He(I) Photoelectron Spectra of Some Transition-metal Sandwich Complexes

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The He(I) photoelectron spectra of $(\pi\text{-}C_6H_3Me_3)_2M$ where M = Cr, Mo, and V; $(\pi\text{-}C_6H_6)_2Mo$, and $(\pi\text{-}C_6H_5Me)_2Mo$; $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)M$ where M = Ti, V, and Cr; and $(\pi\text{-}C_8H_8)(\pi\text{-}C_5H_5)Ti$ are reported. Assignment of the spectra by use of a simple molecular orbital model is followed by a discussion of the electronic structure of these molecules.

In a previous photoelectron study [1] of π-arene complexes of chromium and manganese a satisfactory explanation of the spectra obtained was given in terms of current theories of their electronic structure. Here we extend this study to some bis-π-arene molybdenum and vanadium compounds and various sandwich complexes with cycloheptatrienyl and cyclo-octatetraene rings.

EXPERIMENTAL AND RESULTS

Bis-π-mesitylenevanadium was prepared from VCl_3 following the method of Calderazzo,[2] recrystallized from n-heptane, and sublimed *in vacuo*.

An attempt to prepare bis-π-mesitylenechromium by the reducing Friedel–Crafts method [3] produced a mixture of bis-π-arenechromium compounds which could not be separated. A sample of pure bis-π-mesitylenechromium was made (in conjunction with Mr. D. Young) by co-condensing mesitylene vapour and chromium atoms at liquid-nitrogen temperature. The bis-π-mesitylenechromium was extracted with ethanol and purified by recrystallization and vacuum sublimation.

A sample of bis-π-benzenemolybdenum, kindly donated by Dr. J. Knight, prepared by the method of Fischer and Stahl [4] was purified by washing with light petroleum and vacuum sublimation.

Gifts from Dr. W. E. Silverthorn of bis-π-toluenemolybdenum and bis-π-mesitylenemolybdenum prepared by the method of Green and Silverthorn [5] were purified by vacuum sublimation.

π-Cycloheptatrienyl-π-cyclopentadienyltitanium was prepared from $(\pi\text{-}C_5H_5)TiCl_3$ by the method of van Oven and de Liefde Meijer.[6] It was purified by washing with pentane and two vacuum sublimations.

π-Cycloheptatrienyl-π-cyclopentadienylvanadium was prepared from $(\pi\text{-}C_5H_5)V(CO)_4$ by a previously reported route [7] and purified by two vacuum sublimations.

π-Cycloheptatrienyl-π-cyclopentadienylchromium was prepared from anhydrous $CrCl_3$ by the method of King and Bisnette [8] and purified by washing with pentane and two vacuum sublimations.

π-Cyclo-octatetraene-π-cyclopentadienyltitanium was prepared from $K_2C_8H_8$ and $(\pi\text{-}C_5H_5)_2TiCl_2$ by the method of van Oven and de Liefde Meijer [9] and purified by resublimation *in vacuo*.

Mesitylene was freshly distilled before measurement.

In order to establish the purity and identity of the samples mass spectra were run for all compounds except bis-π-toluenemolybdenum which was too air-sensitive. The parent-ion peaks were identified and the cracking pattern for the various samples examined carefully. I.r. spectra were run on all samples except bis-π-toluenemolybdenum and bis-π-mesitylenemolybdenum and compared with previous i.r. data. We could find no account of the i.r. spectrum of bis-π-mesitylenechromium but the i.r. spectrum of our sample closely resembled that of bis-π-mesitylenevanadium. Bis-π-toluenemolybdenum which proved too air-sensitive for either of these purity tests was checked by means of its ^1H n.m.r. spectrum.

The spectra were obtained by three different instruments. Spectrometer (*a*) [10] combined a 127° analyser with a variable retarding field and possessed no facility for heating the inlet system. Spectrometer (*b*) [11] retarded the photoelectrons before entry into a 90° deflection analyser and possessed a steam-heated inlet system and target chamber. Spectrometer (*c*) was a Perkin-Elmer P.S. 16 instrument modified to take a heated insert probe. Owing

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[1] S. Evans, J. C. Green, and S. E. Jackson, *J.C.S. Faraday II*, 1972, **68**, 249.

[2] F. Calderazzo, *Inorg. Chem.*, 1964, **3**, 810.

[3] E. O. Fischer and W. Hafner, *Z. anorg. Chem.*, 1956, **286**, 146.

[4] E. O. Fischer and H. O. Stahl, *Chem. Ber.*, 1956, **89**, 1805.

[5] M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, 301.

[6] H. O. van Oven and H. J. de Liefde Meijer, *J. Organometallic Chem.*, 1970, **23**, 159.

[7] *Organometallic Syntheses*, 1965, **1**, 140.

[8] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785.

[9] H. O. van Oven and H. J. de Leifde Meijer, *J. Organometallic Chem.*, 1969, **19**, 373.

[10] S. Evans, A. F. Orchard, and D. W. Turner, *Internat. J. Mass Spectrometry Ion. Phys.*, 1971, **7**, 261.

[11] S. Evans and A. F. Orchard, unpublished work.

to the differing methods of scanning employed by these three instruments differing band-intensity distributions are obtained. Spectrometer (*b*) gives a decline in band intensity to *low* IE regions while spectrometer (*c*) gives a decline in band intensities to *high* IE regions.

All samples were run above room temperature in order to produce a sufficiently high count rate. This high temperature was produced with spectrometer (*a*) by directing a stream of hot air on the spectrometer and sample. Run conditions are in Table 1.

TABLE 1

Run conditions for measurement of photoelectron spectra

Compound	Spectrometer	t/°C	Counts/s^{-1} (max)
$(mes)_2Cr$	*c*	80	3000
$(bz)_2Mo$	*c*	110	1000
$(tol)_2Mo$	*a*	40	50
$(mes)_2Mo$	*a*	40	50
$(mes)_2V$	*a*	40	50
(cht)(cp)Ti	*b*	100	100
(cht)(cp)V	*a*	75	150
(cht)(cp)Cr	*a*	25	15
(cot)(cp)Ti	*c*	115	1000
Mesitylene	*a*, *b*	25	500

mes = π-Mesitylene, bz = π-benzene, tol = π-toluene, cht = π-cycloheptatrienyl, cp = π-cyclopentadienyl, cot = π-cyclo-octatetraene.

The spectra were calibrated by use of a mixture of noble gases as described previously.[12] Spectrometer (*c*) can only scan below 5·2 eV on an expanded scale which prevents direct calibration from the noble gas ionizations. In the case of bis-π-mesitylenechromium the first band had to be scanned on this expanded scale and was calibrated with reference to the second band. This placed the first band at 5·01 eV which is coincident with the band due to He(II) in the light source ionizing He atoms (4·98 eV). The first ionization band of π-cyclo-octatetraene-π-cyclopentadienyltitanium was calibrated both with respect to the noble gases (5·67 eV) and, the same linear scale being assumed, with reference to the He(II)/He line (5·62 eV) showing a reasonable agreement.

The spectra are given in Figures 1—10. In Table 2 the vertical ionization energies are tabulated together with those from ref. 1 for comparison. Maximum errors in ionization energies are of the order of 0·1 eV for broad bands and 0·05 eV for sharp bands.

DISCUSSION

Recently two papers have appeared which calculate the ionization potentials of ferrocene[13] and bis-π-allylnickel[14] by means of a full calculation on the ground states of the molecules and the ground and various excited states of the ions. For ferrocene their results give the observed order of ionizations which is not given by their ground state calculation for the molecule and assumption of Koopmans's theorem.[15] The theorem is found to be particularly inaccurate for ionization of electrons largely localized on the iron atom. Whatever the limitations of these calculations it is clear that assignment of a photoelectron spectrum of a metal complex cannot rely with confidence on a calculation of the orbital energies of the molecule and assumption of Koopmans's theorem.

In the subsequent assignment of spectra and their interpretation we will assume that, for a closed-shell molecule, ionization from each orbital or set of degenerate orbitals will give rise to one band in the photoelectron spectrum. The ionizations are labelled according to the symmetry of the orbitals from which they arise. In the case of open-shell molecules the possible number of ion states accessible to the ionizing molecule are considered and where exchange splitting is observed the bands are labelled according to the total symmetry of the ion state. Simple schematic molecular orbital diagrams are given as a convenient aid and are not deemed to represent the result of an accurate calculation.

When discussing variations of ionization energy in a series of closely related molecules such as we are studying here the interpretative problem is more complex. Let us suppose a correction term, X, can be applied to Koopmans's theorem designed to remedy the neglect of orbital reorientation, relativistic energy, and correlation energy,[16] as in equation (1). Here we will assume

$$\text{I.P.} = -\varepsilon i + X \qquad (1)$$

that for a particular ionization in a series of closely related molecules variations in this correction term may be neglected and that *trends* in ionization potential can be discussed in terms of *changes* in the orbital energy. We have no theoretical justification of this approximation but it provides a consistent and satisfying picture of bonding in these molecules, and seems in the absence of conflicting evidence a reasonable procedure.

We choose to divide the compounds studied in this work into two classes, the bis-π-arenemetal complexes and the mixed-ring metal complexes. Examples of both classes have been studied previously by photoelectron spectroscopy[1] and assignment of the present spectra will follow the same lines.

Bis-π-arenemetal Complexes.—Chromium and molybdenum. The electronic structure of the bis-π-arene complexes of chromium and molybdenum is fairly well established;[1] if these molecules are assumed to belong to the $D_{\infty h}$ point group, a simple molecular orbital scheme for the upper occupied and lower unoccupied levels of the molecules can be deduced and is given in Figure 11(a). The e_{1g} molecular level consists of a combination of the metal d_{xz} and d_{yz} orbitals with the symmetric combination of ring $e_1(\pi)$ orbitals. The e_{1u} level corresponds to the antisymmetric combination of the ring $e_1(\pi)$ orbitals possibly stabilized by mixing with the metal p_x and p_y orbitals. Both the metal d_{xy} and $d_{x^2-y^2}$ orbitals and the symmetric combination of the

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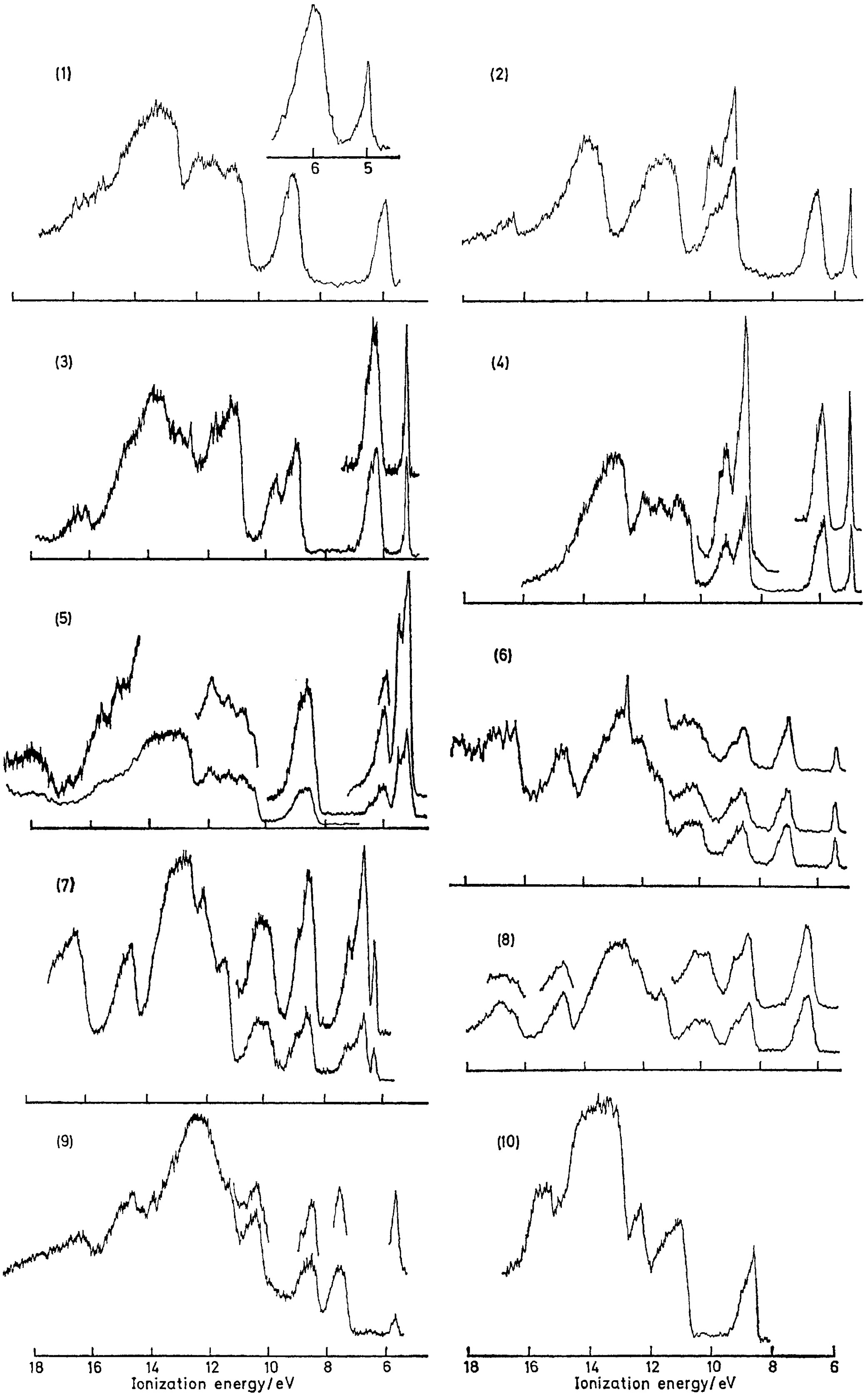
[12] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22.

[13] M. M. Coutière, J. Demuynck, and A. Veillard, *Theoret. Chim. Acta*, 1972, **27**, 281.

[14] M. M. Rohmer and A. Veillard, *J.C.S. Chem. Comm.*, 1973, 250.

[15] T. Koopmans, *Physica*, **1934**, **1**, 104.

[16] W. G. Richards, *Internat. J. Mass Spectroscopy Ion Phys.*, 1969, **2**, 419.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Ionization energy/eV
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Ionization energy/eV

FIGURES 1—10

ring $e_2(\pi)$ orbitals, which are unoccupied in the free arene ligand, can contribute to the e_{2g} molecular level. The a_{1g} level is likely to be almost pure metal d_{z^2}.[1] All these orbitals are filled in the bis-π-arene complexes of molybdenum and chromium.

TABLE 2

Vertical ionization energies/eV

$(bz)_2Cr$ [a]	$(tol)_2Cr$ [a]	$(mes)_2Cr$	$(bz)_2Mo$	$(tol)_2Mo$	$(mes)_2Mo$	$(mes)_2V$ [b]	(cht)(cp)Cr	(cht)(cp)V [b]	(cht)(cp)Ti	(bz)(cp)Mn [a]	(bz)(cp)Cr [b]	(cot)(cp)Ti [b]	Assignment
5·4	5·24	5·01	5·52	5·32	5·13	5·61	5·59	6·42		6·36	7·15	5·67 [c]	a_1
6·4	6·19	5·88	6·59	6·33	6·03	5·33	7·19	6·77	6·83	6·72	6·20	7·62	e_2
						6·08		7·28			7·15		
9·6	9·16	8·90	9·47	9·05	8·63	8·75	8·69	8·66	8·71	8·75	8·76	8·63	e
	9·53		10·15	9·75	9·31		9·00	8·99	9·1	9·25	9·17	8·93	
							10·4	10·2	10·2	9·79	9·68	10·51	
11·5	11·1	10·9	11·7	11·2	10·9	10·9	11·5	11·5	11·5	11·4	11·5	11·5	Ligand
13·8	11·6	11·6	12·1	11·8	11·5	11·4	12·1	12·2	12·3	12·2	12·2		
	13·8	12·1	14·2	13·8	12·0	12·0	12·7	12·8	12·8	14·1	13·8	12·6	
	14·7	13·4	16·6	14·7	13·0	13·0	14·8	14·6	14·6	16·8	17·2	14·8	
	16·2	17·8		16·2		15·6	16·5	16·6	16·2			15·1	
						17·8			16·6			16·6	

[a] Data from ref. 1. [b] 17-Electron molecule. [c] 5·62 eV Calibrated with respect to the He(II)/He line.

Two facts are immediately apparent from an initial examination of the spectra of the bis-π-arene compounds measured in this work and those of bis-π-benzenechromium and bis-π-toluenechromium.[1] First the upper regions of the spectra (*i.e.*, the ionization regions above *ca.* 10·3 eV) closely resemble that of the free arene. Ionization energies and band contours are very similar but the bands are broader in the complexes than in the free ligands. Therefore, we assign these bands in the same way as in previous work on arenes.[17,18] Secondly, in the ionization region below 10·3 eV the spectra of all the 18 electron molecules are similar. The first ionization band is very sharp and of low intensity and is therefore associated with ionization of an electron from the a_{1g} orbital. The second ionization band is broader and more intense and is assigned to ionization from the e_{2g} orbitals. Bands in the region 8—10·5 eV are assigned to ionization from the e_{1g} and e_{1u} orbitals; these will be discussed below.

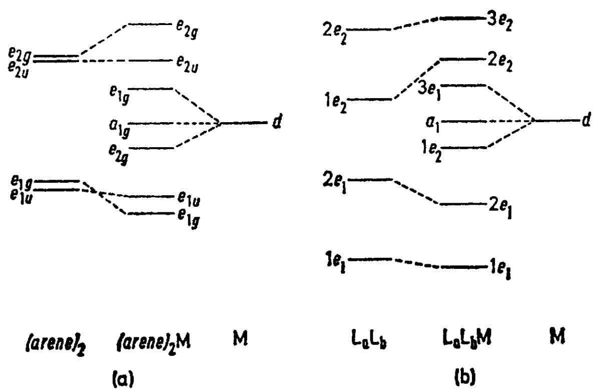

FIGURE 11 Qualitative molecular orbital schemes for (a) bis-π-arene complex; and (b) mixed ligand complex. L_a and L_b represent the two different ring ligands

In Figure 12 we plot the vertical ionization energies of the molybdenum and chromium compounds demonstrating clearly the effects of change of metal and of methyl substitution on the arene rings. The ionization energies of the electrons in the a_{1g} and e_{2g} orbitals are larger for the molybdenum series of compounds

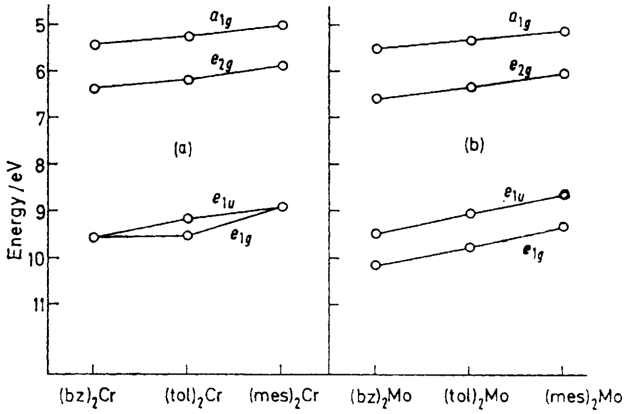

FIGURE 12 The vertical ionization energies of the 18-electron bis-π-arene complexes

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[17] E. Lindholm, C. Fridh, and L. Åsbrink, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 127; A. W. Potts, W. C. Price, D. C. Streets, and T. W. Williams, *ibid.* p. 168.

[18] L. Åsbrink, C. Fridh, and E. Lindholm, *Chem. Phys. Letters*, 1972, **15**, 567.

Captions to Figures 1—10

FIGURE 1 The He(I) photoelectron spectrum of bis-π-mesitylenechromium

FIGURE 2 The He(I) photoelectron spectrum of bis-π-benzenemolybdenum

FIGURE 3 The He(I) photoelectron spectrum of bis-π-toluenemolybdenum

FIGURE 4 The He(I) photoelectron spectrum of bis-π-mesitylenemolybdenum

FIGURE 5 The He(I) photoelectron spectrum of bis-π-mesitylenevanadium

FIGURE 6 The He(I) photoelectron spectrum of π-cycloheptatrienyl-π-cyclopentadienylchromium

FIGURE 7 The He(I) photoelectron spectrum of π-cycloheptatrienyl-π-cyclopentadienylvanadium

FIGURE 8 The He(I) photoelectron spectrum of π-cycloheptatrienyl-π-cyclopentadienyltitanium

FIGURE 9 The He(I) photoelectron spectrum of π-cyclo-octatetraene-π-cyclopentadienyltitanium

FIGURE 10 The He(I) photoelectron spectrum of mesitylene. Vertical ionization energies are 8·45, 11·1, 12·4, 14, and 15·8 eV than for the chromium one, and the separation of the two bands is marginally larger for the molybdenum series. The e_{1u}–e_{1g} splitting is clearly seen in the molybdenum spectra whereas in the chromium series only with bis-π-toluenechromium could it be detected, the band at 9·16 eV having a shoulder at 9·53 eV. In the molybdenum spectra it can be seen that the higher IE band has a shape characteristic of a bonding orbital while the lower of the two bands has a sharp edge indicating that this is less involved in the bonding. The e_{1g} ligand orbitals are of correct symmetry to combine with the metal *d*-orbital whereas the e_{1u} ligand orbitals can only combine with the higher-energy metal *p*-orbitals. The former combination is therefore believed to be the more strongly bonding and the origin of the higher ionization band. This greater splitting in the molybdenum complexes indicates a stronger arene ring–metal e_1 interaction in the molybdenum than in the chromium compounds.

Methyl substitution in the ring decreases the ionization energies of all electrons associated with these highest orbitals. The effect is greatest for ionizations from the e_{1g} and e_{1u} orbitals where decreases of *ca.* 0·4 eV in corresponding bands are found for monomethylation of each ring. The effect of adding one methyl group in passing from benzene to toluene appears comparable with adding two from toluene to mesitylene. The effect on ionizations from the e_{2g} and a_{1g} orbitals is *ca.* 0·2 eV for a_{1g} and 0·3 eV for e_{2g}. As the a_{1g} orbital is nearly non-bonding in character this decrease appears to be a result of increased electron–electron repulsion as the degree of methyl substitution increases. Thus the inductive effect of the methyl group makes these substituted arenes less effective in removing electrons from the metal.

Similar trends have been found for the series of isoelectronic molecules bis-π-cyclopentadienyl-iron, -ruthenium, and -osmium and their methyl derivatives.[19]

Bis-π-mesitylenevanadium. This is a 17-electron compound. E.s.r. evidence [20] indicates that the ground state of the molecule is $^2A_{1g}$, namely that the unpaired electron occupies an orbital of a a_{1g} symmetry. This concurs with the fact that the isoelectronic bis-π-arenechromium cations have $^2A_{1g}$ ground states.[21] Ionization of an electron from a fully occupied level in this molecule can give rise to either a singlet or a triplet ion state. In practice, such states are only likely to be resolved in the photoelectron spectrum when ionization is taking place from an orbital localized on the metal.

The first three bands in the spectrum of bis-π-mesitylenevanadium are assigned to ionizations from the a_{1g} and e_{2g} orbitals which can give rise to $^1A_{1g}$, $^3E_{2g}$, and $^1E_{2g}$ ion states. By analogy with the bis-π-arenechromium compounds an ionization from an a_{1g} orbital is likely to be sharper and less intense than an ionization from an e_{2g} orbital. Also the intensity ratios of the bands $^3E_{2g}:{}^1E_{2g}$ is predicted to be 3 : 1 [1] and Hund's rules predict that the $^3E_{2g}$ state is of lower energy than the $^1E_{2g}$ state. If these points are taken into consideration, the bands can be assigned unambiguously as follows: $^3E_{2g}$ 5·33 eV, $^1A_{1g}$ 5·61 eV, and $^1E_{2g}$ 6·08 eV. It may be noted that the E_{2g} bands have a characteristic asymmetric shape.

The remaining part of the spectrum closely resembles that of the other bis-π-mesitylene complexes and is assigned accordingly to ligand orbitals.

Mixed Sandwich Compounds.—*X*-Ray diffraction studies on $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)V$ [22] and $(\pi\text{-}C_8H_8)(\pi\text{-}C_5H_5)Ti$ [23] show that the two rings are planar and parallel; thus orbitals may be assigned in $C_{\infty v}$. It may reasonably be assumed that the other mixed sandwich compounds studied here have similar structures. In spite of this lower symmetry the molecular orbital treatment of these compounds is similar to that of the bis-π-arene compounds. A simple Hückel MO treatment of the isolated rings predicts that the *e* ring molecular orbitals are progressively stabilized with increase in ring size.[24] Owing to these energy differences the orbitals of the two rings mix less with each other and to differing extents with the metal orbitals. The assignment of the spectra of the mixed sandwich compounds is based on the molecular orbital diagram shown in the Figure 11(b).

π-Cycloheptatrienyl-π-cyclopentadienylchromium. The electronic configuration of this diamagnetic 18-electron molecule is $(1e_1)^4(2e_1)^4(e_2)^4(a_1)^2$. Ionizations of electrons from these four orbitals can be seem in the region below 11·0 eV. The first ionization band at 5·59 eV is sharp and of low intensity and is due to ionization from the a_1 orbital. The second band is well separated from the first and can be assigned to ionization from an e_2 orbital. The third band at 8·69 eV with a slight shoulder at 9·00 eV is characteristic in position and shape of ionization from the cyclopentadienyl e_1 orbitals. The band at 10·4 eV is presumably due to ionization from the corresponding cycloheptatrienyl e_1 orbitals. This assignment corresponds to that previously advanced for the spectrum of the isoelectronic molecule π-benzene-π-cyclopentadienylmanganese.[1]

π-Cycloheptatrienyl-π-cyclopentadienylvanadium. The isotypic vanadium compound has 17 electrons. Its ground state has been shown by e.s.r. studies to be $^2A_1$.[25] As with bis-π-mesitylenevanadium, ionization from any filled orbital can give rise to singlet and triplet ion states. Five ionizations are observed below 11·0 eV. The first band (6·42 eV) is sharp and is assigned to ionization from the a_1 orbital. The next two bands (6·77 and 7·28 eV) overlap but the two vertical ionization

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energies can be clearly distinguished and are assigned respectively to the $^3E_2$ and $^1E_2$ ion states. The bands at 8·66 eV (shoulder 8·99 eV) and 10·2 eV closely resemble those of π-cycloheptatrienyl-π-cyclopentadienylchromium and are similarly assigned to ionization from the cyclopentadienyl and cycloheptatrienyl e_1 orbitals respectively.

π-Cycloheptatrienyl-π-cyclopentadienyltitanium. This 16-electron molecule is diamagnetic[6] and must have the ground-state configuration $(e_2)^4$. The photoelectron spectrum is consistent with this as below 11·0 eV there are two bands characteristic of the cyclopentadienyl e_1 ionization (8·7 eV) and the cycloheptatrienyl e_1 ionization (10·2 eV) and only one other, a broad band at 6·83 eV which we assign to ionization from the e_2 orbital.

π-Cyclo-octatetraene-π-cyclopentadienyltitanium. Magnetic measurements give $\mu_{\text{eff}} = 1{\cdot}60 \pm 0{\cdot}01$ B.M.[9] The photoelectron spectrum has four bands below 11·0 eV. The band at 8·63 eV is assigned to ionization from the cyclopentadienyl e_1 orbital and the band at 10·51 eV presumably is due to ionization from the cyclo-octatetraene e_1 orbital. The first band of the spectrum (5·67 eV) is of low intensity and by analogy with the isoelectronic $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)V$ it can be assigned to the $^1A_1$ ion state. Thus the remaining band at 7·62 eV must be due to ionization from the e_1 orbital. The $^3E_2$ and $^1E_2$ ion states are not resolvable under our experimental conditions, perhaps owing to broadness of the band. This suggests that the exchange interaction with the unpaired electron in the a_1 molecular orbital is smaller than in the other d^5 molecules studied, consistent with more extensive delocalization of the electrons in the e_2 MO on to the cyclo-octatetraene ligand. This is expected as the empty ring e_2 π-levels are stabilized with increase in ring size and thus better able to mix with the metal e_2 orbitals. Also the closer approach of the larger ring to the metal will increase the overlap of these δ-symmetry orbitals.

Trends in Ionization Energies.—The variation in ionization energies in related series of molecules is best illustrated by plotting vertical ionization energies for corresponding bands. When ionization from one molecular orbital gives rise to two ion states, the ionization energies are weighted according to the degeneracies of the ion states and the average is plotted. The separation of the two states is indicated by a bar terminating in the two observed ionization energies.

Figure 13 shows ionization energies for two series of isoelectronic molecules. Figure 13(a) representing the 18-electron compounds $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)Cr$, $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Mn$,[1] and $(\pi\text{-}C_5H_5)_2Fe$,[19] and Figure 13(b) representing the 17-electron compounds $(\pi\text{-}C_8H_8)(\pi\text{-}C_5H_5)Ti$, $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)V$, and $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Cr$.[1] Both metal and ring are changing from one member of the series to the next. We will discuss the trends in terms of orbital energies as mentioned above.

Figure 13(a) shows that the a_1 orbital decreases rapidly in energy across the series. As this orbital has largely metal character this change can be correlated with the decrease of the metal d-orbital energy (Cr 7·2 eV, Mn 7·9 eV, Fe 8·7 eV).[26] The variation of the e_2 orbital energy is both less regular and less marked which is understandable in terms of its composite nature. In the mixed-ring compounds the principal ring contribution to this e_2 orbital will come from the larger ring as this will have the lower e_2 orbital energy; in ferrocene of course both rings must contribute equally. Thus as far as the ring contribution to the e_2 orbital is concerned, the e_2 orbital should rise in energy across the series. Superimposed on this rise will be a decrease in orbital energy due to the metal contribution as the metal is changed from chromium through to iron. The net effect is to produce an irregular variation as shown. This can be compared with the corresponding series $(\pi\text{-}C_6H_6)_2Cr$, $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Mn$, and $(\pi\text{-}C_5H_5)_2Fe$[1] where a small but regular decrease in e_2 orbital energy was found across the series. The substantially greater a_1–e_2 splitting in $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)Cr$ (1·60 eV) than in $(\pi\text{-}C_6H_6)Cr$ (0·9 eV) indicates the high contribution the cycloheptatrienyl e_2 orbital makes to the e_2 molecular orbital. The first ionization energies are however very close, 5·43 eV for $(\pi\text{-}C_6H_6)_2Cr$ and 5·59 eV for $(\pi\text{-}C_7H_7)(\pi\text{-}C_5H_5)Cr$, as one would expect for a virtually non-bonding orbital localized on the chromium atom.

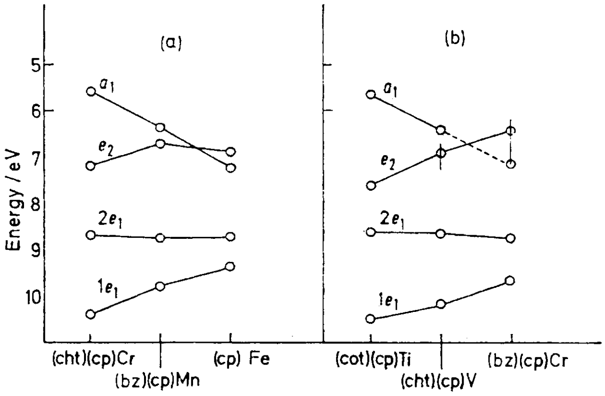

FIGURE 13 The vertical ionization energies of (a) the 18 electron compounds π-cycloheptatrienyl-π-cyclopentadienylchromium, π-benzene-π-cyclopentadienylmanganese, and bis-π-cyclopentadienyliron; and (b) the 17 electron compounds π-cyclo-octatetraene-π-cyclopentadienyltitanium, π-cycloheptatrienyl-π-cyclopentadienylvanadium, and π-benzene-π-cyclopentadienylchromium

The upper e_1 level stays almost constant throughout the series whereas the lower level increases in energy on passing from the chromium to the iron compound. This suggests that in the two mixed-ring compounds the mixing between the two ring e_1 orbitals is small and that the rise in the lower e_1 level across the series is due to the increase in ring orbital energy with decrease in ring size.

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[26] C. J. Ballhausen and H. B. Gray, 'Molecular Orbital Theory,' Benjamin, New York, 1964.

The e_1 orbitals of the 17-electron series of compounds show a similar pattern. The average e_2 ionization energy for this series shows an upward trend indicating that the stability of the larger-ring e_2 orbital is the dominant factor in determining the energy of the e_2 molecular orbital. The separation of the $^3E_2$ and $^1E_2$ ion states increases with decrease in ring size. This is consistent with a greater localization of the e_{2g} electrons on the metal for the smaller rings.

The trend in the energy of the ionization from the a_1 orbital throws light on the assignment of the spectrum of $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Cr$.[1] The a_1 ionization was not resolved in the spectrum of this compound and on intensity grounds we assumed that it lay under the $^3E_2$ ionization band. Extrapolation of the a_1 ionization energy in a manner similar to that of the 18-electron compounds places this $^1A_1$ ion state at the same energy as the $^1E_2$ ion state. On this basis we conclude that this is the more likely assignment. The trend in the metal *d*-orbital energies[26] (Ti —5·6 eV, V —6·3 eV, Cr —7·2 eV) then closely parallels the variation of a_1 ionization in this series of compounds, as in the 18-electron compounds discussed above.

In Figure 14 we examine the effect of a change of metal on the ionizations of isotypic compounds. The change in metal necessarily involves a change in electron number. The e_1 orbital energies are insensitive to change in metal. The e_2 orbital energy decreases with increase in nuclear charge of the metal but not at a rate as large as that of the decrease in a_1 orbital energy in the isoelectronic sequences. This is consistent with a substantial contribution of both metal and ligand to these e_2 molecular orbitals.

In marked contrast there is a decrease in a_1 ionization energy with increase in nuclear charge of the metal. This decrease is attributed to the change from a 17-electron compound with an $(a_1)^1$ configuration to an 18-electron compound with an $(a_1)^2$ configuration. The decrease in a_1 ionization energy is a direct consequence of the increase in electron–electron repulsion in a doubly occupied a_1 orbital. Comparison of the $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)M$ pair, where M = Cr or Mn, with the other isotypic pairs again suggests that the a_1 ionization for the chromium compound occurs at *ca.* 7·2 eV.

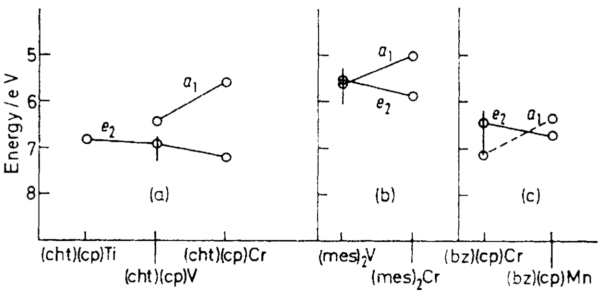

FIGURE 14 The vertical ionization energies of isotypic compounds: (a) π-cycloheptatrienyl-π-cyclopentadienyltitanium, π-cycloheptatrienyl-π-cyclopentadienylvanadium, and π-cycloheptatrienyl-π-cyclopentadienylchromium; (b) bis-π-mesitylenevanadium and bis-π-mesitylenechromium; and (c) π-benzene-π-cyclopentadienylchromium and π-benzene-π-cyclopentadienylmanganese

It is noteworthy that continuation of this trend to $(\pi\text{-}C_8H_8)(\pi\text{-}C_5H_5)Ti$ and the as yet unprepared analogous vanadium compound suggests a first ionization potential for the latter of less than 5 eV.

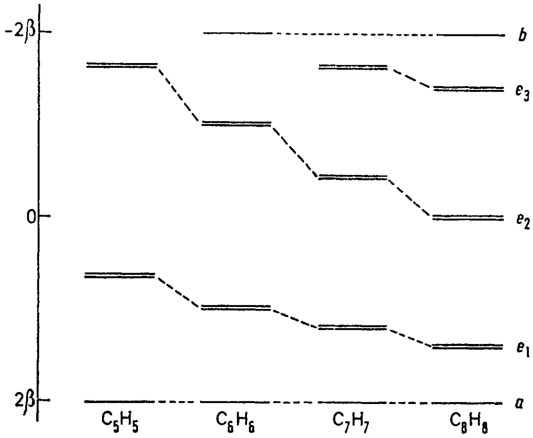

FIGURE 15 Hückel M.O. energies for C_5H_5, C_6H_6, C_7H_7, and C_8H_8

Conclusion.—We compare the function of $(\pi\text{-}C_5H_5)$, $(\pi\text{-}C_6H_6)$, $(\pi\text{-}C_7H_7)$, and $(\pi\text{-}C_8H_8)$ as ligands. As is shown in Figure 15, in the free ligand the *e* levels are progressively stabilized with increase in ring size. This has important consequences in their ability to bond to metals. On grounds of energy separation it can be deduced that the interaction of the e_1 orbitals with a metal is likely to decrease with increase in ring size, while that of the e_2 orbitals is likely to increase. Given that the energy of the metal valence orbitals concerned is more or less intermediate between the e_1 and e_2 orbitals for the early transition metals, this implies that both the e_1 and e_2 molecular orbitals will increase in ligand character with increase in ring size. An indication of this increasing e_2 orbital interaction is given by the increase in a_1–e_2 splitting represented in Figure 13 and also by the decrease in single–triplet splitting for the E_2 ion states. The decrease in e_{1u}–e_{1g} splitting from ferrocene (0·4 eV)[19] to bis-π-benzene-chromium (<0·4 eV) and from ruthenocene (1·42 eV)[19] to bis-π-benzenemolybdenum (0·68 eV) is consistent with a decrease in e_1 orbital interaction from the cyclopentadienyl to the benzene complexes.

When π-cyclopentadienyl is a ligand, interaction of the e_1 orbitals is the most important source of bonding and as these orbitals are not fully occupied in the free ligand, the cyclopentadienyl radical, this interaction is able to remove charge from the metal. When benzene is the ligand these e_1 orbitals are fully occupied and are therefore involved in a donor bond to the metal. This is evidenced by the e_{1g}–e_{1u} splitting observed in the bis-arene complexes. The acceptor action of the e_2 orbitals is more important than for the π-cyclopentadienyl ligand; however, the very low ionization potentials observed for the bis-arene complexes indicate that benzene is less efficient overall at removing electrons from the metal atom. When π-cycloheptatrienyl is a ligand its e_1 interaction with the metal is likely to be very small and the chief source of bonding is the e_2 interaction. This interaction appears even greater for the cyclo-octatetraene ligand where the percentage of ligand character in the e_2 orbital is high. This regular variation in bonding properties is obscured by the oxidation-state formalism which describes these ligands as $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{2-}$.

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