Theoretical Investigation of the Electronic Structures of the Mixed-ring Sandwich Molecules $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ (M = Ti, V, Nb or Ta)†

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Density-functional methods have been used to investigate the valence electronic structures of four mixed-ring transition-metal sandwich molecules, $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ (M = Ti, V, Nb or Ta). Close agreement with previous experimental data is obtained in all cases for the ionisation energies and localisation properties of the highest occupied molecular orbitals. The metal-cyclopentadienyl ring bonding is predominantly ionic, while the interaction of the metal with the cycloheptatrienyl ring is found to have a significant covalent component. Analysis of the composition of the highest occupied molecular orbital corresponding to the metal–cycloheptatrienyl ring bonding of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, for which experimental data are not available, suggests that it is not appreciably different from that in the Group 5 molecules.

The bonding of cycloheptatrienyl (η^7-C_7H_7) rings to early transition metals has recently been the subject of extensive experimental investigation.[1,2] The doubly degenerate e_2 symmetry highest occupied molecular orbital (HOMO) of a cycloheptatrienyl ring contains only one electron, with the consequence that both a +1 and a −3 formal charge satisfy the Hückel $4n + 2$ rule for aromaticity.[3] Synchrotron radiation-based photoelectron spectroscopy (PES),[2] allied with electrochemical, ESR and X-ray crystallographic data,[1] has demonstrated that the principal metal–cycloheptatrienyl ring bonding interaction in mixed-ring sandwich molecules of the type $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4R)]$ (M = Ti, V, Nb or Mo, R = H; M = Ta, R = Me) involves significant mixing of the e_2 HOMO of the cycloheptatrienyl ring with the metal d orbitals of appropriate symmetry ($d_{x^2-y^2}$ and d_{xy} in a coordinate system in which the metal–ring axis is defined as the z axis). Such extensive orbital mixing implies that neither the +1 nor the −3 formalism for the charge on the cycloheptatrienyl ligand is an accurate description of the electron distribution between the metal centre and the seven-membered ring.

The photoelectron (PE) spectroscopic evidence was based upon analysis of the relative partial photoionisation cross-section (RPPICS) behaviour of the first four bands in the PE spectra of $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ (M = Nb or Mo) and $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)]$.[2] The first band is due to ionisation of the essentially metal d-localised HOMO, while the second arises from the metal–cycloheptatrienyl ring bonding MO discussed above. The third and fourth bands are due to MOs localised predominantly on the cyclopentadienyl and cycloheptatrienyl rings respectively. By comparing the RPPICS of these bands over the incident photon-energy range in which the metal's $np \rightarrow nd$ giant resonance[2,4,5] occurs, it proved possible to quantify the degree of mixing in the metal–cycloheptatrienyl ring bonding orbital. For $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ (M = Nb or Mo) it was found to possess 63% metal 4d and 37% cycloheptatrienyl e_2 character, while for $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)]$ 74% Ta 5d and 26% cycloheptatrienyl e_2 contributions were found.

The compound $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, however, is a 16-electron molecule, and as such there are no essentially metal d-localised electrons {the HOMO of the 17- and 18-electron compounds of the Group 5 and 6 metals is the lowest unoccupied molecular orbital (LUMO) in $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$}. Metal 3d involvement in the e_2 symmetry HOMO of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ is strongly indicated by the large increase in the RPPICS of the associated PE band in the region of the Ti 3p subshell ionisation potentials,[2] but without a metal d-based 'internal standard' PE band as a reference this is impossible to quantify.

It was therefore decided to employ computational methods to study these molecules further. This paper reports the results of a density-functional investigation of the electronic structure of four mixed-ring transition-metal sandwich molecules, $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ (M = Ti, V, Nb or Ta). Density-functional methods have frequently been shown to yield accurate results on large molecular systems while retaining computational feasibility.[6] One particular advantage of the Amsterdam density functional[7,8] (ADF) program used in this study is its fragment-based approach, which allows molecular electronic structure to be analysed in terms of the interactions of specific molecular fragments.

Computational Details

All calculations were performed using the Amsterdam density functional program suite.[9] Double-zeta Slater-type orbital atomic basis sets were employed for all orbitals apart from the valence d orbitals of the transition metals, which were of triple-zeta quality including one diffuse function. Frozen cores were used for carbon (1s) and the transition metals [$(n-1)$p]. The local density functional of Vosko *et al.*[10] was employed, with Stoll's correlation correction[11] and Becke's gradient correction[12] to the exchange part of the potential. Quasi-relativistic scalar corrections, Darwin and mass-velocity, were included for $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ *via* the Pauli formalism, in which the first-order scalar relativistic Pauli Hamiltonian is diagonalised in the space of the non-relativistic basis sets. Relativistic core potentials were computed for Ta and C using the ADF auxiliary program DIRAC.

Ionisation energies were computed using the transition-state method.[13] Separate calculations were converged for each ionisation energy. Mulliken population analyses[14] were performed.

Molecular geometries were taken from experimental data where available, $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$,[15] $[Ti(\eta^7\text{-}C_7H_7)\text{-}$

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† *Non-SI unit employed:* eV = 1.6021×10^{-19} J.

$(\eta^{5}\text{-}\mathrm{C_5H_5})]$,[16] $[\mathrm{V}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$,[17] and optimised to C_s symmetry in all cases. The geometry of $[\mathrm{Ta}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$ was assumed to be the same as that of $[\mathrm{Nb}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$.

Results and Discussion

An energy *vs.* composition diagram of the highest occupied and lowest unoccupied MOs of $[\mathrm{Nb}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$ is shown in Fig. 1, with orbital eigenvalues, occupations, compositions and ionisation energies collected in Table 1. Corresponding data for $[\mathrm{Ta}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$ (with both non-relativistic and relativistic frozen cores) are given in Table 2, and those for $[\mathrm{V}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$ and $[\mathrm{Ti}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$ are presented in Tables 3 and 4 respectively. The internal charge distributions and metal d-electron configurations of all four molecules are given in Table 5.

There are only two possible orbital symmetries in the C_s point group, a′ and a″. The labels in parentheses (in the figure, tables and text) relate these to the more frequently encountered $C_{\infty v}$ orbital labels for mixed-ring sandwich molecules, in which infinite axes of rotation are assumed for the carbocyclic rings.[18] Formally, all doubly degenerate e symmetry $C_{\infty v}$ orbitals split into two non-degenerate orbitals in the C_s point group, one

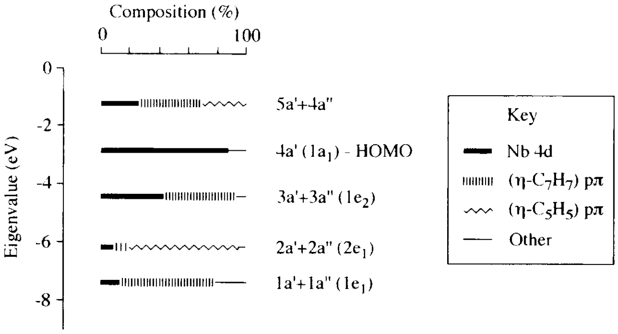

Fig. 1 Eigenvalue *vs.* composition diagram for the highest occupied and lowest unoccupied molecular orbitals of $[\mathrm{Nb}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$

Table 1 Valence molecular orbital eigenvalues, occupations, compositions and ionisation energies for $[\mathrm{Nb}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$

			Fragment contribution (%)			Ionisation energy (eV)	
Orbital	Eigenvalue (eV)	Occupation	Nb	η^7-C$_7$H$_7$	η^5-C$_5$H$_5$	Calculated	Experimental*
4a″	−1.223	0	27 d	43 e$_2$	29 e$_2$		
5a′(LUMO)	−1.225	0	27 d	43 e$_2$	29 e$_2$		
4a′(1a$_1$) (HOMO)	−2.824	1	4 s, 88 d	7 a$_1$		5.57	5.85
3a″ (1e$_2$)	−4.434	2	43 d	50 e$_2$	4 e$_2$	6.93	7.00
3a′ (1e$_2$)	−4.436	2	43 d	50 e$_2$	4 e$_2$	6.93	
2a″ (2e$_1$)	−6.276	2	9 d	11 e$_1$	76 e$_1$	8.79	8.77
2a′ (2e$_1$)	−6.277	2	9 d	11 e$_1$	76 e$_1$	8.79	
1a″ (1e$_1$)	−7.423	2	13 d	81 e$_1$	5 e$_1$	9.99	10.22
1a′ (1e$_1$)	−7.426	2	13 d	81 e$_1$	5 e$_1$	9.99	

* Data from ref. 2.

Table 2 Valence molecular orbital eigenvalues, occupations, compositions and ionisation energies for $[\mathrm{Ta}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$, calculated with both non-relativistic and relativistic (in parentheses) frozen core orbitals for Ta and C

			Fragment contribution (%)			Ionisation energy (eV)	
Orbital	Eigenvalue (eV)	Occupation	Ta	η^7-C$_7$H$_7$	η^5-C$_5$H$_5$	Calculated	Experimental*
4a″	−1.152 (−1.109)	0	24 d (22 d)	40 e$_2$ (36 e$_2$)	36 e$_2$ (41 e$_2$)		
5a′ (LUMO)	−1.153 (−1.109)	0	24 d (23 d)	40 e$_2$ (36 e$_2$)	36 e$_2$ (41 e$_2$)		
4a′ (1a$_1$) (HOMO)	−2.690 (−2.618)	1	7 s, 84 d (87 d)	7 a$_1$ (8 a$_1$)	(5 a$_1$)	5.38 (5.31)	5.47
3a″ (1e$_2$)	−4.469 (−4.393)	2	41 d (39 d)	51 e$_2$ (53 e$_2$)	5 e$_2$ (5 e$_2$)	6.97 (6.89)	6.89
3a′ (1e$_2$)	−4.469 (−4.393)	2	41 d (39 d)	51 e$_2$ (53 e$_2$)	5 e$_2$ (5 e$_2$)	6.97 (6.89)	
2a″ (2e$_1$)	−6.273 (−6.336)	2	8 d (8 d)	15 e$_1$ (14 e$_1$)	75 e$_1$ (76 e$_1$)	8.76 (8.83)	8.73
2a′ (2e$_1$)	−6.274 (−6.337)	2	8 d (8 d)	15 e$_1$ (14 e$_1$)	75 e$_1$ (76 e$_1$)	8.76 (8.83)	
1a″ (1e$_1$)	−7.457 (−7.437)	2	14 d (14 d)	73 e$_1$ (73 e$_1$)	8 e$_1$ (8 e$_1$)	10.01 (10.01)	10.19
1a′ (1e$_1$)	−7.457 (−7.437)	2	14 d (14 d)	73 e$_1$ (73 e$_1$)	8 e$_1$ (8 e$_1$)	10.01 (10.01)	

* Data for $[\mathrm{Ta}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_4Me})]$ from ref. 2.

Table 3 Valence molecular orbital eigenvalues, occupations, compositions and ionisation energies for $[\mathrm{V}(\eta^{7}\text{-}\mathrm{C_7H_7})(\eta^{5}\text{-}\mathrm{C_5H_5})]$

			Fragment contribution (%)			Ionisation energy (eV)	
Orbital	Eigenvalue (eV)	Occupation	V	η^7-C$_7$H$_7$	η^5-C$_5$H$_5$	Calculated	Experimental*
4a″	−1.177	0	40 d	49 e$_2$	10 e$_2$		
5a′ (LUMO)	−1.179	0	40 d	49 e$_2$	10 e$_2$		
4a′ (1a$_1$) (HOMO)	−3.171	1	2 s, 90 d	4 a$_1$	2 a$_1$	6.06	6.49
3a″ (1e$_2$)	−4.319	2	44 d	51 e$_2$	3 e$_2$	6.86	6.86
3a′ (1e$_2$)	−4.320	2	44 d	51 e$_2$	3 e$_2$	6.86	
2a″ (2e$_1$)	−6.216	2	15 d	2 e$_1$	81 e$_1$	8.94	8.72
2a′ (2e$_1$)	−6.216	2	15 d	2 e$_1$	81 e$_1$	8.94	
1a″ (1e$_1$)	−7.367	2	6 d	87 e$_1$	5 e$_1$	10.02	10.40
1a′ (1e$_1$)	−7.372	2	6 d	87 e$_1$	5 e$_1$	10.02	

* Data from ref. 1.

Table 4 Valence molecular orbital eigenvalues, occupations, compositions and ionisation energies for [Ti(η^7-C_7H_7)(η^5-C_5H_5)]

			Fragment contribution (%)			Ionisation energy (eV)	
Orbital	Eigenvalue (eV)	Occupation	Ti	η^7-C_7H_7	η^5-C_5H_5	Calculated	Experimental*
5a′	−0.660	0	72 d	13 e_2	15 e_2		
4a″	−0.664	0	72 d	13 e_2	15 e_2		
4a′ (LUMO)	−2.826	0	2 s, 88 d	6 a_1			
3a″ (1e_2) (HOMO)	−4.215	2	38 d	58 e_2	3 e_2	6.78	6.85
3a′ (1e_2)	−4.215	2	39 d	58 e_2	3 e_2	6.78	
2a″ (2e_1)	−6.184	2	12 d	2 e_1	82 e_1	8.93	8.74
2a′ (2e_1)	−6.184	2	12 d	2 e_1	82 e_1	8.93	
1a″ (1e_1)	−7.359	2	3 p, 7 d	89 e_1	1 e_1	10.05	9.90
1a′ (1e_1)	−7.365	2	3 p, 7 d	89 e_1	1 e_1	10.06	

* Data from ref. 2.

Table 5 Fragment charges and d-electron configurations for [M(η^7-C_7H_7)(η^5-C_5H_5)] {M = Nb, Ta [non-relativistic and relativistic (in parentheses) calculations], V or Ti}

	Fragment charge			Metal d-electron
Compound	η^7-C_7H_7	η^5-C_5H_5	Metal	configuration
[Nb(η^7-C_7H_7)(η^5-C_5H_5)]	−1.14	−0.78	+1.92	3.57
[Ta(η^7-C_7H_7)(η^5-C_5H_5)]	−0.81	−0.57	+1.38	3.75
	(−1.01)	(−0.69)	(+1.70)	(3.66)
[V(η^7-C_7H_7)(η^5-C_5H_5)]	−0.69	−0.36	+1.05	3.86
[Ti(η^7-C_7H_7)(η^5-C_5H_5)]	−1.11	−0.51	+1.62	2.61

each of a′ and a″ symmetry. However, Tables 1–4 clearly indicate that each orbital of an a′/a″ pair has essentially the same energy and composition as its partner, supporting the validity of a $C_{\infty v}$ treatment of these molecules.

Turning first to [Nb(η^7-C_7H_7)(η^5-C_5H_5)], the computational results reinforce the generally accepted features of the valence electronic structure of molecules of this type. The principal interactions between metal and ligands involve the metal d orbitals and the e_1 and e_2 symmetry p_π orbitals of the carbocyclic rings [those orbitals formed from the carbon 2p atomic orbitals (AOs) which lie perpendicular to the plane of the rings]. The 1a′ and 1a″ (1e_1) orbitals are largely localised on the cycloheptatrienyl ring, while the 2a′ and 2a″ (2e_1) levels are made up predominantly of the e_1 orbitals of the five-membered ring. This reflects the trend toward increased stability of the e symmetry p_π MOs of carbocyclic rings with increasing ring size.[3] The slightly greater Nb d contribution to the 1a′ and 1a″ orbitals over the 2a′ and 2a″ is entirely consistent with the PE spectroscopic data,[2] as is the conclusion that the 4a′ (1a_1) HOMO is essentially Nb 4d-localised.

For the crucial 3a′ and 3a″ (1e_2) MOs the theoretical results support the experimental data in finding significant contributions from both metal d and cycloheptatrienyl e_2 fragments. Experiment and theory differ, however, in their assessment of the major contributor to these orbitals, with experiment indicating 63% Nb 4d *versus* only 43% from the calculation. It is difficult to gauge the significance of this difference, as both the theoretical and experimental methods for deriving the MO compositions have some uncertainty associated with them. Population-analysis methods are at their most useful when comparing trends between different molecules with similar basis sets, and the absolute values of percentage compositions are sometimes less reliable.[19] Furthermore, the experimental conclusions are based on the assumption of pure metal 4d in the 4a′ (1a_1) HOMO and pure C 2p in the 2a′ and 2a″ (2e_1) levels, which neither the experimental nor the theoretical data entirely support. It is clear, however, that there is a significant degree of covalency in the 3a′ and 3a″ (1e_2) MOs, reinforcing the experimental conclusions regarding the formal description of the oxidation state of the cycloheptatrienyl ring in these complexes.

It is notable how well the ionisation energies of [Nb(η^7-C_7H_7)(η^5-C_5H_5)] (and those of all the other compounds studied) are reproduced at this level of theory. The *greatest* discrepancy is 0.28 eV for the 4a′ HOMO, which is impressively accurate for a 25-atom transition-metal organometallic and provides further support for the assignments of the PE spectra.

Table 2 presents the results of both non-relativistic and relativistic calculations on [Ta(η^7-C_7H_7)(η^5-C_5H_5)]. In the latter, scalar relativistic effects have been included by use of relativistic frozen-core potentials for Ta and (much less importantly) C. These corrections account for the relativistic modification of AO energies[20] but stop short of a fully relativistic treatment involving spin–orbit coupling and molecular double point groups.[21] It may be seen that the effects of the relativistic corrections on [Ta(η^7-C_7H_7)(η^5-C_5H_5)] are not great. There are slight destabilisations of the MO eigenvalues and concomitant reduction in the associated ionisation energies with respect to the non-relativistic calculations, caused by the relativistic destabilisation of the Ta 5d AOs as a result of increased screening of the nucleus by the inner core s and p electrons. The MO compositions are also largely unaltered in the relativistic calculations, with the 3a′ and 3a″ levels once again being a mixture of cycloheptatrienyl e_2 (53%) and Ta d (39%).

The PE spectroscopic data indicate that there is a *ca.* 10% greater Ta 5d contribution to the 1e_2 MOs of [Ta(η^7-C_7H_7)(η^5-C_5H_4Me)] than is the case for the equivalent orbitals of [Nb(η^7-C_7H_7)(η^5-C_5H_5)].[2] Table 2 does not support this conclusion, and suggests that the electronic structure of the valence orbitals of [Ta(η^7-C_7H_7)(η^5-C_5H_5)]* is very similar to that of its second-row congenor.

Although no RPPICS data are available for [V(η^7-C_7H_7)(η^5-C_5H_5)], density-functional calculations were carried out on this molecule to allow comparison with the heavier

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* It is very unlikely that replacement of η^5-C_5H_5 by η^5-C_5H_4Me will significantly modify the valence electronic structure of [Ta(η^7-C_7H_7)(η^5-C_5H_4R)], and hence comparison of experimental data for [Ta(η^7-C_7H_7)(η^5-C_5H_4Me)] with theoretical data for [Ta(η^7-C_7H_7)(η^5-C_5H_5)] is valid.

Group 5 analogues. The computational data (Table 3) are quite similar to those of the niobium and tantalum compounds discussed above, particularly the composition of the 3a′ and 3a″ MOs (44% V d and 51% cycloheptatrienyl e_2). The relative metal d content of the 1a′ and 1a″ ($1e_1$) and 2a′ and 2a″ ($2e_1$) MOs is reversed in $[V(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, although none of these orbitals has a large metal contribution. The composition of the LUMOs is also a little different in the first-row molecule, with greater metal content and reduced cyclopentadienyl ring character. The ionisation energies are once again reproduced very well by the calculations.

One of the main aims of this study is to assess the degree of Ti 3d AO character in the $1e_2$ HOMO of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$. Table 4 indicates that the composition of the 3a′ and 3a″ ($1e_2$) orbitals is little different to that of the equivalent orbitals in the Group 5 mixed-ring compounds, with a slightly increased cycloheptatrienyl e_2 contribution and a correspondingly smaller metal d involvement. In general, the valence levels of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ display decreased metal–ligand mixing, particularly in comparison with the heavier Group 5 molecules. This is best illustrated by the composition of the 4a″ and 5a′ unoccupied orbitals, which are much more metal d-localised than in the other systems studied. The reduced metal–ring mixing may well be a reflection of the relative energies of the d orbitals of Ti *versus* those of V, Nb and Ta. As the transition-metal rows are crossed from left to right the d orbitals become increasingly stabilised, bringing them into closer energetic proximity with the ligand p_π orbitals. This results in greater mixing of metal and ligand valence orbitals.

The present data suggest that the metal d contribution to the $1e_2$ HOMO of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ is no greater than in the corresponding orbital in the Group 5 molecules. If this is indeed true it provides another illustration of the invalidity of comparing the magnitudes of $p \longrightarrow d$ giant resonant cross-section enhancements between compounds containing different metals. Although the RPPICS increase of the first band in the PE spectrum of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ in the region of the metal 3p subshell binding energies is larger than that of the equivalent bands in the spectra of $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, $[Mo(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ and $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)]$, the theoretical data indicate that this does not reflect greater metal character in the associated $1e_2$ MO.

Table 5 gives an indication of the location of charge within the molecules under investigation, together with their metal d-electron configurations. Formally the cyclopentadienyl ring is considered to carry a -1 charge when complexed to transition metals, and the data in Table 5 are reasonably consistent with this description {more so for $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ and $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ than for the first-row compounds}. In contrast, the *ca.* -1 charge on the cycloheptatrienyl ring is intermediate between the two possible formal descriptions ($+1$ and -3). This is reflected in the metal d-electron configurations. A $+1$ formal charge for the cycloheptatrienyl ring results in a d^5 metal centre for the Group 5 molecules and a d^4 configuration for $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$. The -3 formalism produces d^1 and d^0 electron counts respectively. The calculated d-electron configurations are intermediate between the two formal electron-counting schemes.

In all cases the calculated charges on the metals are quite large and positive, with those of the carbocyclic rings being correspondingly negative. This suggests that there is an appreciable amount of ionic bonding within the molecules. Such an assertion is supported by the MO compositions given in Tables 1–4, in that most of the orbitals are either predominantly ligand-based or metal-localised. Significant covalency is confined to the 3a′ and 3a″ ($1e_2$) metal–cycloheptatrienyl ring bonding orbitals. The conclusion, therefore, is that the metal–cyclopentadienyl ring interaction is largely ionic, with the metal–cycloheptatrienyl bonding being a mixture of ionic and covalent.

Conclusion

The results of the present study strongly support the band assignments of the valence PE spectra of $[M(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4R)]$ (M = Ti, V, Nb or Mo, R = H; M = Ta, R = Me),[1,2] and reinforce previous conclusions concerning the localisation properties of the associated MOs. While the valence π orbitals of the cyclopentadienyl ring undergo little mixing with the metal d orbitals, the interaction between the metal and the cycloheptatrienyl ring is much more covalent, as evidenced by the mixed metal–cycloheptatrienyl ring character of the 3a′ and 3a″ ($1e_2$) MOs and the distribution of charge within the molecules.

There is some discrepancy between experimental and theoretical estimates of the relative metal and ligand content of the 3a′ and 3a″ ($1e_2$) orbitals of $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ and $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4R)]$ [R = Me (experiment) or H (theory)], with experiment suggesting a 20% greater metal d contribution in the second-row compound and a *ca.* 35% greater d content for $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_4Me)]$. Although such differences are not insignificant, they do not preclude a theoretical assessment of the Ti d character of the 3a′ and 3a″ ($1e_2$) HOMOs of $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, for which experimental data are unavailable. There is found to be slightly less metal d contribution to these orbitals than in $[V(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, $[Nb(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ and $[Ta(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$, although at 39% Ti d: 58% cycloheptatrienyl e_2 there is still extensive covalency. The theoretical conclusion, therefore, is that the metal–cycloheptatrienyl ring bonding in $[Ti(\eta^7\text{-}C_7H_7)(\eta^5\text{-}C_5H_5)]$ is not significantly different from that in the Group 5 analogues.

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