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Preliminary communication

INFRARED SPECTROSCOPIC EVIDENCE FOR THE EXISTENCE OF THE (η^5-CYCLOHEPTATRIENYL)TRICARBONYL(HYDRIDO)MOLYBDENUM INTERMEDIATE TRAPPED IN FROZEN GAS MATRICES AT 12 K

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Summary

Infrared spectra of matrices obtained by co-condensing sublimed (η^6-C_7H_8)-$Mo(CO)_3$ (I) with matrix gas at 12 K reveal a novel species, produced by thermal rearrangement of I in the gas phase and proposed to be the metal hydride complex (η^5-C_7H_7)$Mo(CO)_3H$ (II).

There are several reports [1—3] of thermal rearrangement reactions of organometallic compounds in which ring-to-metal hydrogen transfer and the reverse process are thought to be involved. A metal-assisted pathway has been proposed for the specific migration of the equatorial 7-*endo* hydrogen in complexed cycloheptatrienes of the type *exo*-(η^6-C_7H_7R)$M(CO)_3$ e.g. (R = H, Me, Ph; M = Cr, Mo) [4—7]. Very recently this particular rearrangement has been confirmed to involve a 1,5-hydride shift [7]. Low temperature matrix isolation studies have shown that photoinduced hydrogen migration [8] from cyclopentadiene to rhenium occurs on irradiation of (η^5-C_5H_5)(η^2-C_5H_6)$Re(CO)_2$ to give (η^5-C_5H_5)(η^1-C_5H_5)$Re(CO)_2H$ [9]. In relation to these thermal and photochemical intramolecular hydrogen transfers we report here infrared spectroscopic evidence for a matrix-trapped species which is produced on subliming the known complex (η^6-C_7H_8)$Mo(CO)_3$ (I).

Infrared spectra of frozen gas matrices of the parent I* in CH_4, Ar, CO, N_2 and SF_6 at 12 K exhibited three carbonyl bands assigned to I [10] together with other bands. For example, the spectrum of a CO matrix (Fig. 1(a)) showed three parent bands at 1993.7 cm^{-1} (A′), 1924.1 cm^{-1} (A′) and 1907.2 cm^{-1} (A″) (cf. solution spectrum (Fig. 2): IR bands at 1996.8,

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*Prepared by refluxing $Mo(CO)_6$ with cycloheptatriene (ref. [10]) in petroleum ether (b.p. 100—120°C) for 16 h under N_2.

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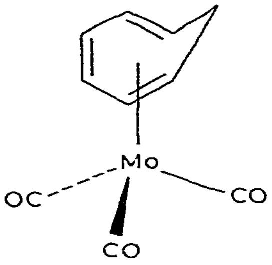
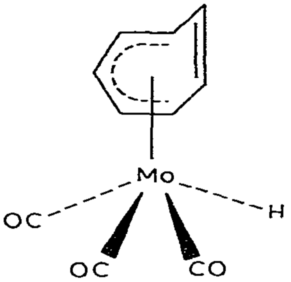


(I)



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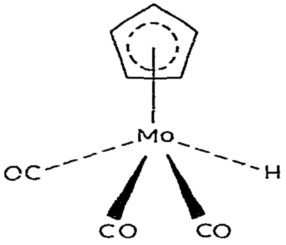

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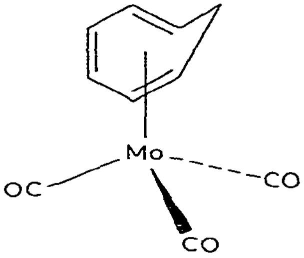

(IV)

1932.5 and 1907.9 cm^{-1}) and two other bands at 2042.3 and 1956.8 cm^{-1}. This matrix was obtained by depositing the sample I from a long spray head. Another matrix deposited using the same head but with a higher sample temperature* gave the spectrum shown in Fig. 1(b). A subtraction of the former spectrum from the latter gave the full spectrum in the terminal carbonyl region of the other species present in the matrices (Fig. 1(c)), revealing a third band at 1909.2 cm^{-1}. Comparisons of Fig. 1(a) and Fig. 1(b) with Fig. 2 show that this species is not some sample impurity and that its production increases with the sample sublimation temperature. The relative amount of this compound was also found to increase significantly, for a given sample temperature and matrix gas flow rate, with the distance travelled** by the sample before deposition. Sublimation of I at 50°C from a long hot tube onto a cold finger at 77 K gave a light orange deposit. On warming from 77 K to 25°C the colour of the deposit appeared to change (ca. 100 K) from light orange to red and a solution spectrum obtained subsequently indicated that only I was present on the finger after warming. These observations and the fact that three similar extra IR bands were seen regardless of matrix gas suggest that the other matrix-isolated species is produced by thermal rearrangement of I in the gas phase.

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*The matrix gas deposition rate was increased to compensate for the drop in dilution, caused by the higher sample temperature, which would have favoured unwanted bimolecular reactions.

**Varied between 12 and 45 cm.

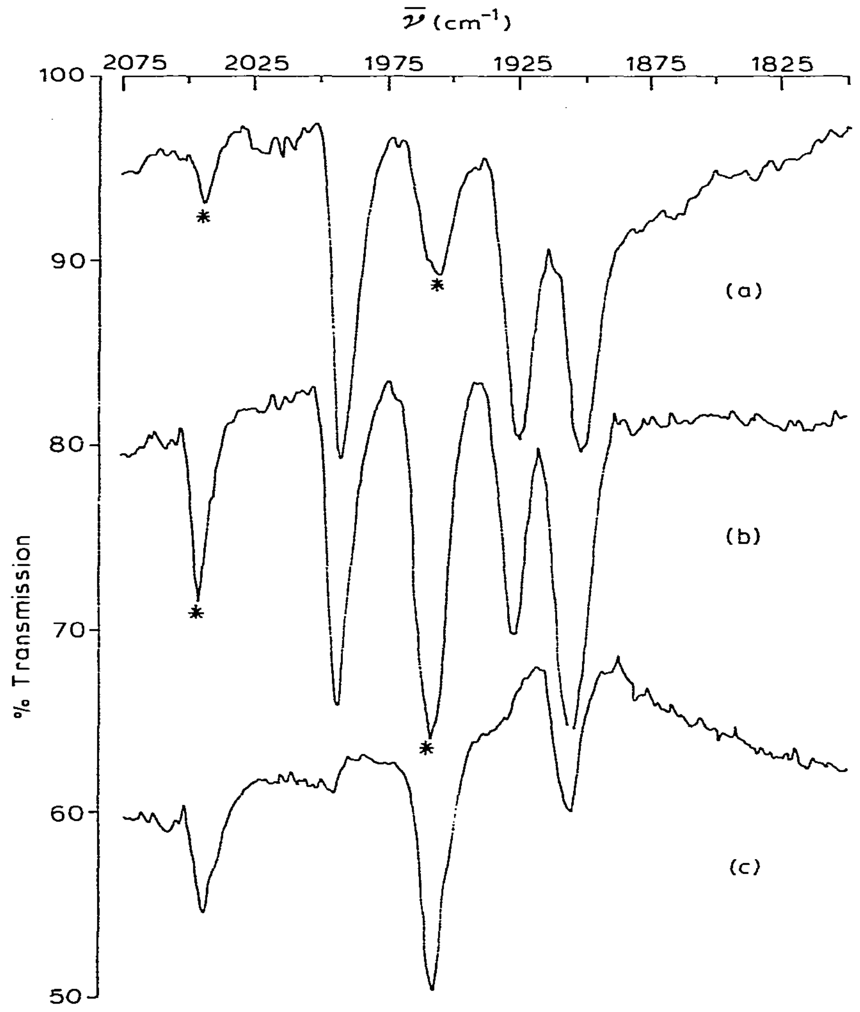

Fig. 1. Infrared spectra in the 2100—1800 cm^{-1} region (Nicolet 7199 FTIR spectrometer) showing (η^6-C_7H_8)Mo(CO)$_3$ (I) and another species (bands marked with an asterisk) isolated in CO matrices (1/2000) at 12 K: (a) after co-condensing a sample of I, sublimed at 28°C in a 45 cm long spray-head, with CO for 55 min; (b) as in a but with the sample sublimed at 45°C; (c) difference spectrum, b − a.

The most probable identity of the new species is the 18 valence electron metal hydride complex II frozen out of a gas phase reaction in which the 7-*endo* hydrogen in I migrates to the metal. The IR bands are at higher energy than those associated with I and are at quite similar wavenumbers to those of the stable complex (η^5-C_5H_5)Mo(CO)$_3$H (III) (ν(CO) at 2030, 1945 and 1941 cm^{-1} in a CO matrix at 12 K). No IR band for a Mo—H linkage was seen. Such a band, however, is expected to be weak; it was not possible to observe this band for III when it was isolated in gas matrices at 12 K. The well known thermal 1,5-hydrogen shift for I has been proposed [6,7] to proceed through the same metal hydride II which could undergo an internal rearrangement so that the hydride can return to the ring with a net 1,5-shift.

Experiments repeated with the complex (η^6-C_7H_8)Cr(CO)$_3$ under the same

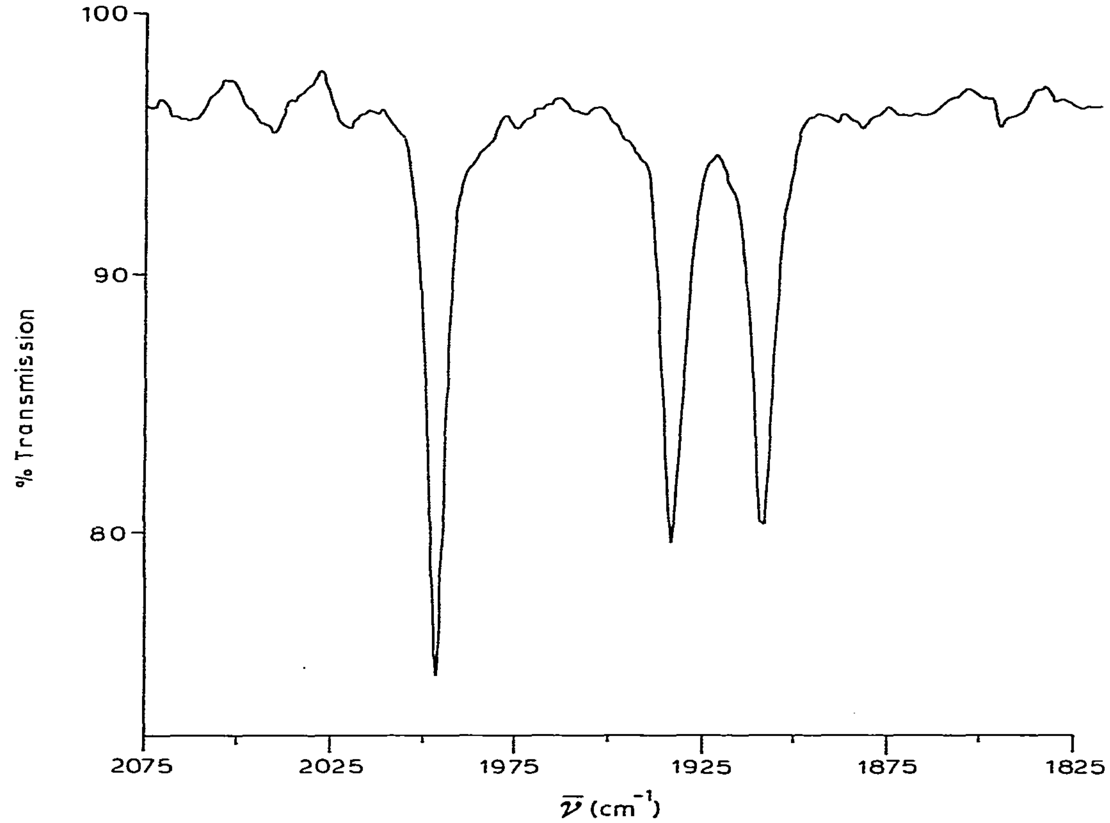

Fig. 2. Infrared spectrum of similar sample of I in hexane at 25°C (Nicolet 7199 FTIR spectrometer).

conditions showed no evidence for a chromium analogue of the trapped Mo species. The possibility of a high energy conformation* (IV) being trapped, rather than a metal hydride, seems therefore unlikely as such an isomer would also be expected to be frozen out in the matrices on subliming the chromium complex. Further work with the isotopically labelled complexes $(\eta^6\text{-}C_7H_8)Mo(^{12}CO)_n(^{13}CO)_{3-n}$ and $(\eta^6\text{-}C_7H_7D)Mo(CO)_3$ should assist in identifying the trapped species. Details of the matrix photochemistry of I will be presented elsewhere [12].

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References

1 A.D. Humphries and S.A.R. Knox, J. Chem. Soc. Dalton, (1975) 1710.
2 G.A.M. Munro and P.L. Pauson, J. Chem. Soc. Chem. Comm., (1976) 134.

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* ^{13}C NMR studies have shown that rapid rotation of the ring about the metal-ring axis in I and the chromium and tungsten analogues in solution occurs at room temperature (ref. [11]).

3 S.G. Davies, H. Folkin and O. Watts, J. Chem. Soc. Chem. Comm., (1980) 159.

4 W.E. Roth and W. Grimme, Tetrahedron Lett., (1966) 2347.

5 M.I. Foreman, G.R. Knox, P.L. Pauson, K.H. Todd and W.E. Watts, J. Chem. Soc. Chem. Comm., (1970) 843; J. Chem. Soc. Perkin II, (1972) 1141.

6 J.W. Faller, Inorg. Chem., 19 (1980) 2957.

7 W.J. Albery, J.M. Brown and I. Midgley, J. Chem. Soc. Perkin II, in press.

8 J. Shelly and T.H. Whitesides, J. Organometal. Chem., 92 (1975) 215.

9 J. Chetwynd-Talbot, P. Grebenik and R.N. Perutz, J. Chem. Soc. Chem. Comm., (1981) 452.

10 E.W. Abel, M.A. Bennett, R. Burton and G. Wilkinson, J. Chem. Soc., (1958) 4559.

11 C.G. Kreiter and M. Lang, J. Organometal. Chem., 55 (1973) C27.

12 R.H. Hooker and A.J. Rest, J. Chem. Soc. Dalton, in press.