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Preliminary communication

UV PHOTOELECTRON STUDIES OF $Cr(\eta\text{-}C_3H_5)_3$, $Cr_2(\eta\text{-}C_3H_5)_4$ AND $Mo_2(\eta\text{-}C_3H_5)_4$

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Summary

The He(I) and He(II) photoelectron spectra of $Cr(\eta\text{-}C_3H_5)_3$, $Cr_2(\eta\text{-}C_3H_5)_4$ and $Mo_2(\eta\text{-}C_3H_5)_4$ have been determined and assigned. Comparisons are made between the allyl dimers and the quadruply bonded chromium and molybdenum carboxylate dimers.

The binuclear allyl complexes, $Cr_2(\eta\text{-}C_3H_5)_4$ and $Mo_2(\eta\text{-}C_3H_5)_4$ are representative of a small but particularly interesting sub-group of the extensive class of quadruply bonded metal dimers. The catalytic properties of allyl complexes towards olefin isomerization and polymerization have received considerable attention and are well documented [1,2]. Detailed interpretation of the reported spectroscopic data is, however, sparse. We have measured the photoelectron spectra of these dimers, and that of the monomer $Cr(\eta\text{-}C_3H_5)_3$, in the gas phase, in order to gain insight into their electronic structure.

The three compounds have been structurally characterized by X-ray crystallography at low temperatures [3—6]: representations of the structures are given in Fig. 1. Although the global symmetry of the molecules is very low, it is possible to draw some conclusions from symmetry based arguments if several basic assumptions are made. The first of these concerns the principal metal—allyl bonding interactions. By analogy with $Ni(\eta\text{-}C_3H_5)_2$ and $Pd(\eta\text{-}C_3H_5)_2$ (which have been extensively studied both theoretically [7—10] and experimentally [11,12]), the metal *d*-orbitals are expected to mix most strongly with the $1a_2$ (non-bonding) orbital of the allyl moiety. In the $1a_2$ level the charge density is distributed equally between the two terminal carbon atoms, and, if only these atoms are considered, it is apparent that $Cr(\eta\text{-}C_3H_5)_3$ has approximate D_{3h} symmetry and $M_2(\eta\text{-}C_3H_5)_4$ have approximate D_{2d} symmetry. On these assumptions it is possible to draw up qualitative interaction schemes for the two types of molecules, shown in Fig. 2. In the monomer, the strongest interaction is expected to be a π-interaction between the chromium d_{xz} and d_{yz} orbitals and the non-bonding allyl π-orbital ($1a_2$), whereas in the dimer, the principal metal—allyl

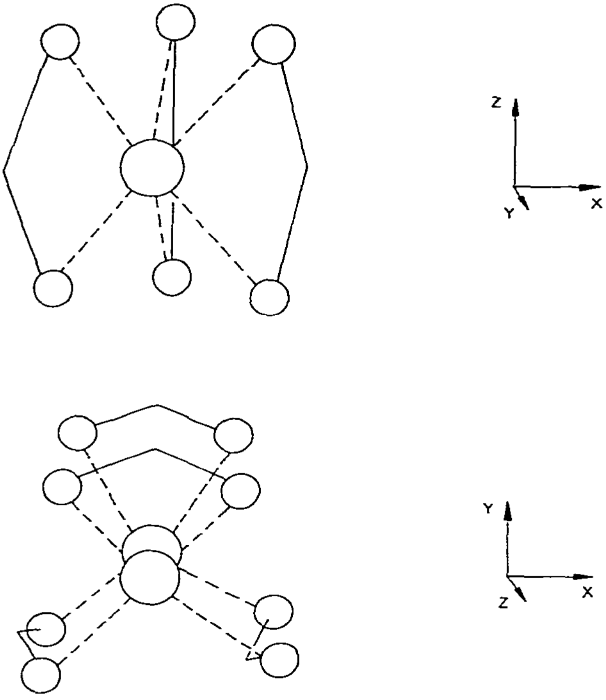

Fig. 1. Symmetry approximations for $Cr(\eta\text{-}C_3H_5)_3$ and $M_2(\eta\text{-}C_3H_5)_4$.

bonding interaction is expected to involve the metal d_{xy} orbitals, and the allyl $1a_2$ orbitals.

The photoelectron spectra of all three compounds show bands above 12 eV similar to those observed for several other allyl compounds [11,12]. These are assigned to ionizations from allyl σ-bonding levels and are not discussed further.

The He(I) spectrum of $Cr(\eta\text{-}C_3H_5)_3$ shows five bands below 12 eV, A—E (see Fig. 3, Table 1). The He(I)/He(II) intensity ratios do not vary much, but it is apparent, that bands B and D gain in intensity, relative to band F, on changing from He(I) to He(II) radiation. In the light of our interaction scheme and the ionization energy and intensity pattern, we assign the spectrum as follows. The three essentially non-bonding metal *d*-electrons (in the a'_1 and e' levels) are assigned to bands A and B. The levels correlating with the allyl $1a_2$ orbitals (e'' and a''_2) constitute the rest of band B and band C. Band D and possibly the shoulder E are attributed to the allyl π-bonding levels ($1b_2$).

The He(I) spectra of $Cr_2(\eta\text{-}C_3H_5)_4$ and $Mo_2(\eta\text{-}C_3H_5)_4$ (see Fig. 3, Table 1) are broadly similar in appearance: the low energy region consists of an isolated band, A, below 7.0 eV, and two extremely broad bands at ca. 7.9 eV and between 10.0 and 10.7 eV, of which the low band shows some evidence of fine structure. This band is more resolved in the case of the molybdenum compound than for the chromium compound, which is a general trend between first and second row transition metals. Band A is relatively more intense in the Mo spectrum than in the Cr spectrum. This indicates it has a high degree of metal *d*-character, substantial increases being normally found between 3*d* and 4*d* ionization cross sections [13]. Band A is therefore assigned to ionization from the M—M δ orbital. Band B

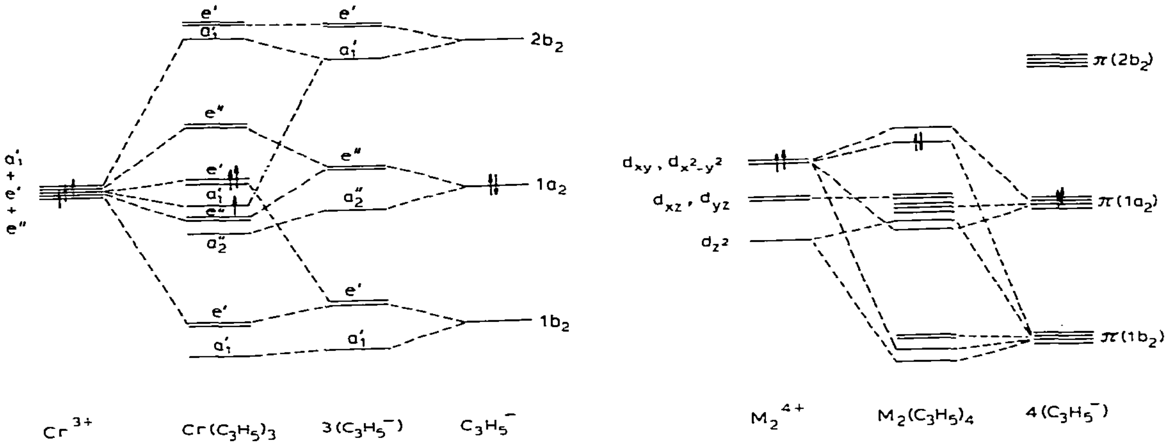

Fig. 2. Interaction schemes for $Cr(\eta\text{-}C_3H_5)_3$ and $M_2(\eta\text{-}C_3H_5)_4$.

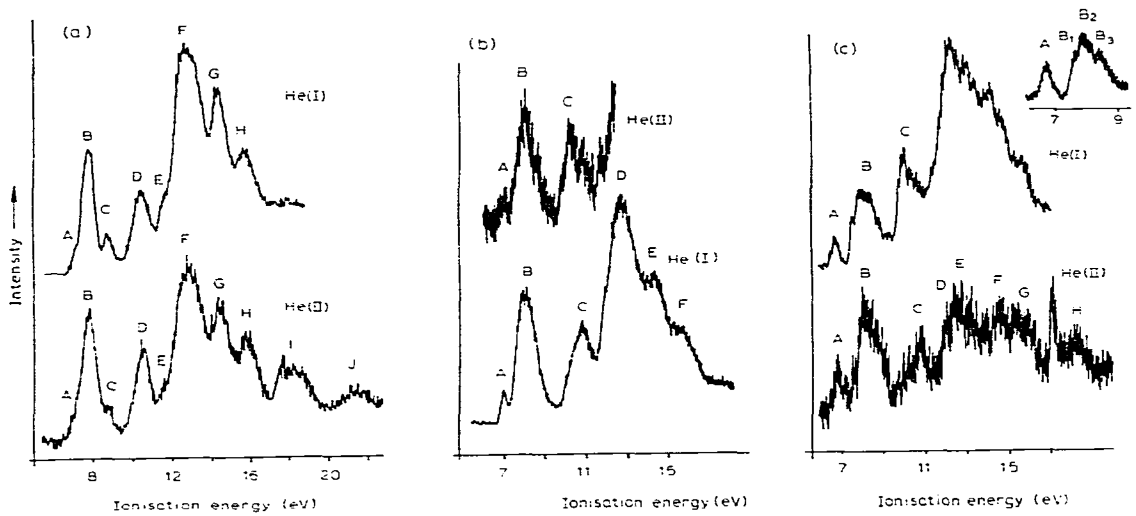

Fig. 3. Photoelectron spectra of (a) $Cr(\eta\text{-}C_3H_5)_3$, (b) $Cr_2(\eta\text{-}C_3H_5)_4$ and (c) $Mo_2(\eta\text{-}C_3H_5)_4$.

TABLE 1

IONIZATION ENERGY DATA FOR $Cr(\eta\text{-}C_3H_5)_3$, $Cr_2(\eta\text{-}C_3H_5)_4$ AND $Mo_2(\eta\text{-}C_3H_5)_4$

$Cr(\eta\text{-}C_3H_5)_3$	$Cr_2(\eta\text{-}C_3H_5)_4$	$Mo_2(\eta\text{-}C_3H_5)_4$	Assignment
	6.90 (A)	6.72 (A)	M—M δ
7.20 (A)	7.94 (B)	7.61 (B_1)	$M_d + 1a_2$
7.84 (B)		7.94 (B_2)	
8.80 (C)		8.46 (B_3)	
10.54 (D)	10.73 (C)	10.04 (C)	$1b_2$
11.79 (E)			
12.86 (F)	12.72 (D)	12.46 (D)	allyl σ
14.36 (G)	14.27 (E)	13.36 (E)	
15.48 (H)	15.63 (F)	14.52 (F)	
17.9[a] (I)		15.98 (G)	
21.2[a] (J)		18.2 (H)	

[a] Calculated from the He(II) spectrum.

is likely to contain ionizations from levels correlating with the ligand $1a_2$ levels as well as those from M—M π- and σ-bonding orbitals.

Though detailed assignment is not possible due to overlapping of the ionization bands, several useful comparisons may be made between these two compounds and other Cr and Mo quadruply bonded dimers. We will focus attention on the ionization energies of the σ-, π- and δ-levels of the quadruple bond. These may be considered to depend on two factors: the interaction between the two metal centres and the more intimate interaction with the ligand levels; the latter will depend crucially on the symmetry and energy relationship of the particular M—M bonding orbital and the appropriate ligand orbitals. Such a situation has been demonstrated in comparison of three triply bonded dimolybdenum complexes [14]. Most useful comparisons may therefore be made between metals within a particular ligand class. In this context it is interesting that the allylchromium and -molybdenum dimers show closely similar spectra, whereas, for the carboxylates, $M_2(O_2CR)_4$ (M = Cr or Mo), the spectra have very different profiles in the low energy region [15]. In the spectra of $Cr_2(O_2CR)_4$, the δ-, π- and σ-ionization overlap, whereas for $Mo_2(O_2CR)_4$ the δ- and π- (and probably also the σ-) bands are well separated. This drawing together of ionization for the Cr compounds has been associated with the anomalously long M—M bond in the chromium carboxylate dimers [15]. ($Cr_2(O_2CMe)_4$ 0.2288 nm [16]; $Mo_2(O_2CMe$ 0.2093 nm [17]). In the cases of $M_2(\eta\text{-}C_3H_5)_4$ the bond length relationship between the two compounds is more normal ($Cr_2(\eta\text{-}C_3H_5)_4$ 0.197 nm [5]; $Mo_2(\eta\text{-}C_3H_5)_4$ 0.2183 nm [6]) so the compounds would be expected to have more similar orbital splittings.

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