Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

PRELIMINARY NOTE

Structure and bonding of $(OC)_4Cr(PMe_2)_2Cr(CO)_4$ and $(OC)_4Mn(PMe_2)_2Mn(CO)_4$ in solution as established by IR combination spectra

We have extended the usefulness of infrared spectra for the determination of the structures of metal carbonyl derivatives in solution[1], by making use of combination spectra[2-5] to assess symmetry and furnish evidence for metal–metal bonding. Theory[6] predicts that when two conditions are satisfied, and only then, dinuclear metal carbonyls will have a "high frequency inactive mode", ν_1, in the CO stretching region, such that the following relationships hold:

$$\nu_{\max}(\mathrm{c}) = \nu_1 + \nu_2 \tag{1}$$

$$\nu_{\max}(\mathrm{f}) = \nu_2 \tag{2}$$

$$\nu_1 > \nu_2 \tag{3}$$

These conditions are:

(a) the point group of the molecules must be of suitably high symmetry. Specifically, it must include C_i, C_{nh}, S_n or D_n. (C_{2h}, which contains C_i, satisfies this condition; C_{2v} does not).

(b) there must exist a direct interaction between CO groups on different metals, such as could arise[2,3,6] from a metal–metal bond.

If (a) is not satisfied, ν_1 will itself be IR active. If (b) is not satisfied, ν_1 will differ from the IR active ν_2 only to a small extent (because of non-bonded interactions).

We have examined the fundamental and combination spectra of several dinuclear metal carbonyls in order to assess these predictions. The results are shown in Table 1.

(I) is known[7] to be of symmetry C_{2h} (staggered) in the solid. In solution it could be eclipsed (C_{2v}), gauche, or intermediate (C_2). Our results show, however, that the staggered configuration is retained. (II) is known to be transoid (C_{2h}) in the solid[8] but cisoid (C_{2v}) in solution[9]. As predicted, it does not have a high frequency inactive mode.

(III) may be assumed to be D_{2h}, in analogy with $Mn_2(CO)_8Br_2$[10], satisfying condition (a). Our results confirm this assumption. However, condition (b) is satisfied only by non-bonding interactions, and the separation between ν_1 and ν_2 is only 22 cm^{-1}. This is 0.4 of the value found in $Mn_2(CO)_{10}$[2,3], where there is a metal–metal bond, although simple theory indicates[6] a value of 0.71 for this ratio, if we could treat the cases as comparable.

(IV) is presumed[11] C_{2v} by analogy with $Fe_2(CO)_6(SEt)_2$[12], a suggestion supported by Mössbauer studies[13] and since (a) is not satisfied it has no high frequency inactive mode. The excellent agreement between $\nu_{\max}(\mathrm{c})$ and $\nu_{\max}(\mathrm{f})$ in (II) and (IV) indicates that the neglect of anharmonicity in Eqn. (1) does not lead to major errors.

It was not known for certain at the start of this work whether (V) had a D_{2h}

TABLE 1

HIGHEST OBSERVED COMBINATION AND FUNDAMENTAL BANDS

Substance	*Possible symmetry in solution*	*Conditions satisfied by assigned symmetry*	$\nu_{max}(c)^b$	$\nu_{max}(f)^a$	$\nu_{max}(c)-\nu_{max}(f)$	*Inference*
I = $\{C_5H_5Mo(CO)_3\}_2$	C_{2h} C_{2v} C_2	a,b b b	3958	1961	1997	C_{2h} correct
II = $\{C_5H_5Fe(CO)_2\}_2$	C_{2v}	b	4110	2054	2056	
III = $(OC)_4Mn(PMe_2)_2Mn(CO)_4$	D_{2h} (?)	a (?)	4106	2042	2064	D_{2h} correct
IV = $(OC)_3Fe(PMe_2)_2Fe(CO)_3$	C_{2v}	b	4098	2049	2049	
V = $(OC)_4Cr(PMe_2)_2Cr(CO)_4$	D_{2h} C_{2v}	a,b	4058	2011	2047	D_{2h} correct; effect (b) considerable

[a] CCl_4 solution; Perkin-Elmer 225. Cyclohexane solution gives better resolution but slight shift. [b] CCl_4 solution, saturated, 1 cm path length. Beckman DK2-A spectrometer (grant of Science Research Council to P.S.B.) 90–100% transmission range. Base lines and calibration (with *p*-dichlorobenzene) essential for each run. Estimated error ~ ±2 cm^{-1}.

structure with a planar M_2P_2 ring [as in (III)], or a C_{2v} structure with the ring buckled [as in (IV)]. As Table 1 shows, the D_{2h} structure is correct, and the metal–metal bond required to explain the observed diamagnetism[14] gives rise to an increased interaction. $\nu_1 - \nu_2$ is nearly twice as large as in (III) (having 0.66 of the value in $Mn_2(CO)_{10}$ where theory[6] requires 0.71), and is equal to that observed in (I) where the metal–metal bond must be real since it is the only factor holding the two halves of the molecule together. The exact agreement between (I) and (V) is presumably fortuitous. These conclusions are supported by the results of an independent crystallographic study[15] of a derivative of the molybdenum equivalent of (V).

The combination band method of structure investigation has unique advantages for determination of the structure of polynuclear metal carbonyls in solution. Normal IR evidence from the fundamental region has been used as evidence for high symmetry but the method rests on the absence of bands which could have been "lost" through accidental degeneracy. Combination studies eliminate this source of error by evaluating the "missing" frequency. Raman studies (for which combination studies are to some extent a substitute) require equipment less widely available, and may be difficult with coloured and photosensitive materials. X-ray studies are lengthy and give information only about the solid.

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Received July 5th, 1967