Photoelectron Studies of some Bent Bis(η-cyclopentadienyl)metal Complexes. Part I. Some Eighteen-electron Systems with Hydride, Alkyl, Olefin, Allyl, and Carbonyl ligands

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Photoelectron spectra of some bent bis(η-cyclopentadienyl)metal complexes, namely [(cp)$_2$ReH], [(cp)$_2$MH$_2$] (M = Mo and W), [(cp)$_2$TaH$_3$], [(cp)$_2$MMe$_2$] (M = Mo and W), [(cp)$_2$MoL] (L = CO and η-C$_2$H$_4$), [(cp)$_2$WL] (L = η-C$_2$H$_4$ and η-C$_3$H$_6$), and [(cp)$_2$Nb(η-C$_3$H$_5$)] have been measured. A unified bonding model is proposed which accounts for the observed spectra.

BENT bis(η-cyclopentadienyl) metal complexes were first treated theoretically by Ballhausen and Dahl[1] who proposed, in accord with chemical experience, that a (cp)$_2$M unit has three orbitals available for further bonding. The stereochemistry of this type of complex has been extensively investigated[2-5] and it is now clear that when the metal is bonded to two further ligands the unused orbital is not located between the two bonding orbitals as originally proposed by Ballhausen and Dahl. A further weakness of their model is that it is based on a hybrid scheme which utilizes equally the *s*, five *d*, and three *p* valence orbitals of the the metal. Obviously a more flexible molecular orbital (m.o.) scheme is desirable. Such a scheme has been outlined in an earlier publication[3] and here we describe photoelectron (p.e.) studies which substantiate it. Subsequent e.s.r. studies[5-7] on d^1 complexes confirm the proposal of this scheme that the upper a_1 orbital is chiefly a hybrid of the metal $d_{x^2-y^2}$ and d_{z^2} orbitals. Unfortunately the various authors favour different co-ordinate systems for the C_{2v} molecules so care must be taken in comparing their results.

We have studied the p.e. spectra of bis(η-cyclopentadienyl)metal complexes containing hydride, methyl, olefin, allyl, and carbonyl ligands in order to investigate the nature of the bonding. Studies with halides and tetrahydroborate as ligands are already underway and will form Part II of this series.

EXPERIMENTAL

As most of the complexes studied were air sensitive, the preparations were carried out *in vacuo* or under an atmosphere of nitrogen using standard techniques. Solvents were dried by heating under reflux for several hours over calcium hydride and were distilled immediately before use. In most cases the purity of the complex was checked by mass and i.r. spectrometry and the spectra compared with previously published results. Where no such data existed, which was mainly the case for mass spectrometry, the spectra were carefully checked for impurity. In all cases the mass spectra showed no peaks above the parent-ion peak and a characteristic cracking pattern. The complexes had the same physical properties as described in the literature, with particular reference to appearance, sublimation temperatures, and m.p.s. The p.e. spectra were constant over a period of time and within a limited range of temperature and showed no trace of well known likely volatile impurities such as solvent or possible decomposition products.

Bis(η-cyclopentadienyl)hydridorhenium was prepared[8] from ReCl$_5$, Na(cp), and NaBH$_4$. Sublimation at 120 °C *in vacuo* yielded yellow needle-shaped crystals. Bis(η-cyclopentadienyl)trihydridotantalum was prepared[9] from TaCl$_5$, Na(cp), and NaBH$_4$. The sample was sublimed twice at 140 °C *in vacuo* to produce pure white crystals. No parent-ion peak could be seen in the mass spectrum. The highest peak was due to [(H$_{11}$C$_{10}$)Ta]$^+$, and the rest of the cracking pattern was very similar to that of the bis(η-cyclopentadienyl)metal hydrides. Bis(η-cyclopentadienyl)dihydridomolybdenum was prepared[9] by Dr. G. A. Moser from MoCl$_5$, Na(cp), and NaBH$_4$. Two sublimations at 120 °C *in vacuo* produced lemon-yellow crystals. Bis(η-cyclopentadienyl)dihydridotungsten was prepared similarly[9] from WCl$_6$ by Mr. J. Kenward. It was sublimed twice at 140 °C *in vacuo* to yield lemon-yellow crystals. Bis(η-cyclopentadienyl)dimethylmolybdenum and its tungsten analogue were prepared[10] by Drs. F. W. Benfield and G. A. Moser from [(cp)$_2$MCl$_2$] (M = Mo and W) and MeMgCl. The red crystals were purified by sublimation *in vacuo* at 80 (M = Mo) and 120 °C (M = W). Bis(η-cyclopentadienyl)(η-ethylene)molybdenum was prepared[11] from [(cp)$_2$MoCl$_2$] and ethylaluminium dichloride. It was recrystallized twice from light petroleum (b.p. 30—40 °C) and sublimed at 80 °C *in vacuo*. Bis(η-cyclopentadienyl)(η-ethylene)- and bis(η-cyclopentadienyl)(η-propene)-tungsten were prepared[11] by Mr. N. J. Cooper and Dr. F. W. Benfield from [(cp)$_2$WCl$_2$] and ethylaluminium dichloride or isopropylaluminium dichloride. The red crystals were further purified by sublimation at 80 and 40—60 °C *in vacuo* respectively. (η-Allyl)bis(η-cyclopentadienyl)niobium was prepared[12] from [(cp)$_2$NbCl$_2$] and allylmagnesium bromide. The green-black crystals were purified by recrystallization from n-pentane and

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sublimation at 130 °C *in vacuo*. Carbonylbis(η-cyclopentadienyl)molybdenum was prepared[13] by Dr. G. A. Moser and Mr. I. Packer from $[(cp)_2MoH][MgBr(C_6H_{11})][MgBr(C_4H_{10}O)]_2$ and carbon dioxide in a toluene suspension. Hydrolysis with methanol followed by chromatography on alumina and light petroleum elution gave $[(cp)_2MoCO]$. The product was further purified by sublimation at 140 °C *in vacuo*.

Spectra were obtained on Perkin-Elmer P.S.16 instruments modified to take heated insert probes. The conditions used for the various complexes are given in Table 1. The spectra were calibrated using a mixture of rare gases. Maximum errors in ionization energies are of the order of 0·1 eV.*

TABLE 1

Spectrometer conditions

Complex	θ_c/°C	Counts s^{-1}
$[(cp)_2ReH]$	94	1 000
$[(cp)_2TaH_3]$	83	1 000
$[(cp)_2MoH_2]$	60	1 000
$[(cp)_2WH_2]$	85	1 000
$[(cp)_2MoMe_2]$	61	1 000
$[(cp)_2WMe_2]$	65	1 000
$[(cp)_2Mo(\eta\text{-}C_2H_4)]$	84	1 000
$[(cp)_2W(\eta\text{-}C_2H_4)]$	94	1 000
$[(cp)_2W(\eta\text{-}C_3H_6)]$	110	1 000
$[(cp)_2Nb(\eta\text{-}C_3H_5)]$	90	1 000
$[(cp)_2MoCO]$	63	400

RESULTS AND DISCUSSION

In order to assign the spectra we require a molecular-orbital (m.o.) scheme for these molecules. In general they may be taken as belonging to the C_{2v} point group and a symmetry treatment quickly leads to a labelling of the m.o.s with their appropriate transformation properties. However it gives no indication of the relative ordering of the energy levels. Calculations give some indication of this but have only been carried out for a few specific molecules of this type.[5,6] We require a flexible general model which can be adapted for each member of the series. The $(cp)_2M$ unit which is common to each member of the series has been shown crystallographically[3,4] to be very constant in its dimensions when a wide variety of ligands are bonded to it. We therefore adopted a ' molecules in molecules ' approach of first deriving a m.o. scheme for this unit, and then further combining it with the appropriate ligands.

The energy-level scheme of a closed-shell metallocene such as ferrocene is now well established.[14] The upper levels of symmetry e_{2g} and a_{1g} are chiefly metal d in character, and though argument continues as to their relative ordering this is irrelevant for our purposes. The next set of levels of symmetry e_{1g} and e_{1u} may be regarded as chiefly cyclopentadienyl in character the former being the main source of bonding of the rings to the metal. Our procedure for deriving an energy-level scheme for the $(cp)_2M$ unit was to start with the scheme for a metallocene unit with D_{5h} symmetry, and by bending the molecule lower the symmetry to C_{2v}, the orbitals being relabelled. In order to clarify the relation between the linear and bent $(cp)_2M$ unit, we maintained the same set of axes as shown in Figure 1, namely the z axis as the principal axis in the ' linear ' molecule and unconventionally the x axis as the two-fold axis in the bent molecule. The derived m.o. scheme is shown in Figure 1. Mixing between the top three orbitals and the next set was neglected to a first approximation.

Our thesis is that the metal–cyclopentadienyl orbitals ($a_1 + b_2 + a_2 + b_1$) remain roughly constant in energy throughout this series as the electronegativity of the other ligands bonded to the metal is fairly constant, though we may well expect changes with change of the metal itself. The simplest case where it is possible to identify these orbitals is $[(cp)_2MoCO]$ and we start by discussing the spectrum of this molecule.

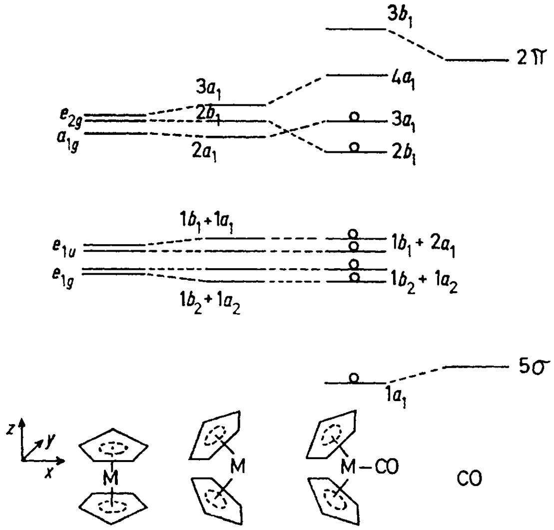

FIGURE 1 M.o. scheme for $[(cp)_2MoCO]$

Carbonylbis(η-cyclopentadienyl)molybdenum.— Carbon monoxide binds to transition metals by donation of the electron pair occupying the 5σ orbital and acceptance of metal d electrons into the empty 2π-antibonding orbital. In the presumed C_{2v} symmetry of the carbonyl complex, the 5σ orbital transforms as a_1 and the 2π orbitals as $b_1 + b_2$. The metal orbitals available for bonding the carbonyl ligand are $2a_1$, $2b_1$, and $3a_1$ (see Figure 1) which, by analogy with ferrocene, will be chiefly composed of the metal d_{z^2} and $d_{x^2-y^2}$ orbitals (a_1 symmetry) and the d_{xy} orbital (b_1 symmetry). These can therefore provide an acceptor orbital and a donor orbital necessary for bonding the carbon monoxide. The unequal population of the two carbon monoxide π-antibonding orbitals should lead to bending of the M–CO axis. An m.o. scheme is given in Figure 1.

The first ionization energy (i.e.) of free carbon monoxide occurs at 14·01 eV[15] and is assigned to ionization of the 5σ orbital. We can therefore assume that

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* 1 eV ≈ $1{\cdot}60 \times 10^{-19}$ J.

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TABLE 2

Vertical ionization energies (eV) of the carbonyl, olefin, and allyl complexes

$[(cp)_2MoCO]$	$[(cp)_2Mo(C_2H_4)]$	$[(cp)_2W(C_2H_4)]$	$[(cp)_2W(C_3H_6)]$	$[(cp)_2Nb(C_3H_5)]$	Assignment C_{2v}	C_s
5·9	6·0	6·0	5·9	5·7	$3a_1$	$4a'$
6·8	6·9	7·1	7·0	8·0	$2b_1$	$3a''$
8·8	8·8	9·0	8·9	8·6	$2a_1 + 1b_2 + 1b_1 + 1a_2$	$2a' + 3a' + 1a'' + 2a''$
9·3	9·2	9·3	9·5	9·2		
9·6		9·5				
	11·3	11·3	11·0		$1a_1$	$1a'$
12·6	12·6	12·5		13·0		
13·6	13·2	13·0	13·2	15·0		
16·8	17·0	16·7	16·9	16·9		

ionizations arising from the ligand and from the $1a_1$ orbital of the complex will all occur above 14 eV and are thus likely to be hidden under the amorphous CH and CC ionization bands. The assignment of the spectrum is given in Table 2. The first band at 5·9 eV is assigned to electron loss from the $3a_1$ orbital, its sharp profile indicating the non-bonding nature of the orbital. The second band at 6·8 eV has a shape indicating bonding character and is assigned to the $2b_1$ orbital, the ' back-donation ' orbital. Ionizations from the metal–cyclopentadienyl orbitals occur in the region 8·5—10·0 eV. Only three vertical ionization energies could be distinguished (8·8, 9·3, and 9·6 eV). An interesting feature is the sharp edge to low ionization energy similar to that found in a wide variety of bis(η-cyclopentadienyl)metal complexes.[14] In these it is assigned to ionization from the e_{1u} orbital and the sharp edge attributed to the fact that metal *p* orbitals contribute little to the e_{1u} m.o. Analogous reasoning in these bent bis(η-cyclopentadienyl)metal complexes would lead to assignment to the $2a_1$ or $1b_1$ ionizations. The next complex band is assigned to ionizations from orbitals concerned with C–H and C–C bonding in the cp ligands. The upper ionization region, *i.e.* above 12 eV, was similar in all the complexes discussed here and a similar assignment will be assumed for each spectrum discussed subsequently.

Olefin Complexes.—The nature of the bonding of olefin ligands to a transition metal is formally similar to that of carbon monoxide, the olefin π-electrons donating into an empty metal orbital and the metal *d* electrons back donating to the π^*-olefin antibonding orbital. The spectra of the olefin complexes are shown in Figure 2. A direct comparison may be made between these spectra and that of the carbonyl complex and they are assigned accordingly (Table 2 and Figure 3).

The first i.e. of ethylene is 10·51 eV [15] and is assigned to ionization of the π-electrons. The peaks at 11·3 and 11·4 eV in the spectra of $[(cp)_2Mo(\eta\text{-}C_2H_4)]$ and $[(cp)_2W(\eta\text{-}C_2H_4)]$ have no analogue in the spectrum of $[(cp)_2MoCO]$ and are reasonably assigned to the $1a_1$ orbital which is composed of the olefin π-orbital mixed with a metal a_1 orbital. Thus the olefin π-electrons are stabilized by *ca.* 0·8 eV on complexing to the metal. The ionization band at 11·0 eV in the spectrum of $[(cp)_2W(\eta\text{-}C_3H_6)]$ is similarly assigned, the lower ionization energy in comparison with the ethylene complexes being in accord with the known inductive effect of the methyl group. The bands in the region 8—10 eV are due to ionization from the cyclopentadienyl–metal orbitals $2a_1 + 1b_2 + 1b_1 + 1a_2$. The sharp band at

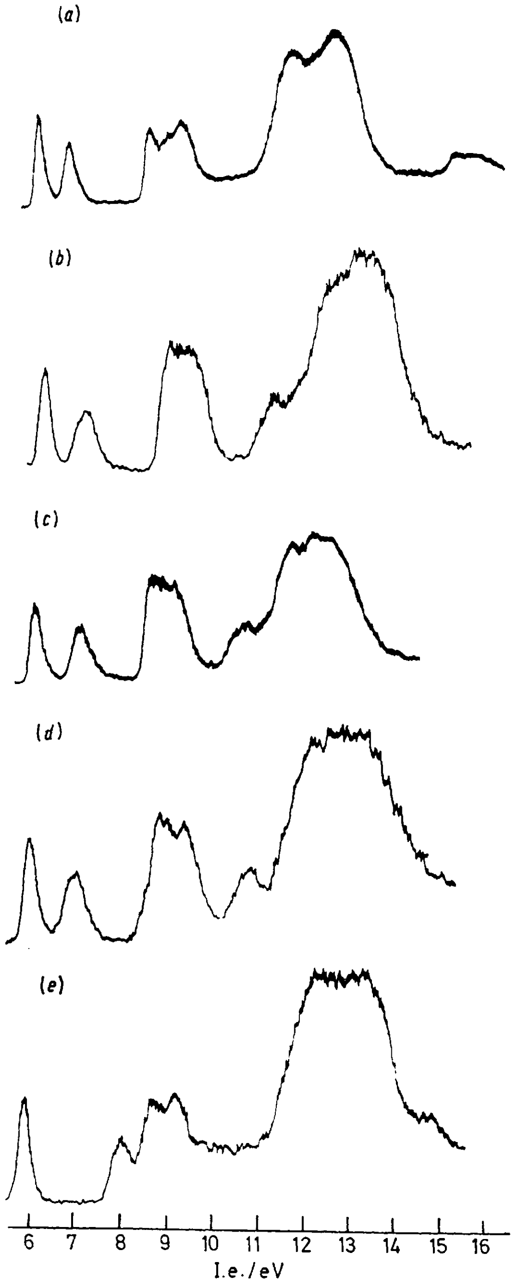

FIGURE 2 P.e. spectra of (*a*) $[(cp)_2MoCO]$, (*b*) $[(cp)_2Mo(\eta\text{-}C_2H_4)]$, (*c*) $[(cp)_2W(\eta\text{-}C_2H_4)]$, (*d*) $[(cp)_2W(\eta\text{-}C_3H_6)]$, (*e*) $[(cp)_2Nb(\eta\text{-}C_3H_5)]$

lowest i.e. in all the spectra is assigned to the metal non-bonding $3a_1$ orbital and the broader band to the $2b_1$ orbital. That the metal provides an orbital of b_1 symmetry for back donation will fix the preferred orientation of the ethylene in these molecules as being in the *xy* plane (as defined in Figure 1).

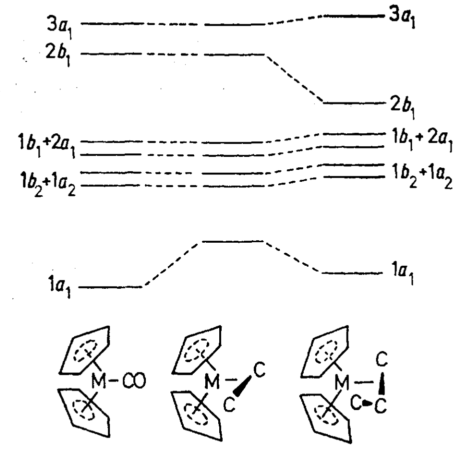

FIGURE 3 M.o. correlation diagram for $[(cp)_2MoCO]$, $[(cp)_2Mo(\eta\text{-}C_2H_4)]$, and $[(cp)_2Nb(\eta\text{-}C_3H_5)]$

(η-Allyl)bis(η-cyclopentadienyl)niobium.—The η-allyl group of necessity will lower the symmetry of the molecule. If we assume the structure in Figure 3 we may deduce a m.o. scheme in C_s symmetry (see Figure 3). The spectrum is shown in Figure 2. The band at 5·65 eV is immediately assigned to the $4a'$ orbital, the niobium lone pair, as it is a typically narrow band of low i.e. well separated from the other bands. The bands at 8·6 and 9·2 eV may be assigned to the metal–cyclopentadienyl orbitals $1a'' + 2a'' + 2a' + 3a'$. The band at 8·0 eV is assigned to ionizations from the $3a''$ orbital formed by the metal d_{xy} orbital and the allyl non-bonding π-orbital.

The molecule is like $[(cp)_2Mo(\eta\text{-}C_2H_4)]$ and, in accord with this, the two spectra showed marked similarities. The correlation between the non-bonding metal orbitals ($3a_1$ and $4a''$) and the metal–cyclopentadienyl orbitals is immediately obvious. The bands at 6·90 eV in $[(cp)_2Mo(\eta\text{-}C_2H_4)]$ and 8·0 eV in $[(cp)_2Nb(\eta\text{-}C_3H_5)]$ are also analogous, being due in each case to ionizations from an orbital formed by overlap of the metal d_{xy} orbital with a ligand π-orbital antisymmetric with respect to reflection in the *xz* plane. The empty π*-orbital of ethylene is higher in energy than the occupied a'' non-bonding allyl orbital. On energy grounds the interaction between the metal *d* orbitals and the ethylene π-orbital is expected to be less. Hence the 6·9 eV band of $[(cp)_2Mo(\eta\text{-}C_2H_4)]$ has more metal character than the 8·0 eV band of $[(cp)_2Nb(\eta\text{-}C_3H_5)]$. A band assignable to the $1a'$ orbital was not observed and thus ionization probably occurs above 11·6 eV which would be reasonable extrapolating from the olefin complexes.

TABLE 3

Vertical ionization energies (eV) of the hydride and methyl complexes

$[(cp)_2ReH]$	$[(cp)_2MoH_2]$	$[(cp)_2WH_2]$	$[(cp)_2TaH_3]$	$[(cp)_2MoMe_2]$	$[(cp)_2WMe_2]$	Assignment
6·4	6·4	6·4	8·1	6·1	6·0	$3a_1$
7·0	8·9	8·9	8·7	8·3	8·3	$2b_1$
8·8	9·5	9·6	9·6	8·9	8·8	$1a_2 + 1b_2 + 2a_1 + 1b_1$
9·2					9·0	
9·9						
			10·6	9·6	9·6	$1a_1$
				11·3	11·3	CH_3
12·6	12·5	12·6	12·7	12·6	12·6	
13·4	13·5	13·7	13·5		13·3	
17·0	16·8	17·0	16·9	17·1	17·1	

Bis(η-cyclopentadienyl)hydridometal Complexes.—In the series of molecules $[(cp)_2ReH]$, $[(cp)_2MH_2]$, and $[(cp)_2TaH_3]$ the hydrogens are assumed to lie in the *xy* plane and the molecules are again assumed to have C_{2v} symmetry. The symmetry-adapted combinations of hydrogen 1*s* orbitals appropriate for bonding to the $(cp)_2M$ unit are a_1 for H_1, $a_1 + b_1$ for H_2, and $2a_1 + b_1$ for H_3. These will on bonding involve one, two, and three metal orbitals respectively. The m.o. schemes are given in Figure 4. Comparison of the m.o. schemes shows that $[(cp)_2ReH]$ has two lone pairs of electrons located mainly on the metal, $[(cp)_2MH_2]$ one, and $[(cp)_2TaH_3]$ none. This was clearly displayed in the p.e. spectra in the region below 7·5 eV (Figure 5). The complex $[(cp)_2ReH]$ had two equally intense bands at 6·3 and 6·9 eV assigned to ionizations from the $3a_1$ and $2b_1$ orbitals; the spectra of $[(cp)_2MH_2]$ (M = Mo and W) were very alike, one band at 6·4 eV corresponding to ionization from the $3a_1$ orbital $[(cp)_2TaH_3]$ had a spectrum with no bands below 7·5 eV. Characteristically the metal lone-pair ionizations are expected to decrease in i.e. along the series Re, W, Ta. The average metal i.e. for $[(cp)_2ReH]$

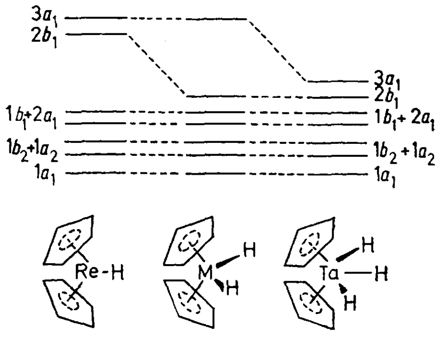

FIGURE 4 M.o. correlation diagram for $[(cp)_2ReH]$, $[(cp)_2MH_2]$, and $[(cp)_2TaH_3]$

is 6·6 eV, that of $[(cp)_2WH_2]$ is 6·4 eV, and so if Ta had a 'lone-pair' ionization it would be expected below 6·4 eV. The spectral observations correlate with the well known basic properties of the Re, Mo, and W hydrides.[16]

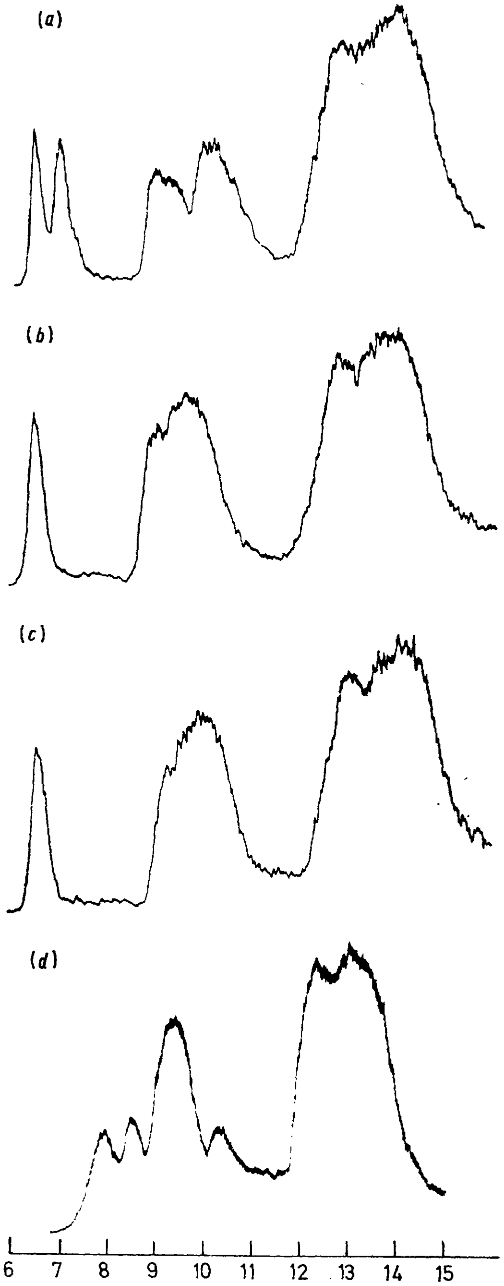

FIGURE 5 P.e. spectra of (*a*) $[(cp)_2ReH]$, (*b*) $[(cp)_2MoH_2]$, (*c*) $[(cp)_2WH_2]$, (*d*) $[(cp)_2TaH_3]$

The next series of bands with i.e.s of 8—11 eV must in part be due to ionization from the mainly cp orbitals. The varying complexity of these bands in the different molecules indicates that ionization from the M–H bonding orbitals also occurs in this region. The spectrum of $[(cp)_2ReH]$ with only one M–H bonding orbital is expected to be most like the corresponding third-row metallocene. In 1,1'-dimethylosmocene[14] the e_{1u} and e_{1g} ionizations are widely separated and occur in the regions 8·2—8·5 and 9·7—10·0 eV respectively. The corresponding a_1, b_1, a_2, and b_2 ionizations of $[(cp)_2ReH]$ are expected in the same region. The bands at 8·8, 9·2, 9·9, and 10·2 eV are assigned to ionizations from these orbitals together with ionization from the M–H a_1 orbital.

For $[(cp)_2MH_2]$ (M = Mo and W) there was one broad ionization band in this region with a maximum at *ca.* 9·5 eV and a shoulder at 8·9 eV. This broad band must correspond to ionizations from the $2a_1$, $1b_1$, $1a_2$, and $1b_2$ metal–cyclopentadienyl orbitals and from the $2b_1$ and $1a_1$ M–H bonding orbitals. The shoulder at 8·9 eV is tentatively assigned to the $2b_1$ M–H bonding orbital. The complex $[(cp)_2TaH_3]$ had four distinct ionization maxima in the region 8—11 eV, a broad intense band and three smaller bands. The intense band at 9·6 eV is assigned to ionizations from the metal–cyclopentadienyl orbitals and the bands at 8·1, 8·7, and 10·6 eV to the $3a_1$, $2b_1$, and $1a_1$ M–H bonding orbitals.

Bis(η-cyclopentadienyl)dimethylmetal Complexes.—The p.e. spectra of CH_4,[15] $M(CH_3)_4$,[17] and $W(CH_3)_6$ [18] indicate that ionizations from the CH_3 framework may be expected above 11 eV and are likely to be hidden under the amorphous region of the spectra. They are therefore not included in the m.o. scheme. A similarity of the spectra of these dimethyl derivatives to the corresponding dihydride spectra is expected and found. Again the spectra of the molybdenum and tungsten complexes were similar (Figure 6).

The single sharp band at lowest i.e. is assigned to ionizations from the $3a_1$ orbital, the metal lone pair. The next region of the spectrum between 7·5 and 11 eV consisted of several overlapping bands. These are assigned, as for the dihydrides, to ionizations from the $2a_1$, $1b_1$, $1a_2$, and $1b_2$ cyclopentadienyl–metal orbitals together with those from the $1a_1$ and $2b_1$ M–CH_3 bonding orbitals. The most intense band, definitely showing some splitting when M = W, probably corresponds to the cp orbitals; its ionization energy of 8·9—9·6 (M = Mo) and 8·8—9·5 eV (M = W) corresponds to that found for $[(cp)_2MoCO]$. The smaller band to low i.e. at 8·3 eV probably corresponds to the $2b_1$ M–CH_3 bonding orbital. The i.e.s of all bands in this region were lower than the corresponding bands of the hydride molecules, in line with the inductive effect of the methyl group. The area of ionization above 11 eV was largely the same as that of the other complexes in this study. However a distinct shoulder at 11·6 eV was observed which is absent from the hydride spectra. This is assigned to ionizations from the CH_3 framework.

Conclusions.—The spectra of the olefin complexes

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[18] S. Craddock and W. Savage, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 753.

provide an elegant demonstration of synergic bonding. The π-bonding level of the olefin is clearly lowered in energy on complexing of the olefin with the metal. That back donation also occurs may be seen by comparing the spectra of the olefin complexes with that of [(cp)$_2$ReH]. In the spectrum of the latter complex the first two bands are interpreted as lone-pair ionizations, have consequently sharp profiles, and are separated by 0·6 eV. In the spectra of the olefin complexes the second band is broader and is separated by 0·9 eV from the first thus establishing its bonding origin.

If the familiar σ-donation–π-acceptance of the bonding model for π-olefins is replaced by an equivalent ring-bonding scheme involving M–C σ-bonds, the similarity of the π-olefin complexes to the dimethyl complexes is readily apparent. The a_1 and b_1 bonding orbitals involving the ethylene π- and π^*-orbitals respectively correspond to a_1 and b_1 orbitals formed by two M–C σ-bonds in C_{2v} symmetry. The interaction between two such metal–carbon bonds is expected to increase as the distance between them decreases and thus the a_1–b_1 splitting is expected to be substantially greater in the ethylene complexes than in the dimethyl complexes. Although the a_1 and b_1 bands are not clearly resolved in the dimethyl complexes, their splitting must be less than 2 eV. The corresponding a_1–b_1 splitting in the olefin complexes is *ca.* 4·5 eV.

The splitting of the cyclopentadienyl–metal orbitals appears to be very similar for molybdenum and tungsten complexes. This is in contrast to the iron group where the splitting is found to increase substantially from ruthenium to osmium.[14] It appears that the degree

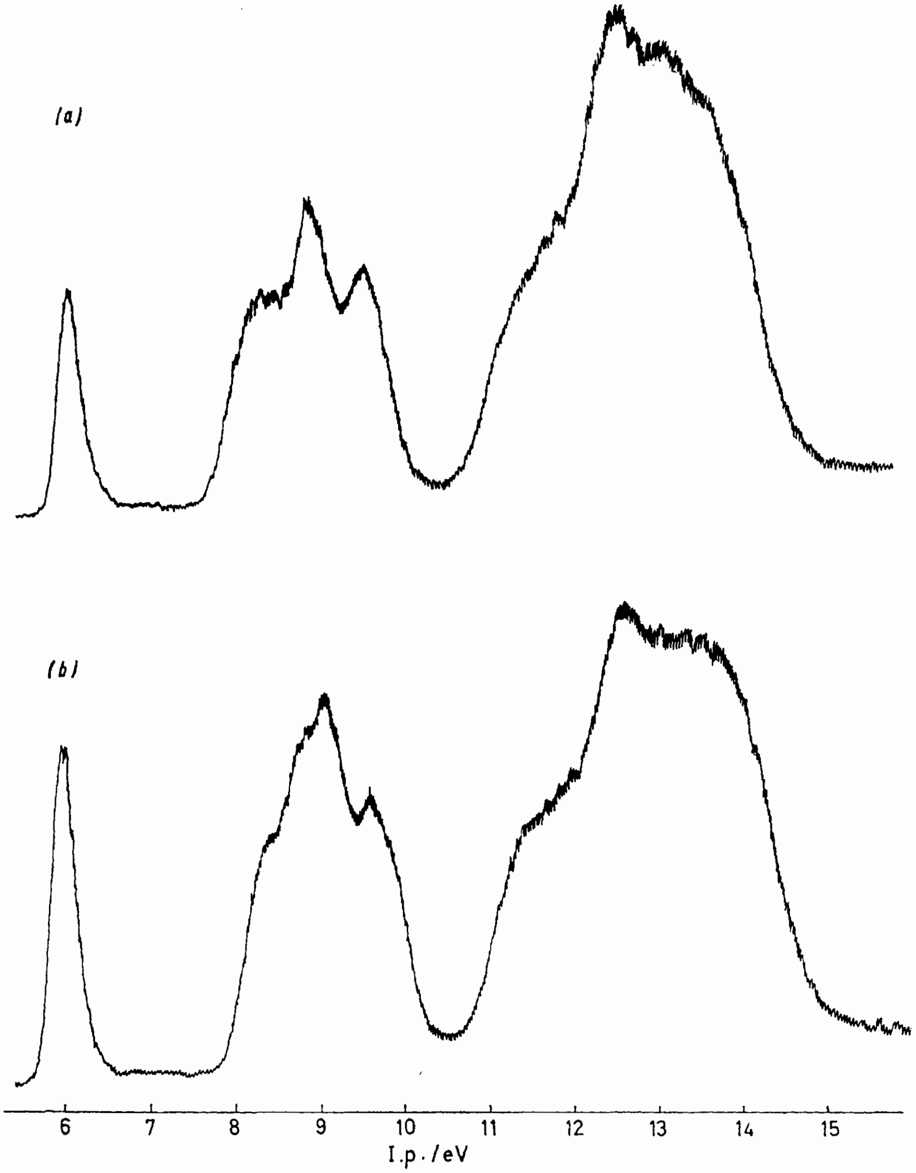

FIGURE 6 P.e. spectra of (*a*) [(cp)$_2$MoMe$_2$], (*b*) [(cp)$_2$WMe$_2$]

of splitting is less in the complexes of the earlier members of the transition series.

The p.e. spectra give no information as to the exact composition of the $3a_1$ orbital in these complexes, but it may be strongly argued that it is largely metal *d* in character and thence, on symmetry grounds, composed of $d_{x^2-y^2}$ and d_{z^2} orbitals. This is compatible with the crystallographic evidence[3] that this upper orbital lies outside the X–M–X angle and that its occupation reduces this angle. The orthogonal $2a_1$ orbital is then well disposed for covalent bonding of the X_2 unit.

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