

## Infrared Spectra of the Metal Carbido Cluster Complexes $M_5C(CO)_{15}$ ( $M = Fe, Ru$ and $Os$ )

IAN A. OXTON\* and DONALD B. POWELL

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

ROBERT J. GOUDSMIT, BRIAN F. G. JOHNSON, JACK LEWIS, WILLIAM J. H. NELSON, J. NICOLA NICHOLLS, MARIA J. ROSALES, MARIA D. VARGAS and KEN H. WHITMIRE

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

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### Introduction

Recent interest in the structural and spectroscopic properties of metal carbido cluster complexes stems mainly from the topographical similarity which is likely to exist between molecular species of this type and species present as adsorbates on metal surfaces, the latter being believed to play a crucial rôle in catalytic hydrogenation reactions such as the Fischer–Tropsch syntheses (*cf.* ref. 1).

Several vibrational spectroscopic studies have now been reported in which metal–carbido stretching modes of metal carbido cluster complexes have been assigned; the situations of the carbido atoms may be divided conveniently into two types: (i) interstitial, such as in  $Co_6C(CO)_{12}(\mu_3-S)_2$  [2] and  $[Os_{10}C(CO)_{24}]^{2-}$  [3], and (ii) exposed, or semi-interstitial, as in  $Ru_5C(CO)_{15}$  [4]. The present paper is concerned with carbido clusters of the latter type and reports the vibrational frequencies associated with the carbido ligands in polycrystalline  $Fe_5C(CO)_{15}$  and  $Os_5C(CO)_{15}$ , permitting a comparison with data already reported for the third member of this series  $Ru_5C(CO)_{15}$  [4]. Characterisation of the  $\nu_{MC}$  modes in these clusters is especially desirable in view of the flexibility of the metal skeleton [4, 5], the geometry of which may be readily deduced from the infrared spectrum [6].

One result of the earlier study of  $Ru_5C(CO)_{15}$  which made extension to the Fe and Os analogues rather important was the observation of an anomalously large number of absorptions due to  $\nu_{RuC}$  in the infrared spectrum. Five such bands were observed, instead of the maximum of three which would be expected. Possible reasons for this observation were suggested [4], the two most likely origins being

thought to lie in correlation-field ('factor-group') coupling of the  $\nu_{RuC}$  modes in the crystal, or a 'multiple-site' splitting effect, resulting from the presence in the crystal of non-equivalent sets of cluster molecules. Crystallographic data for the three  $M_5C(CO)_{15}$  cluster complexes are given in Table I, where it may be seen that only the Ru and Os complexes are isomorphous, possessing a different space group from that of  $Fe_5C(CO)_{15}$ . However, all three cluster species are isostructural, each possessing a square-based pyramidal structure in which the carbido atom is located *ca.* 0.1 Å below the centre of the square face (Fig. 1). The Fe complex is composed of a single set of equivalent cluster molecules in the crystal, whereas two such sets exist in crystals of both the Ru and Os complexes. A comparison of the infrared spectra of three cluster complexes might thus be expected to identify the origin of the multiplicity of  $\nu_{MC}$  bands in the spectrum of  $Ru_5C(CO)_{15}$ .

TABLE I. Crystallographic Data for  $M_5C(CO)_{15}$  ( $M = Fe, Ru, Os$ ) Complexes.

Species	$Fe_5C(CO)_{15}$ [7]	$Ru_5C(CO)_{15}$ [8]	$Os_5C(CO)_{15}$ [5]
Space Group	$C2/c$ ( $C_{2h}^6$ ; no. 15)	$P2_1/c$ ( $C_{2h}^5$ ; no. 14)	$P2_1/c$ ( $C_{2h}^5$ ; no. 14)
Z	8	8*	8*
$\bar{r}_{MM}$ (Å)	2.64	2.84	2.87
$\bar{r}_{MC}$ (Å)	1.75	2.04	2.06

\*The eight cluster molecules per unit cell occupy two equally-populated sets of inequivalent sites; the overall geometries of the two types of cluster molecule in each case are very similar [5, 8].

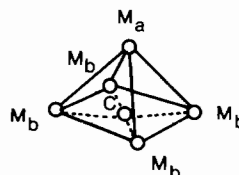


Fig. 1. Schematic configuration of the  $M_5C$  skeletons of the metal carbido clusters  $M_5C(CO)_{15}$  ( $M = Fe, Ru, Os$ ). The subscripts 'a' and 'b' refer to apical and basal metal atoms, respectively.

### Experimental

The complex  $Fe_5C(CO)_{15}$  was synthesised by a modification of the method of Tachikawa and Muetterties [9] and was recrystallised from hot toluene. The cluster  $Os_5C(CO)_{15}$  was isolated by the vacuum pyrolysis at 533 K of  $Os_3(CO)_{12}$  and sub-

\*Author to whom correspondence should be addressed.

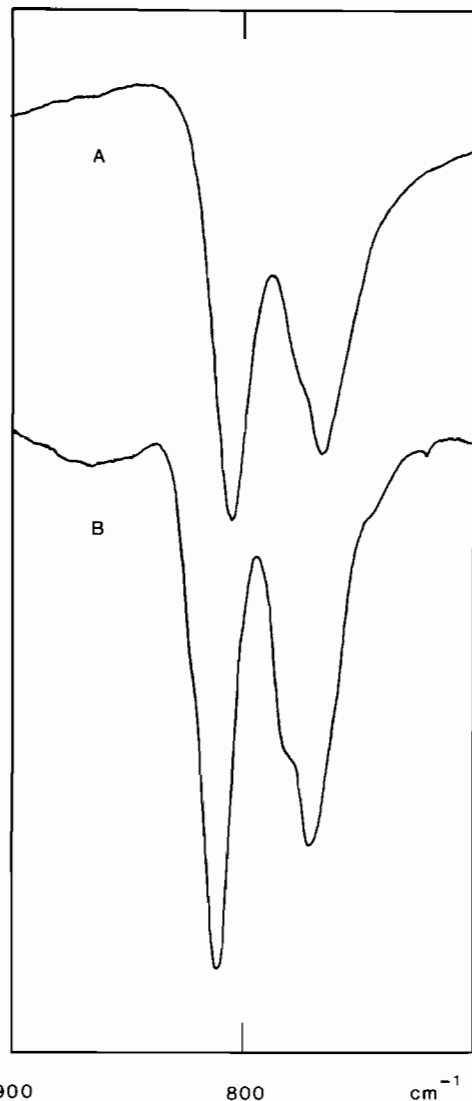


Fig. 2. The 900–700  $\text{cm}^{-1}$  region of the infrared spectrum of  $\text{Fe}_5\text{C}(\text{CO})_{15}$  at 300 K (A) and 95 K (B).

sequent crystallisation from an ethyl acetate solution containing a mixture of cluster products.

Infrared spectra of the complexes, as CsBr discs at 300 K and *ca.* 95 K, were measured using Digilab FTS-14 and FTS-20 Fourier transform spectrophotometers at a resolution of  $1.0 \text{ cm}^{-1}$ .

### Results and Discussion

The absorption arising from the metal–carbido stretching modes in  $\text{Fe}_5\text{C}(\text{CO})_{15}$  and  $\text{Os}_5\text{C}(\text{CO})_{15}$  are shown in Figs. 2 and 3, respectively, and vibrational frequencies of these modes are given in Table II, along with the corresponding data for  $\text{Ru}_5\text{C}(\text{CO})_{15}$  [4].

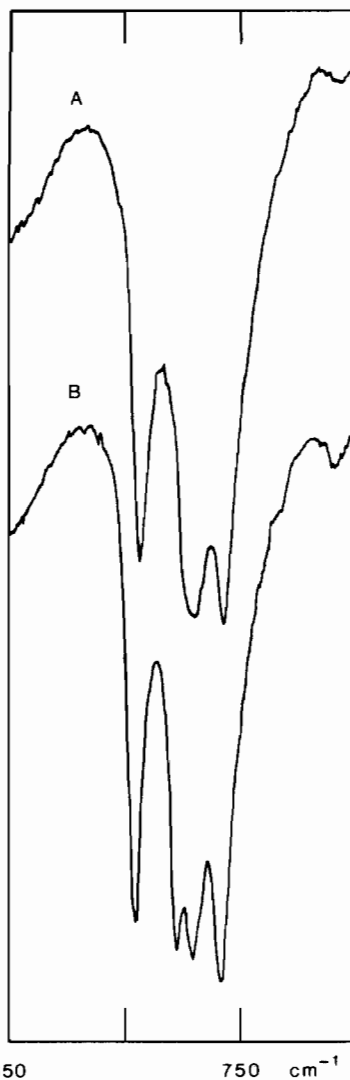


Fig. 3. The 850–700  $\text{cm}^{-1}$  region of the infrared spectrum of  $\text{Os}_5\text{C}(\text{CO})_{15}$  at 300 K (A) and 95 K (B).

Some years ago Braye *et al.* [7] reported bands at  $790 \text{ cm}^{-1}$  and  $770 \text{ cm}^{-1}$  in the infrared spectrum of  $\text{Fe}_5\text{C}(\text{CO})_{15}$  in cyclohexane solution and tentatively assigned these absorptions to the two Fe–C stretching modes ( $\text{C}_{4v}$  symmetry;  $a_1 + e$ ). The present data confirm these assignments, both modes undergoing slight shifts to higher frequency and the e mode being split by the crystal environment. The spectra of 300 K for the three complexes are thus similar, with a single absorption at somewhat higher frequency than a poorly-resolved doublet being observed in each case. This is entirely in agreement with the crystallographically-determined molecular structures [5, 7, 8].

By contrast, the low-temperature spectra of these complexes are of two types, with that of  $\text{Fe}_5\text{C}(\text{CO})_{15}$  being essentially similar to the 300 K spectrum and

TABLE II. Metal–Carbido Stretching Frequencies ( $\text{cm}^{-1}$ ) in  $\text{M}_5\text{C}(\text{CO})_{15}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ) Complexes at Room and Liquid-Nitrogen Temperatures.

$\text{Fe}_5\text{C}(\text{CO})_{15}$		$\text{Ru}_5\text{C}(\text{CO})_{15}^*$		$\text{Os}_5\text{C}(\text{CO})_{15}$	
300 K	95 K	300 K	95 K	300 K	95 K
805 (vs)	811 (vs)	757 (s)	767 (sh)**	793 (s)	799 (sh)
			764 (s)**		795 (s)
775 (sh)	779 (sh)	738 (s)	752 (s)	769 (vs)	777 (s)
			745 (s)		770 (s)
766 (s)	771 (s)	730 (vs)	735 (vs)	757 (s)	758 (vs)

\*Ref. 4. \*\*The two highest-frequency absorptions in the 95 K spectrum of  $\text{Ru}_5\text{C}(\text{CO})_{15}$  were incorrectly given in ref. 4 as  $772 \text{ cm}^{-1}$  and  $769 \text{ cm}^{-1}$ . Abbreviations: s – strong, sh – shoulder, v – very.

those of the Ru and Os analogues displaying a greater complexity. It is thus apparent that the 'extra' bands observed in the spectra of the Ru and Os clusters at low temperatures arise as a consequence of the multiple-site occupancy displayed in the crystal by these species and do not result from intermolecular vibrational coupling. It is a measure of the sensitivity of the metal–carbido stretching absorptions to the environment of the carbido atom that distinguishable absorptions from the two sets of cluster molecules in each case are, in fact, observed, in view of the close geometrical similarity which exists between the molecules of each corresponding set [5, 8]. That the additional complexity observed in the spectra of the Ru and Os complexes is *not* due to correlation-field coupling is reassuring from the point of view of the complication such an effect would introduce into the deduction of molecular symmetry from the observed  $\nu_{\text{MC}}$  absorptions.

It is somewhat surprising to note that the  $\nu_{\text{MC}}$  frequencies in  $\text{Os}_5\text{C}(\text{CO})_{15}$  are *ca.*  $25 \text{ cm}^{-1}$  higher than those in  $\text{Ru}_5\text{C}(\text{CO})_{15}$ , the overall order of frequencies being  $\text{Re} > \text{Os} > \text{Ru}$ . This trend, whilst superficially anomalous, may be readily rationalised in terms of the opposing factors of metal mass and M–C bond stretching force constant,  $k_{\text{MC}}$ . The data are consistent with a steady increase in  $k_{\text{MC}}$  on going to progressively heavier metals, in opposition to the increasing metal mass. At this level of approximation there is probably little effective difference between the metal masses of the  $\text{Ru}_5$  and  $\text{Os}_5$  clusters and the frequency differences between these species may be regarded as being almost wholly due to the difference in the values of  $k_{\text{MC}}$ .

\*It is assumed that each type of cluster molecule will possess two such force constants, corresponding to the  $\text{M}_a$  and  $\text{M}_b$  bonds (Fig. 1).

There is an obvious analogy between the environment of the carbido atom in the square-pyramidal  $\text{M}_5\text{C}(\text{CO})_{15}$  clusters and a superficial carbide atom adsorbed on the (100) or (110) faces of a f.c.c. metal, assuming that interaction between the carbido atom and the metal atom, located in the second layer, directly below the centre of the fourfold site is feasible. It has been observed that superficial carbido adsorbates may be formed by the dissociative adsorption of carbon monoxide on certain metal surfaces [10, 11]; the resulting overlayer may not, however, provide a good spectroscopic analogy with the molecular carbido clusters in that vibrational coupling between the motions of the C and O atoms is distinctly possible [12, 13]. The alternative source of adsorbed carbido atoms, from the dissociative adsorption of hydrocarbons [14], would be expected to permit a more straightforward comparison.

An example of the geometric situation of a superficial carbido atom is provided by the Ni (100) surface. Low-energy electron diffraction analysis of this system is consistent with a  $c(2 \times 2)$  overlayer in which the (distorted) top layer of nickel atoms accommodates carbido atoms in hollow fourfold sites, with Ni–C =  $1.803(15) \text{ \AA}$  and the carbido atoms  $0.1(1) \text{ \AA}$  out of the plane of the nickel atoms [15]. There is, however, a paucity of vibrational data for carbidic overlayers on the later transition metals and a comparison of such data for metal clusters and metal surface species cannot be made at present.

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