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UV PHOTOELECTRON SPECTRAL AND THEORETICAL STUDIES ON TRIS(BUTADIENE)-MOLYBDENUM AND -TUNGSTEN

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Summary

The UV photoelectron spectra of tris(butadiene)molybdenum and -tungsten have been recorded and assigned with the assistance of extended Hückel molecular orbital calculations. The spectra and calculations indicate substantial electron transfer from the metal to the ligand. The molecular orbital calculations have also indicated why these molecules adopt a trigonal prismatic rather than a octahedral geometry about the metal atom. The unusual C—C bond lengths in these complexes have been confirmed by a redetermination of the structure of tris(butadiene)molybdenum by X-ray crystallographic techniques and are discussed in the light of the calculations.

The tris(butadiene) complexes of molybdenum and tungsten, $M(C_4H_6)_3$, are the only well characterised homoleptic transition metal butadiene complexes [1]. If the butadiene ligand is considered in the conventional fashion as a neutral 4-electron ligand then these complexes would be classified as zero-valent, d^6, molybdenum and tungsten complexes respectively. Thus these complexes are formally analogous to the sandwich complexes $M(\eta\text{-}C_6H_6)_2$ and closely related to the carbonyl complexes $M(CO)_6$. However, the remarkable stability of the tris(butadiene) complexes (they are reported to be stable in air for periods up to a week) compared to the corresponding bis(arene) complexes suggested that in practice the bonding in the two types of complex might not be too closely related. This view is supported by the recent synthesis and structural characterisation of tris(*ortho*-xylyl) complexes of tungsten by Lappert and his coworkers [2]. Although these complexes are formally complexes of tungsten(VI), structurally they are closely related to the formally zero-valent tris(butadiene) complexes, c.f. I and II, since in both types of complexes the ligands adopt a η^4-coordination mode and are trigonal prismatic. These structural similarities suggest that such complexes are poorly represented

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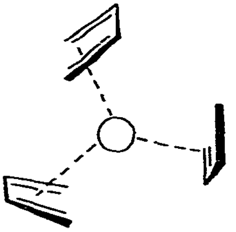
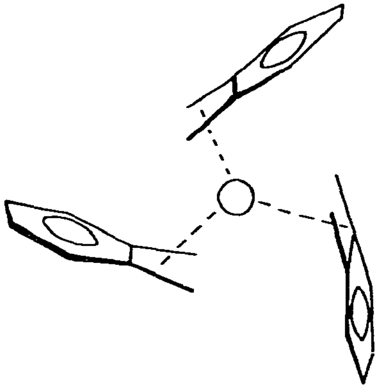


[$Mo(\eta-C_4H_6)_3$]

(I)



[$W(CH_2C_6H_4CH_2\text{-}o)_3$]

(II)

by either M^0 or M^{VI} valence bond representations and the true bonding situation is better represented by a resonance hybrid of these extreme formulations.

The preliminary details of the crystal structure of $Mo(\eta\text{-}C_4H_6)_3$ [1] have suggested that all the Mo—C bond lengths are equal and that the butadiene ligand retains a high degree of multiple bond character in the terminal C—C bonds, which are approximately 0.3 Å shorter than the central C—C bond. This type of bond length alternation is very unusual for η^4-diene complexes of the transition metals, since in general the C—C bond lengths are found to be equal within experimental error [3]. This equalisation of bond lengths has been attributed to effective back donation from filled metal *d*-orbitals to the lowest unoccupied molecular orbital of the butadiene ligand [4]. The unusual structural and chemical features of the tris(butadiene) complexes merited, in our opinion further investigation using He-I and He-II UV photoelectron spectroscopy and molecular orbital calculations based on the extended Hückel approximation.

Results and discussion

Molecular orbital calculations

The type of extended Hückel molecular orbital calculation employed and the relevant geometric and electronic parameters are described in the Appendix. This type of calculation is based on severe approximations, nonetheless, when used sensibly in association with symmetry and perturbation theory arguments, can lead to a consistent and accurate description of the bonding in organometallic complexes [5,6].

The π-molecular orbitals of the butadiene ligand will be familiar to organometallic chemists, but for completeness sake are reproduced at the left hand side of Fig. 1. In $Mo(\eta\text{-}C_4H_6)_3$, which belongs to the C_{3h} point group, the butadiene ψ_1 and ψ_3 π-molecular orbitals which are symmetric to the horizontal mirror plane give rise to linear combinations of a' and e' symmetry, and the ψ_2 and ψ_4 π-molecular orbitals which are antisymmetric with respect to this mirror plane give rise to a'' and e'' linear combinations. The transformation

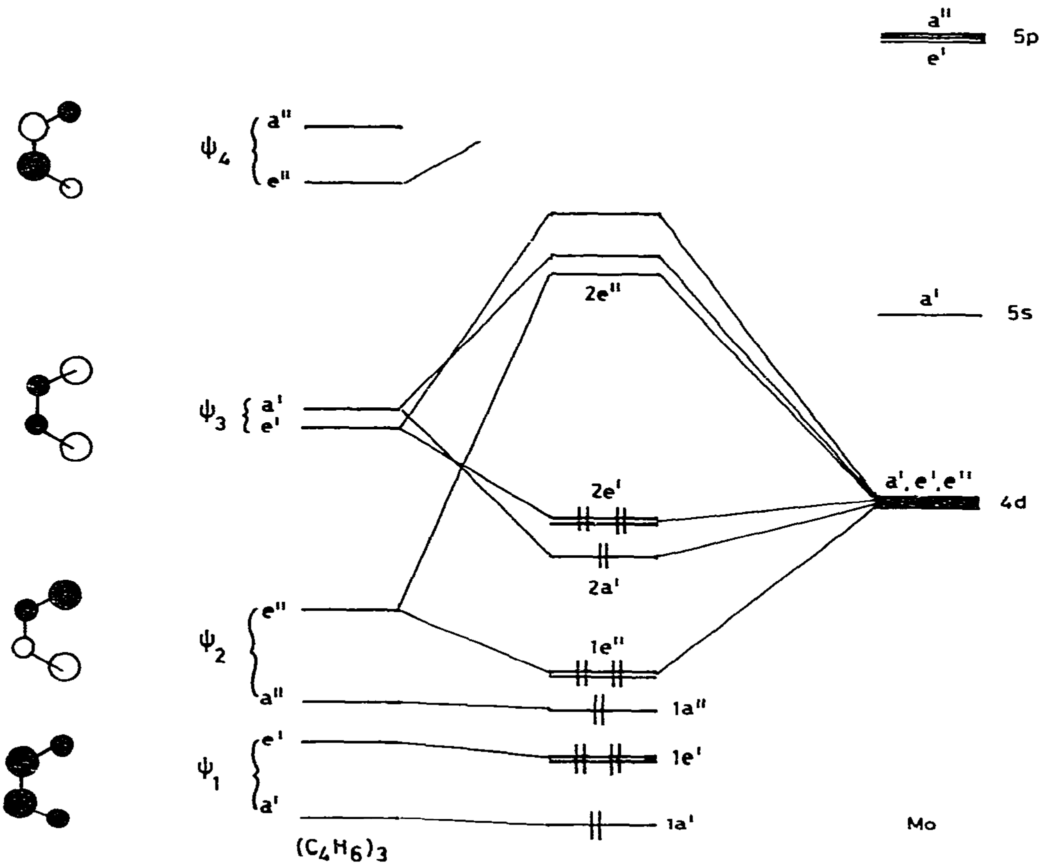


Fig. 1. Schematic molecular orbital interaction diagram for Mo(C_4H_6)$_3$ derived from extended Hückel calculations.

properties of the metal valence orbitals in this point group are summarised below:

4d	x^2-y^2, xy	e'
	xz, yz	e''
	z^2	a'
5s		a'
5p	x, y	e'
	z	a''

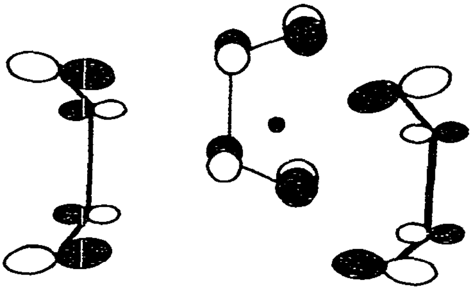
The symmetry partitioning described above limits substantially the allowed metal—ligand interactions. The computed metal—ligand group overlap integrals summarised in Table 1 suggest pseudo-symmetry effects also play an important role in simplifying the analysis of the bonding situation in Mo(η-C_4H_6)$_3$. For example, the ψ_1 and ψ_3 molecular orbitals of the diene and the molybdenum 5s and $4d_{z^2}$ atomic orbitals give rise to orbitals of a' symmetry. However, the ψ_3 combination illustrated in III has supplementary nodes compared to the

TABLE 1

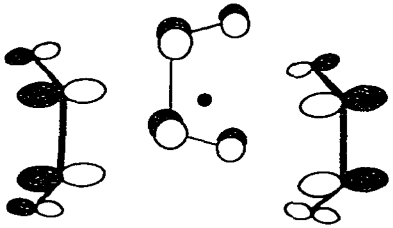
COMPUTED GROUP OVERLAP INTEGRALS FOR Mo(η-C_4H_6)$_3$

$\langle \Psi_3(a')s \rangle$	0.0547	$\langle \Psi_1(a')s \rangle$	0.4018
$\langle \Psi_3(a')z^2 \rangle$	0.1619	$\langle \Psi_1(a')z^2 \rangle$	0.0646
$\langle \Psi_4(a'')z \rangle$	0.0245	$\langle \Psi_2(a'')z \rangle$	0.4659
$\langle \Psi_3(e')xy, x^2-y^2 \rangle$	0.1185	$\langle \Psi_1(e')xy, x^2-y^2 \rangle$	0.2974
$\langle \Psi_3(e')x, y \rangle$	0.1481	$\langle \Psi_1(e'), x, y \rangle$	0.1068
$\langle \Psi_4(e'')xz, yz \rangle$	0.1082	$\langle \Psi_2(e'')xz, yz \rangle$	0.2188

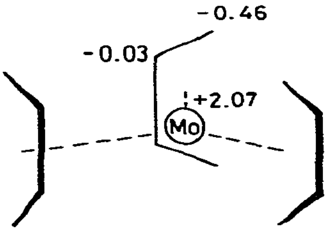
corresponding linear combination derived from ψ_1 (see IV) and therefore overlaps more effectively with the metal $4d_z2$ orbital. Similarly the linear combination illustrated in IV overlaps more effectively with the metal 5s orbital. These pseudo-symmetry arguments when taken together with considerations based on the relative energies of the metal and ligand orbitals illustrated in Fig. 1 can readily explain the qualitative features of the interaction diagram for Mo(η-C_4H_6)$_3$ shown in the Figure 1.



(III)



(IV)



(V)

The primary component of electron donation from ligand to metal orbitals arises from the overlap of the ligand $\psi_2(e'')$ combination with the metal d_{xz}, d_{yz} orbitals, also of e'' symmetry. The lowest unoccupied molecular orbital in Mo(η-C_4H_6)$_3$ is the antibonding component of this interaction and has a high contribution (44%) from the metal $4d_{xz}$ and $4d_{yz}$ orbitals. This forward donation component is supplemented by the donation of electron density from the ligand $\psi_2(a'')$ combination to the higher lying and empty metal 5p_z orbital.

The back donation from filled metal orbitals to the ligand ψ_3 orbitals is most effective and arises primarily from the overlap of $\psi_3(e')$ with the metal $d_{x^2-y^2}$ and d_{xy} orbitals and the ligand $\psi_3(a')$ combination with the metal d_{z^2} orbital. The highest occupied molecular orbitals of the Mo(η-C_4H_6)$_3$ molecule of e' and a' symmetry illustrated in Fig. 1 represent the bonding components of these interactions. These molecular orbitals are extensively delocalised and for example the e' orbital has only a 30% contribution from the metal and 65% from the ligand ψ_3 e' combination, and the a' orbital has a 54% contribution from the metal d_{z^2} orbital and 42% from the ligand ψ_3 combination.

Therefore, although the molecular orbital interaction diagram in Fig. 1 is qualitatively similar to that for a zero valent bis(arene) complex with the metal $d_{z^2}(a')$ and $d_{x^2-y^2}$, d_{xy} (e') occupied and the metal d_{xz}, d_{yz} (e'') orbitals vacant [7], it differs in the important respect that the degree of back donation is far more extensive in the butadiene complexes. In particular, for bis(benzene)molybdenum the back donation from the metal $d_{x^2-y^2}$, d_{xy} orbitals to the arene e_2 orbitals is far less effective because they are higher lying and do not overlap as effectively with the metal orbitals. Furthermore, the d_{z^2} orbital in the bis(arene) complex enters into a weak four-electron destabilising interaction with the arene a_1 orbitals and does not effectively back donate. Therefore, the bonding in Mo(η-C_4H_6)$_3$ resembles more closely the bonding in Mo(CO)$_6$ as far as the degree of back donation is concerned. The effective back donation is reflected in the computed atomic charges for Mo(η-C_4H_6)$_3$ illustrated in V.

The analogy with Mo(CO)$_6$ described above raises the more general geometric question of why Mo(η-C_4H_6)$_3$ adopts a trigonal prismatic coordination rather than an octahedrally based geometry. A pseudo octahedral geometry for Mo(η-C_4H_6)$_3$ can be generated by rotating each butadiene ligand by 30° about the metal—butadiene centroid axis. The extended Hückel calculations suggest that such a geometry is 3.54 eV less stable than the trigonal prismatic geometry. The principal cause of this destabilisation is a steric one since the rotation of the ligands by 30° brings three pairs of hydrogen atoms into contact distances of only 1.48 Å and a further three pairs into contact distances of 1.83 Å. The calculations suggest that these steric effects contribute 2.40 eV to the destabilisation. The remaining 1.14 eV has an electronic origin which can be easily understood in terms of the simplified interaction diagram in Fig. 2. for the interconversion of an octahedral ML$_6$ complex into a trigonal prismatic complex. The octahedral splitting t_{2g} below e_g for the octahedral complex should be familiar. In the absence of π-bonding the t_{2g} set is localised exclusively on the metal. If a trigonal twist occurs the triple degeneracy is split with one level a'_1, z^2, little affected by the rotation because the ligands lie approximately in the nodal surface of the d_{z^2} orbital. The e' component is destabilised by the trigonal twist because it interacts with a lower lying and filled ligand e' orbital set [10]. It is this destabilisation which in general leads to a preference for the octahedral geometry in d^6 metal complexes. However, in Mo(η-C_4H_6)$_3$ the butadiene ligands have low lying empty orbitals of e' and a' symmetry derived from the ψ_3-molecular orbitals which can effectively stabilise the e' and a' orbitals illustrated in Fig. 2. In particular the ψ_3 metal e' interactions are maximised for the trigonal prismatic geometry and therefore this geometry is favoured in preference to the alternative octahedral geometry.

The extensive back donation between metal and the butadiene ligands described above for Mo(η-C_4H_6)$_3$ should lead to an equalisation of the C—C distances in the coordinated butadiene ligands similar to that noted for other diene complexes [3]. Indeed, the extended Hückel calculations performed on Mo(η-C_4H_6)$_3$ with equal C—C bond lengths result in larger computed overlap populations for the central C—C bond than the terminal C—C bond lengths suggesting that this bond length should be shorter. The reported structural data for Mo(η-C_4H_6)$_3$, however, suggested the opposite trend in bond lengths. Since the full details of this structural determination were never reported we have redetermined the structure in order to confirm the C—C bond lengths [1]. The C—C bond lengths we have determined, viz. 1.336(11) Å and 1.560(18) Å, are closely similar to those reported previously, i.e. 1.32(2) Å and 1.55(3) Å for the terminal and internal C—C bonds, respectively. Therefore, this aspect of the structure of Mo(η-C_4H_6)$_3$ remains unresolved. We have noted that the thermal parameters associated with the butadiene carbon atoms in this complex are large and anisotropic; however, in the absence of a low temperature crystallographic investigation it is difficult to evaluate the effect of these motions on the C—C bond lengths.

UV photoelectron spectra of tris(butadiene)molybdenum and tungsten

The photoelectron spectra of dienes bound to Fe(CO)$_3$ fragments have been reported and interpreted in the basis of ab initio calculations [8,9]. These spectral results are summarised in Table 2. Connor et al. [8] ascribed the first band (A) in the spectrum of Fe(CO)$_3$(η-C_4H_6) to the ionization of electrons largely localised on the metal atom. The second peak (B) is assigned to an orbital, which correlates with the highest filled π-molecular orbital of *cis*-butadiene (ψ_2). The third band (C) arises through ionisation from the lower filled π-level of butadiene (ψ_1). The bands (D) at higher ionization energies are attributed to loss of electrons from σ-levels of the diene.

The photoelectron spectra of Mo(η-C_4H_6)$_3$ and W(η-C_4H_6)$_3$ using He-I and He-II radiation are very similar (see Fig. 3). Three bands (A, B, and C) occur with ionisation energies <11 eV and may be associated with the metal—ligand bond-

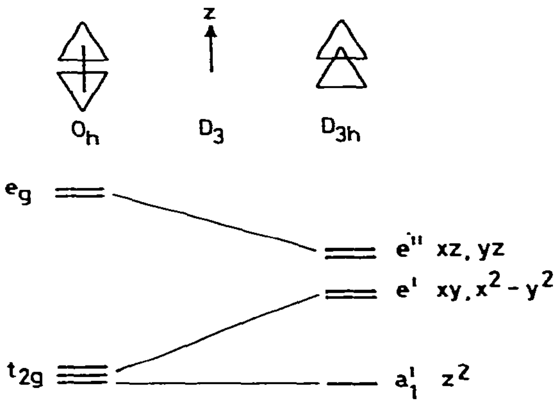


Fig. 2. Schematic interaction diagram for the molecular orbitals of predominantly *d* character in octahedral and trigonal pyramidal ML$_6$ complexes (adapted from ref. 10).

TABLE 2

VERTICAL IONIZATION ENERGIES FOR TRIS(BUTADIENE)-MOLYBDENUM AND -TUNGSTEN

	2a'2e'	1a"1e"	1a'1e'	
$Mo(C_4H_6)_3$	(7.23) 7.44	9.10	10.49	12.25
$W(C_4H_6)_3$	(7.34) 7.74	9.18	10.48	12.30
	A	B	C	
$Fe(CO)_3(C_4H_6)$	(8.16) 8.67 $d + \psi_3$	9.82 ψ_2	11.43 ψ_1	

ing derived from the ligand π-molecular orbitals. No marked changes in intensity of the bands A, B and C are observed when the radiation source is changed from He-I to He-II, indicating that none of the bands results from ionization of an occupied molecular orbital of predominantly metal *d* character. There is a slight rise in relative intensity for band B in the tungsten complex when the radiation is changed, indicating that the orbital from which this ionization derived may have marginally more *d* character compared with those that give rise to bands A and C. An assignment of the spectra which is consistent with previous studies on diene complexes and the molecular orbital calculations described above is the assignment of band C to ionisations from $1a'$, $1e'(\psi_1)$, band B to ionisations from $1a''$, $1e''(\psi_2)$ and band A to ionisations from $2a'$, $2e'(\psi_3)$ in Fig. 1. The fact that the calculations indicated that the highest occupied molecular orbitals are extensively delocalised on the ligands is consistent with the lack of intensity changes in the bands when the He-I source is replaced by He-II.

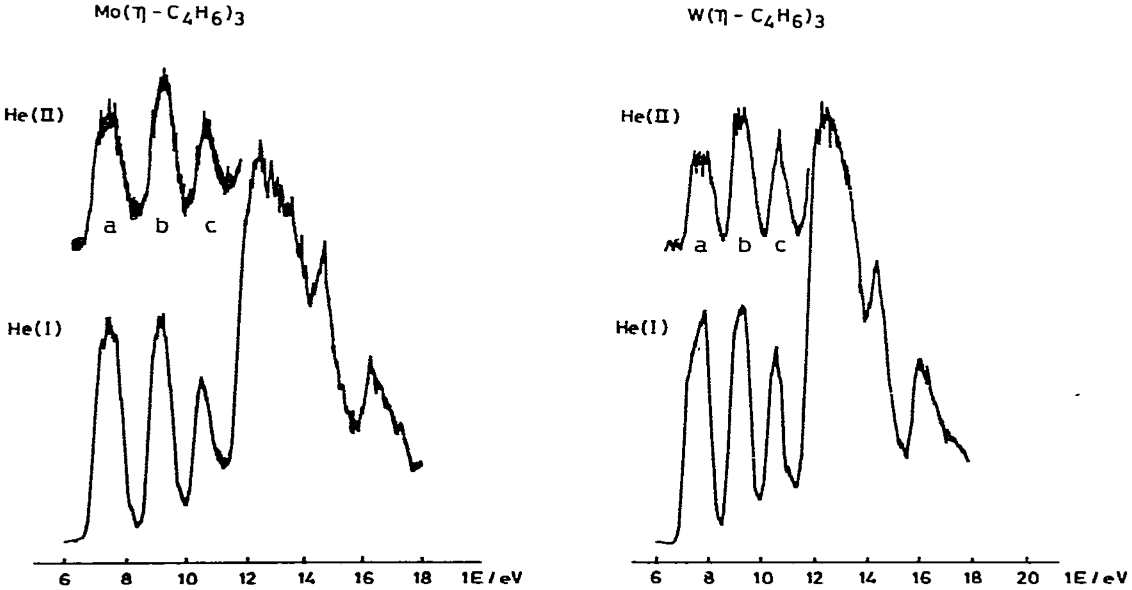


Fig. 3. The UV photoelectron spectra of $Mo(C_4H_6)_3$ and $W(C_4H_6)_3$ using He-I and He-II radiation.

That the first ionization energies of the tris(butadiene) complexes (Mo 7.23 eV, W 7.34 eV) are significantly higher than the values for the corresponding arene compounds (Mo 5.52 eV [15], W 5.40 eV [16]) confirms the suggestion of a more positive charge on the metal in the former case. The ionisation energy of ψ_1 is lowered compared to that reported for the free *trans*-butadiene ligand (11.34 eV) suggesting that there is an overall negative charge on the ligands, which is in agreement with the computed charge densities for the molecule.

Experimental

The compounds $M(\eta\text{-}C_4H_6)_3$, where M = Mo or W, were prepared by the cocondensation of the appropriate metal atoms with butadiene at —195°C [10]. The products were purified by sublimation and recrystallised from 40—60° petrol.

Photoelectron spectra were obtained using a Perkin-Elmer PS 16 18 spectrometer fitted with a Helectros hollow cathode discharge lamp capable of producing both He-I and He-II radiation. The spectra were calibrated using a mixture of xenon and nitrogen and also by reference to the $He(1s)^{-1}$ band. Vertical ionization energies are given in Table 2.

Crystal data

The structure was determined from 290 unique reflections with $I > 3\sigma(I)$ and refined to $R = 0.0365$ ($R_w = 0.0422$). $C_{12}H_{18}Mo$, $M = 423.3$, hexagonal $a = b = 7.264(2)$, $c = 11.904(2)$, $U = 544$ Å^3, $z = 2$, $D_c = 1.58$ g cm^{-3}, μ(Mo-K_α) = 11.2 cm^{-1}, λ(Mo-K_α) 0.71069 Å, space group $P6_3/m$.

The structure yielded unit cell parameters and molecular dimensions essentially identical to those reported earlier [1]. The C—C distances were found to be very sensitive to the locations of the hydrogen atoms, therefore these were located from electron density difference maps and refined isotropically. The hydrogen atoms were, however, constrained to coordinates which maintained a C—H bond length of 1.00 Å. The remaining atoms were refined anisotropically. An analysis of the thermal ellipsoids of the carbon atoms after the final cycle of least squares refinement indicated large concerted movements of the carbon atoms, therefore a redetermination of the structure at low temperatures might significantly improve the determination of the C—C bond lengths of the coordinated butadiene. The structural determination yielded the following bond lengths: Mo—C(1) 2.301(8), Mo—C(2) 2.317(7), C(1)—C(2) 1.336(11), and C(2)—C(2′) 1.560(18) Å, where C(1) and C(2) refer to the outer and inner carbon atoms respectively.

Appendix

All calculations were performed using the extended Hückel method [12,13] and were based on the following parameters.

	Orbital	Slater exponent	H_{ii} (eV)	ref.
H	1*s*	1.300	—13.600	13
C	2*s*	1.625	—21.400	13
	2*p*	1.625	—11.400	13
Mo	5*s*	1.920	—8.340	14
	5*p*	1.920	—5.420	14
	5*d*	4.540(0.590) 1.900(0.590)	—10.50	14

The calculations were done on the ICL2900 computer at the University of Oxford Computer Centre using the ICON8 program developed by Hoffmann and his coworkers at Cornell University [13,14].

In the calculations the C_4H_6 ligand were constrained to be planar and the Mo—C distances were approximated to those obtained from the crystallographic determination. The C—C distances were initially set equal initially to an average value of 1.45 Å in order not to weight the overlap population analysis.

Acknowledgements

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