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Preliminary communication

Photoisomerism and steric stability in a five-coordinate photolytic fragment, $Mo(CO)_4P(C_6H_{11})_3$

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SUMMARY

$Mo(CO)_4PCx_3$ (Cx = cyclohexyl), generated by photolysis of $Mo(CO)_5PCx_3$ in hydrocarbon glass, exists as two isomers with the phosphine and the vacancy in the coordination octahedron mutually *cis* and *trans* and the *trans* isomer may be converted into *cis*, using visible light, by a truly photochemical, non-thermal process.

The photochemistry of hexacarbonyls in rigid media has been closely studied in recent years[1–3]. We are now extending our own studies to substituted derivatives, in which we observe a number of novel effects, and report here some observations on pentacarbonylmolybdenum phosphines.

When $Mo(CO)_5PCx_3$ (I) (Cx = cyclohexyl) is irradiated at 77K[*] in a hydrocarbon glass (approx. $10^{-2}M$ in 4/1 methylcyclohexane/isopentane, medium pressure Hg discharge lamp) with light of wavelength greater than 305 nm, two new species are formed with CO stretching bands at 2027.5 m, 1916 (sh), 1907 s, and 1864 m cm^{-1} (species II) and 1883 cm^{-1} (species III)[**]. Since a C_{4v} geometry for the photochemical fragment $Mo(CO)_5$ is well established[1–4], we assign II and III as the isomers of the incomplete octahedron $Mo(CO)_4(PCx_3)$(vacancy). The 4-band pattern of II is as expected for species of the type *cis*-$M(CO)_4LL'$, while in III the 1883 cm^{-1} band must correspond to the intense E mode of the C_{4v} (pseudo-D_{4h}) *trans* isomer[***]. The higher frequency A_1 band, predicted weak, has so far escaped detection.

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[*] Temperature of cell block in direct contact with sample

[**] Species distinguished by constancy or otherwise of relative intensities. Abbreviations m, medium, (sh), shoulder, s, strong.

[***] The only other possibilities are species $Mo(CO)_3$, $Mo(CO)_nL_m$ ($n < 4$, $m = 0$ or 1) polynuclear species, and products of reaction with the solvent glass. We can rule out these on grounds of number and position of peaks in the IR; the ready formation of species related to III from a range of parents $Mo(CO)_5L$ (L = $P(i\text{-}C_3H_7)_3$, $P(n\text{-}C_4H_9)_3$, $P(p\text{-}C_6H_4CH_3)_3$, and $P(i\text{-}OC_3H_7)_3$), in amounts comparable to II even at concentrations of approximately 10^{-2} M, the ready disappearance of these species on warming, and the failure of $Mo(CO)_5$[2,4] or of $Mo(CO)_4$[9] (identical with these species prepared in inert gas matrices[8]) to react with aliphatic solvents.

When the glass is allowed to warm up to 98K, the 1864 cm^{-1} band of II becomes sharper and loses its initial asymmetry. These changes are maintained on recooling, and we assign them to the annealing out of differences in matrix environment (for related effects in crystalline matrices, see refs.)[3,5]. Further warming to 105K caused disappearance of II, with regeneration of I, while III persisted at the rate of warm-up used (approx. 5 degrees/min.) up to 110 - 115K.

Irradiation of I with light of wavelength greater than 420 nm produced no significant photolysis. However, irradiation of a mixture of I, II and III with such light led to an increase in the amount of II and a decrease in the amount of III. It follows that the light used is causing conversion of III directly to II. In contrast to recombination photoreversal[1-3] , this process is unlikely to be due merely to local lattice softening, since the effects of warming appear different from this, and in any case II is expected, on general grounds[6] and by analogy with species of the type *cis*-$Mo(CO)_4(PR_3)_2$ [7], to show a richer low energy electronic spectrum than III. We conclude that the conversion

$$\mathrm{III} \xrightarrow[\lambda > 420]{h\nu} \mathrm{II}$$

is a genuine photochemical process (Eqn.1).

Secondary photolysis of a mixture of I, II and III in hydrocarbon glass apparently gives a single species which we assign as the *fac* isomer of $Mo(CO)_3(PCx_3)(vacancy)_2$ [ν(CO) = 1955 (A_1); 1847, 1824 (E in idealised C_{3v})], such an assignment is consistent with the 4-band pattern observed by others[8] and confirmed by ourselves[9] for $Mo(CO)_4$ in hydrocarbon matrices.

By way of contrast photolysis of I in a 2-methyltetrahydrofuran (MeTHF) glass produces $Mo(CO)_4(PCx_3)$(MeTHF) exclusively as the *cis* isomer and photolysis of $Mo(CO)_5$(MeTHF)[2] to $Mo(CO)_4(MeTHF)_2$ also gives the *cis* isomer only.

Further studies of steric and electronic factors in determining the range of accessible products, and of the relationship of the photoisomerism described here to that in the coordinatively saturated species $Fe(CO)_4I_2$, are under way in these laboratories.

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