Electronic Structure of 20-Electron Bis(cyclopentadienyl)-metal Oxo Compounds of Group 6: Investigation by Photoelectron Spectroscopy[†]

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The He I and He II photoelectron spectra have been recorded for $[Mo(\eta-C_5H_4Me)_2O]$, $[W(\eta-C_5H_4Me)_2O]$ and $[W(\eta-C_5Me_5)_2O]$. All show two low-ionization-energy bands, the lowest being assigned to the two metal d electrons and the second to an orbital based primarily on the cyclopentadienyl rings and an oxygen 2p orbital. Other cyclopentadienyl ionization bands and metal–oxygen bonding ionizations are also identified. The spectra confirm the SCF-Xα-SW bonding model presented previously. Extended-Hückel calculations, which are in agreement with the SCF-Xα-SW calculations, have been used to model the orbital interactions. The metal–oxygen bonding and the nucleophilic character of the molecules is discussed in the light of the spectroscopic and theoretical results.

Bis(cyclopentadienyl)-molybdenum and -tungsten oxo compounds are formed by the action of aqueous base on the bis(cyclopentadienyl)metal dichlorides.[1-3] The determination of the crystal structure of $[Mo(\eta-C_5H_4Me)_2O]$[4] confirmed the monomeric nature of this class of molecules.

The oxide ligands of both $[Mo(\eta-C_5H_5)_2O]$ and $[W(\eta-C_5H_5)_2O]$ show enhanced nucleophilic character and the metal–oxygen bonds undergo [2 + 2] cycloaddition reactions with both organic and organometallic substrates to yield stable metallocycles.[5-8] These reactions proceed in a stepwise fashion and are initiated by oxygen attack on the electrophilic carbon atoms of the various substrates. Photolysis of $[Mo(\eta-C_5H_5)_2O]$ and $[Mo(\eta-C_5H_4Me)_2O]$ results in the liberation of O_2 and formation of molybdenocene intermediates; net oxygen-atom transfer from the excited state to nucleophiles does not occur.[9]

Exceptional reactivity has been shown for $[W(\eta-C_5Me_5)_2O]$[3] which reacts with H_2 to give $[W(\eta-C_5Me_5)_2H_2]$ and with O_2 to give $[W(\eta-C_5Me_5)(OC_5Me_5)O_2]$. Oxygen exchange between $[W(\eta-C_5Me_5)_2O]$ and water is very rapid; the dihydroxo derivative $[W(\eta-C_5Me_5)_2(OH)_2]$ is assumed to be a likely intermediate.

These oxo compounds are members of a class of neutral transition-metal compounds in which the metal centre would achieve an 18-electron configuration with the oxygen atom donating only two electrons to the metal rather than the full potential complement of four. At its highest symmetry the bent metallocene fragment only possesses a two-fold rotational axis so the interactions with the metal orbitals of the two $2p_\pi$ orbitals of the oxygen atom, which lies on the $C_2(z)$ axis, must differ from one another. A bent metallocene fragment is generally regarded as presenting three orbitals for further bonding which lie in the plane perpendicular to the direction connecting the centroids of the two rings (we take this as the xz plane).[10-12] If this were strictly true the O p_x orbital would have a bonding partner in the metallocene fragment, whereas the O p_y orbital would have no single empty orbital of suitable energy in the metallocene fragment with which to bond. This simple model leads to the assumption of a double M–O bond in these compounds.

The Mo–O distance in $[Mo(\eta-C_5H_4Me)_2O]$[4] is 1.721 Å, somewhat longer than mean bond length of 1.678 Å found for other molybdenum d^2 monooxo compounds, but comparable to the mean for *fac*-trioxo compounds of 1.726 Å.[13] All the C–C distances are of normal length for a molybdenum cyclopentadienyl compound and there is no evidence that the cyclopentadienyl groups are unsymmetrically co-ordinated to the molybdenum as is found in the case of the analogous imido compound $[Mo(\eta-C_5H_5)_2(NBu^t)]$.[14]

The electronic structure of $[Mo(\eta-C_5H_5)_2O]$ has been investigated by the self-consistent field Xα-scattered-wave method (SCF-Xα-SW).[9] This showed the Mo–O bond order to lie between 2 and 3, though it was noted that for $[Mo(\eta-C_5H_4Me)_2O]$ the Mo–O bond length and stretching frequency suggested the presence of not much more than a Mo–O double bond.

In a continuing study of metal oxo and imido compounds by photoelectron spectroscopy,[14-16] we are interested in identifying the ionizations associated with metal–ligand multiple bonds, assessing the range of ionization energies involved and gaining a more detailed, experimentally based picture of the electronic structure of these molecules. Methylcyclopentadienyl derivatives were chosen for the present study as the unsubstituted bis(cyclopentadienyl)metal oxo compounds were not sufficiently thermally stable for spectral measurement.

Experimental

The compounds $[M(\eta-C_5H_4Me)_2O]$ (M = Mo or W)[1] and $[W(\eta-C_5Me_5)_2O]$[2] were prepared by the literature methods.

Table 1 Parameters used in the extended-Hückel calculation on $[Mo(\eta-C_5H_5)_2O]$

Atom	Orbital	H_{ii}/eV	Exponent
Mo	4d	−10.5	4.542 (0.589 86), 1.901 (0.589 86)
	5s	−8.34	1.956
	5p	−5.24	1.900
C	2s	−21.4	1.625
	2p	−11.4	1.625
H	1s	−13.6	1.300
O	2s	−32.3	2.275
	2p	−14.8 to −12.5	2.275

[†] *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

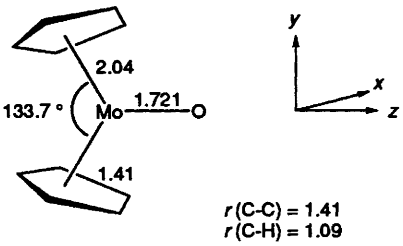

Fig. 1 Structure assumed for $[Mo(\eta\text{-}C_5H_5)_2O]$ in the extended-Hückel calculation; distances in Å

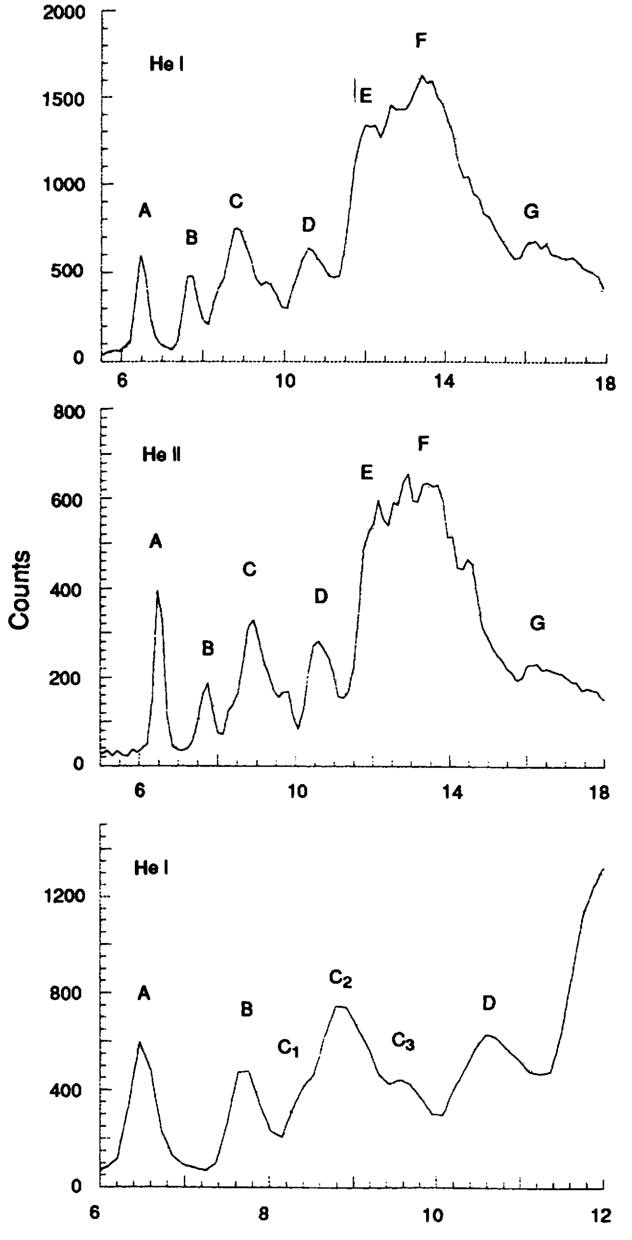

Fig. 2 The He I and He II PE spectra of $[Mo(\eta\text{-}C_5H_4Me)_2O]$

Table 2 Vertical ionization energies (eV) of the principal bands in the PE spectra of $[Mo(\eta\text{-}C_5H_4Me)_2O]$ **1**, $[W(\eta\text{-}C_5H_4Me)_2O]$ **2** and $[W(\eta\text{-}C_5Me_5)_2O]$ **3**; cp = cyclopentadienyl

	Complex			
Band label	1	2	3	Assignment
A	6.53	6.45	5.81	$3a_1$, metal d
B	7.70	7.70	6.97	$2b_2$, cp–O
C_1	8.4	8.90	7.74	$2b_1$, cp
C_2	8.91	9.35	8.17	$1a_2$, cp
C_3	9.52	9.75	8.66	$2a_1$, cp
D	10.67	10.65	9.84	$1a_1$, $1b_1$, $1b_2$, M–O
E	12.1	12.2	11.0	
F	13.5	13.4	13.4	
G	16.2	16.2	16.3	

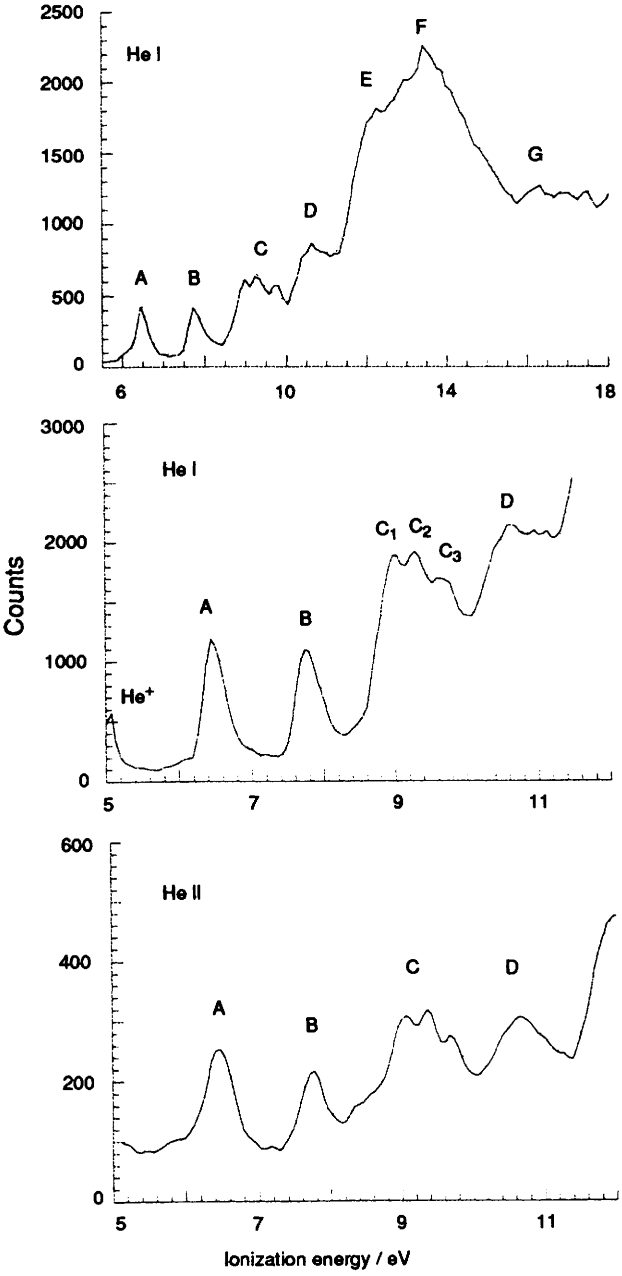

Fig. 3 The He I and He II PE spectra of $[W(\eta\text{-}C_5H_4Me)_2O]$

The photoelectron (PE) spectra were measured using a PES Laboratories 0078 spectrometer which has a hollow-cathode helium discharge lamp capable of providing both He I and He II radiation. The samples were held at a constant temperature between 90 and 110 °C $\{[M(\eta\text{-}C_5H_4Me)_2O]$ (M = Mo or W)$]\}$ and between 140 and 155 °C $\{[W(\eta\text{-}C_5Me_5)_2O]\}$ and data collected by repeated scans on an Atari microprocessor. The spectra were calibrated with reference to N_2, Xe and He.

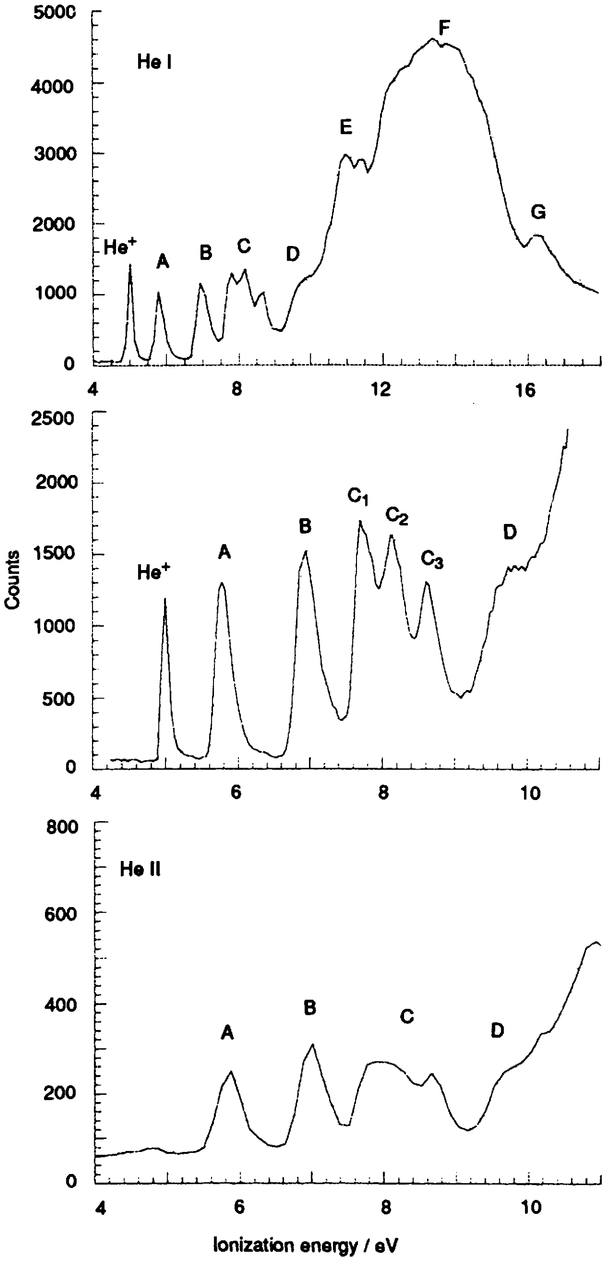

Fig. 4 The He I and He II PE spectra of [W(η-C_5Me_5)$_2$O]

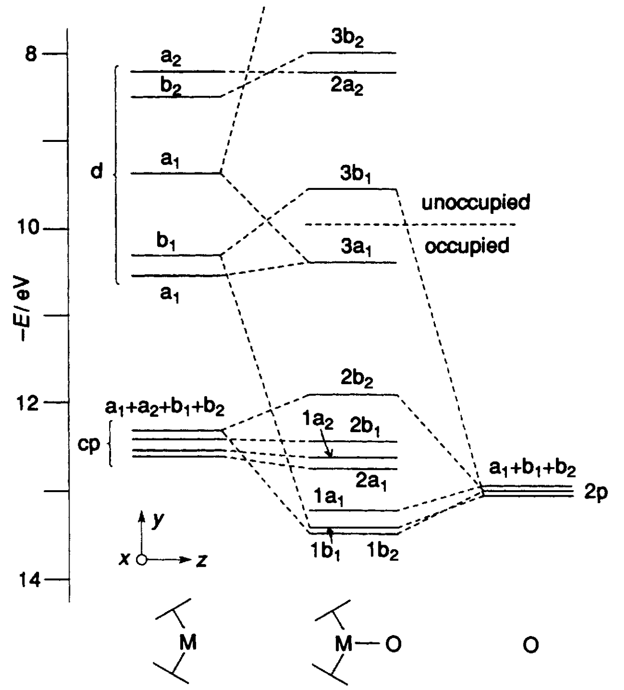

Fig. 5 A MO scheme for [Mo(η-C_5H_5)$_2$O] derived from the frontier orbitals of a bent metallocene and the 2p orbitals of an oxygen atom

Extended-Hückel molecular-orbital (EHMO) calculations[17] were performed on [Mo(η-C_5H_5)$_2$O]. The molecular structure was idealized to C_{2v} symmetry with each metal-to-ring centroid vector perpendicular to the plane of the cyclopentadienyl ring. Fig. 1 shows the coordinate system, ring orientation, distances and angles assumed in the calculation. The atomic parameters used are given in Table 1. The Mo 4d orbitals were represented by a linear combination of two Slater functions. In addition to a calculation using standard parameters,[18] we studied the effect of varying H_{ii} for the O 2p orbitals on the energy level scheme. Values were taken at 0.5 eV intervals between −14.5 and −12.5 eV.

Results and Discussion

The PE spectra of [M(η-C_5H_4Me)$_2$O] (M = Mo or W) and [W(η-C_5Me_5)$_2$O] are shown in Figs. 2–4 and principal ionization energy (i.e.) features given in Table 2. All three compounds show two low i.e., well separated ionization bands, A and B, which lie below the normal i.e. regions for bands associated with the upper π orbitals of the cyclopentadienyl ligand that they contain.[19–21] For C_5H_4Me complexes these bands tend to occur between 8 and 10 eV whereas for C_5Me_5 the range is somewhat lower between about 7 and 9 eV. In the case of [Mo(η-C_5H_4Me)$_2$O] band A shows a relative increase in intensity in the He II spectrum, suggesting assignment to the two Mo d electrons. The lack of such a relative increase in the case of the tungsten compounds is compatible with a similar assignment as the ionization cross-section of W 5d electrons has been shown to fall more steeply with increasing photon energy than that of Mo 4d electrons.[22] Lying in the cyclopentadienyl ionization region are in all cases at least three bands, C_1, C_2 and C_3. These are most separate in the case of [W(η-C_5Me_5)$_2$O], where the band profiles and intensities suggest that there are only three bands in this region. We, therefore, assume that this is also the case for the methylcyclopentadienyl compounds where the bands overlap more. Bands D ionize in the window normally found for metallocenes between the upper occupied cyclopentadienyl π ionizations and those of the lowest π orbital and the σ orbitals of the ring which constitute the main band in these spectra; for C_5H_4Me derivatives the main band starts at *ca.* 11.5 eV,[19,20] whereas for C_5Me_5 derivatives the onset is earlier at *ca.* 10 eV and there is a prominent feature, E, at *ca.* 11.0 eV associated with the methyl substitution.[21] Band D is best resolved in the molybdenum case. The spectrum of [W(η-C_5H_4Me)$_2$O] has a rising background in this region which spoils the definition of D. In the case of [W(η-C_5Me_5)$_2$O] the lower onset of the main band led to a greater overlap between bands D and E. The occurrence of D in the PE spectra of these oxo compounds and its absence in homoleptic cyclopentadienyl compounds strongly suggest that it is associated with the oxide ligand. Bands E–G are entirely characteristic of those found for other metallocenes and will not be discussed further.

To proceed further with the assignment we need a MO description of the bonding in the molecule. This can be generated by considering the interaction of a bent metallocene fragment[10–12] with an oxygen atom (Figs. 5 and 6). We have used extended-Hückel calculations to model this interaction but the resulting energy level scheme and orbital description is similar to the results of the SCF-Xα-SW calculation.[9] Indeed the principal features may be deduced by symmetry

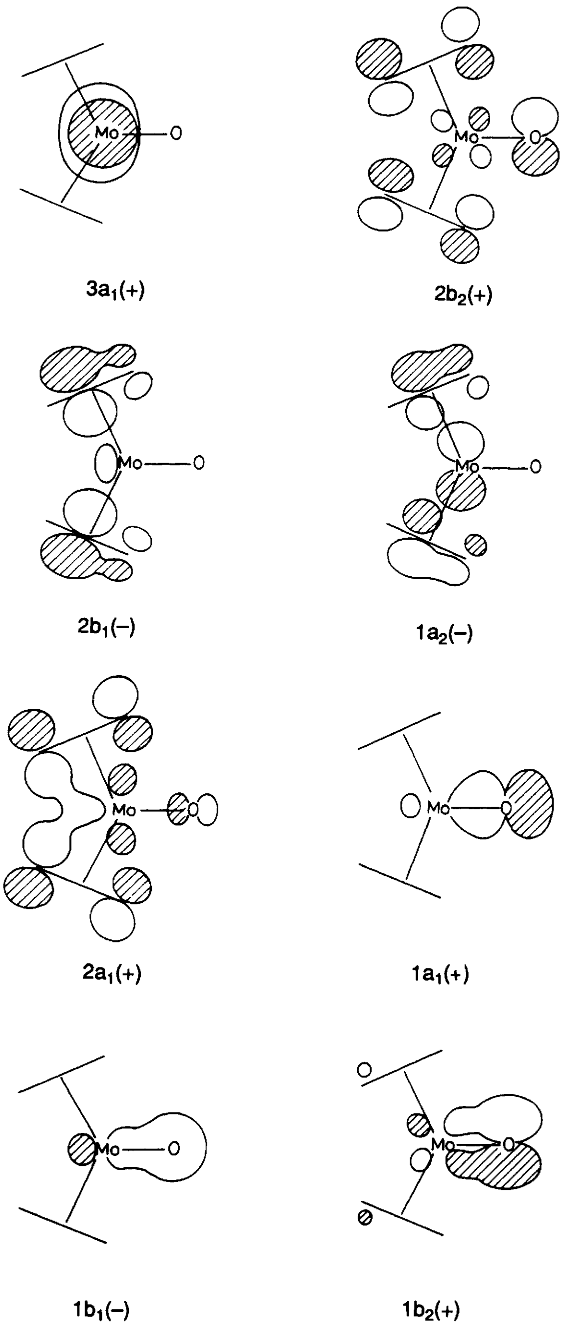

Fig. 6 Diagrammatic representation of the upper occupied orbitals of $[Mo(\eta\text{-}C_5H_5)_2O]$. The orbitals are shown as projections onto the *yz* plane. Their symmetry with respect to reflection in this plane is indicated by the signs + (symmetric) and − (antisymmetric)

considerations. The O 2p orbitals transform as a_1 (p_z), b_1(p_x) and b_2(p_y). Of these the a_1 and b_1 orbitals find a match in the three frontier orbitals of the metallocene fragment (two of a_1 symmetry and one of b_1) which lie in the *xz* plane, forming a σ and a π bond. The extra a_1 orbital, $3a_1$, is d_{x^2} in character and houses the two metal d electrons. The b_2 O 2p orbital has no symmetry match among the frontier orbitals but may interact with the b_2 combination of cyclopentadienyl π orbitals with the metal d_{yz} orbital. In a classic three-centre four-electron interaction, one strongly bonding orbital, $1b_2$, and one more or less non-bonding orbital, $2b_2$, result, both of which are occupied, together with one strongly antibonding orbital, $3b_2$, which is unoccupied. Diagrammatic representations of the occupied b_2 orbitals are given in Fig. 6. Both the SCF-Xα-SW and the extended-Hückel calculations indicate the central $2b_2$ orbital to be slightly Mo–O antibonding while remaining molybdenum–cyclopentadienyl bonding as in the parent metallocene fragment. The three remaining cyclopentadienyl orbitals, $2b_1$, $1a_2$ and $2a_1$, are all bonding to the metal, as are the three largely oxygen orbitals, $1a_1$, $1b_1$ and $1b_2$.

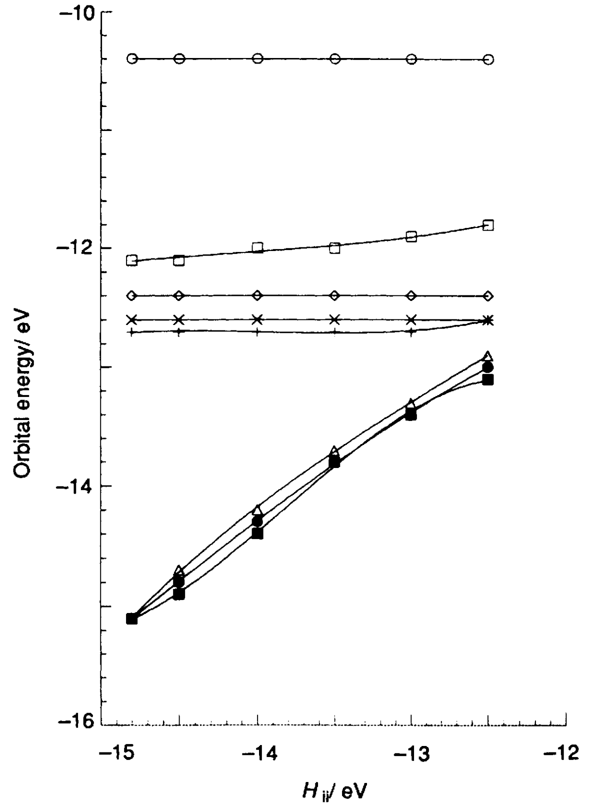

Fig. 7 Variation in the calculated energy, E_i of the upper occupied orbitals of $[Mo(\eta\text{-}C_5H_5)_2O]$ with the value of H_{ii} of the O 2p orbitals: $3a_1$ (○), $2b_2$ (□), $2b_1$ (◇), $1a_2$ (×), $2a_1$ (+), $1a_1$ (△), $1b_1$ (●) and $1b_2$ (■)

The destabilization of the resulting $2b_2$ orbital relative to the other cyclopentadienyl π orbitals may be explored by varying the H_{ii} value of the O 2p orbitals relative to the metallocene fragment. The results of several calculations are shown in Fig. 7. The other cyclopentadienyl orbitals, $2a_1$, $2b_1$ and $1a_2$, show little energy variation. Even when the value of the O 2p H_{ii} lies 2 eV below that of the cyclopentadienyl π orbitals, the $2b_2$ orbital lies *ca.* 0.3 eV above the next highest cyclopentadienyl orbital. The separation pattern which most resembles that of the PE bands is achieved with an H_{ii} value of −13.0 eV, and it is this value that is used to produce the energy-level scheme shown in Fig. 5.

A more detailed spectral assignment may now be achieved (Table 2). Band A is assigned to ionization from orbital $3a_1$, and the other low-lying band, B, to ionization from orbital $2b_2$. Bands C_1–C_3 are assigned to the cyclopentadienyl orbitals $2b_1$, $1a_2$ and $2a_1$. Band D must include some of the M–O bonding ionizations, $1a_1$, $1b_1$ and $1b_2$, though it is possible that one or two of these overlap with the main band. For the two tungsten compounds the largest shift on methylation is found for the three C bands, consistent with their cyclopentadienyl character. That B shifts less is good confirmation that it has some oxygen localization. The trend from Mo to W between the two C_5H_4Me compounds is for the C ionizations to increase, indicating stronger bonding by the third-row atom.

The most novel feature of the PE spectra of this series of compounds is the very low ionization energy, between 7 and 8 eV, found for band B, which is associated with an ionization

$$\begin{tikzcd}
M + H^{+} \arrow[rr, "\text{proton affinity}"] \arrow[dr, swap, "\text{i.e. (M)} - \text{i.e. (H)}"] & & {[M{-}H]^{+}} \\
& M^{+} + H \arrow[ur, swap, "\text{bond energy}"] &
\end{tikzcd}$$

Scheme 1

which has some oxygen character. The first i.e. of OsO_4, for example, is 12.35 eV.[16] Most organic compounds with oxygen lone pairs have ionization energies > 9.5 eV.[23] Low ionization energies may be related to high proton affinities by the thermodynamic cycle, in Scheme 1. Making a crude assumption of constant O–H bond energies, we would expect a lowering of ionization energy by 1 eV to correspond to an increase of 96.5 kJ mol^{-1} in the absolute magnitude of a proton affinity. Thus such oxo compounds would be expected to exhibit exceptional basicities and high nucleophilicity. As pointed out in the Introduction, this is indeed the case. The inability of these compounds to transfer oxygen atoms to nucleophiles is also understandable.

Conclusion

The 20-electron nature of the bis(cyclopentadienyl) oxo compounds of Group 6 metals leads to the occupation by two electrons of a high-lying orbital largely localized on the cyclopentadienyl ligands and the oxygen. These high-lying electrons are responsible for the unusual basic and nucleophilic character of these oxo-metal compounds.

Acknowledgements

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