the rigidity of the low temperature cage. This conclusion is supported by the observation of a very close similarity of far IR bands for I and its photoproduct in either CsI discs (5 mg in 200 mg) or PVC films at ca. 12 K.

The results demonstrate the posibility of using alternative materials, e.g. polymer films, for carrying out low temperature experiments in order to characterize species derived from metal phosphine complexes. This suggests that the species proposed in many catalysis cycles involving such precursors can now be investigated. Interestingly, in the particular case of I, it was the single CO ligand rather than one of the three PMe_2Ph ligands that was ejected.

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[*] Prepared by the published method [5] and having satisfactory melting point, C and H analysis, and ^1H, ^{13}C and ^{31}P NMR spectra.

[**] The casting of PVC films, IR and UV–VIS spectrometers, the photolysis lamp and the closed-cycle He refrigerator have been described elsewhere [7].