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Charges Distribution and Chemical Bonding in Mixed-Ring Sandwich Compounds: *Ab Initio* Calculations on Some Neutral and Charged Cyclopentadienylcycloheptatrienyl Metal Compounds

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Small basis set SCF-LCAO-MO calculations are described for the molecules (C_5H_5)M(C_7H_7) with M = Ti, V and Cr. Basis set effects have been investigated by means of calculations with different basis sets on the free atoms, the free rings and the moieties (C_5H_5)Ti and (C_5H_5)Cr. These calculations indicate that the near minimum basis set results provide a reasonable basis for a discussion of the trends in the charge distributions of the mixed sandwich compounds. Within the framework of Mulliken's population analysis it is shown that the negative charge on the C_7H_7 ring decreases in the order Ti, V, Cr, while the negative charge on the C_5H_5 ring increases in this order. Details of the bonding are discussed. The observed trends in metal 2p and 3s, and carbon 1s ionization energies are quite well reproduced by the corresponding ground state orbital energies. Independent SCF calculations on a number of electronic configurations of the positive ions show large reorganizations of the charge distributions in all cases. The corresponding relaxation energies depend strongly on the amount of metal character of the ionized ground state orbitals. The trends in the calculated ionization energies agree only partly with those derived from the measured photoelectron spectra.

Introduction

The mixed sandwich complexes (C_5H_5)M(C_7H_7) with M = Ti, V, and Cr have been the subject of several chemical and physical investigations. Structural information, summarized in Table I, is reported in ref. 1–3. The molecular point group is C_s. The results of metallation reactions [4], of photoelectron spectroscopy (UPS and XPS) [5–7], and of ^{13}C and ^{1}H nuclear magnetic resonance studies [5, 8] all show characteristic trends as a function of the metal. These trends have been rationalized [5] on the basis of qualitative molecular orbital (m.o.) considerations, the essence of which concerns the relative position of the valence state ionization potentials of the metal 3d orbitals with respect to that of the e_2 π-m.o.'s of the seven membered ring. The e_1 π-m.o.'s of both rings are thought to combine with the 3dπ and 4pπ metal orbitals to form two bonding m.o.'s of mainly ligand character. The e_2 m.o. of C_7H_7 forms a bonding orbital with the metal 3dδ orbitals which, presumably, has mainly ligand character in the titanium compound and mainly metal character in the chromium compound. As a consequence the C_7H_7 ring would carry an appreciable negative charge in the titanium complex which decreases rapidly in the sequence Ti, V, Cr. Furthermore it is assumed that in the titanium compound the C_5H_5 ring carries less negative charge than C_7H_7. This charge might also decrease in the sequence given but much less pronounced so that in the chromium complex C_5H_5 is more negatively charged than C_7H_7. Quantitative estimates of the charge on the metals are obtained from ESCA data pertaining to the ionisation of 2p and 3s core electrons [7]. To this end a linear relationship is assumed between the metal charge and

TABLE I. Interatomic Distances in Å in the Mixed Sandwich Complexes (C_5H_5)M(C_7H_7), M = Ti, V, Cr.

	(C_5H_5)Ti(C_7H_7)	(C_5H_5)V(C_7H_7)	(C_5H_5)Cr(C_7H_7)
C–C(C_5H_5)	1.396	1.42	1.395
C–C(C_7H_7)	1.397	1.40	1.409
M–C(C_5H_5)	2.32	2.23	2.18
M–C(C_7H_7)	2.19	2.25	2.16

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the core level binding energies measured in a series of compounds containing the same metal. The charge scale is determined by putting the charges in the pure metals and the metal oxides equal to the formal oxidation states in these compounds. Additional assumptions lead to charges on the C_7H_7 ring which are consistent with the trends sketched above and with earlier extended Hückel calculations on $(C_5H_5)V(C_7H_7)$ [9].

Motivation and Scope of the Present Work

In spite of its quantitative flavor the description summarized above of the charge distribution and its relation to various experimental findings is mainly of a qualitative nature. Thus, while the trend inferred for the charge on the C_7H_7 ring as a function of the metal is entirely reasonable, the conclusions concerning the magnitude of this charge, its relation to that of the C_5H_5 ring and the trend in the charges on this latter ring are much more speculative. A fundamental difficulty here is of course that the concept of charge on a metal or on a ring does not refer to an observable quantity. Any definition must be based on some theoretical representation of the molecular charge distribution. A very simple representation is that of ions carrying effective charges to be determined by fitting certain experimental data. There is no a priori assurance, however, that a set of effective charges obtained from one type of experiment such as ESCA will coincide with the set inferred from other types of data such as NMR or chemical reactivities. In principle the same can be said for trends in effective charges "observed" in a series of molecules. Alternatively a well defined quantum chemical representation can be obtained by applying Mulliken's population analysis [10] to electronic wavefunctions built from m.o.'s of the linear combination of atomic orbitals (l.c.a.o.) type. Such wavefunctions can be calculated by some semi-empirical method or *ab initio*. In either way there is no a priori reason for a simple relationship to exist between the calculated charges on the one hand and measured or calculated molecular properties on the other.

A purely theoretical assessment of properties like charge distributions and ionization energies and their trends in the molecules at hand would therefore be of interest. Moreover such an approach would provide insight in matters like the role of the ring σ-m.o.'s and the relative importance of the π and δ bonds between the metal and the respective rings.

In the following we report and discuss the results of *ab initio* self-consistent field (s.c.f.) m.o. calculations on the ground states and a number of positive ion states of the molecules $(C_5H_5)M(C_7H_7)$, M = Ti, V, Cr with the nuclei fixed in their experimentally determined positions. Because of the large size of the molecules and their low symmetry we were forced to expand the m.o.'s in terms of a near minimal basis set of a.o.'s in order to make the calculations feasible. The question then arises whether the results can still be trusted to exhibit realistic trends and not artifacts caused by basis set deficiencies. We will therefore also report results of exploratory calculations on smaller systems with basis sets of varying size which were undertaken first. We shall see that particularly the results for the moieties $Ti(C_5H_5)$ and $Cr(C_5H_5)$ make it likely that the main features of the charge distributions in the mixed sandwich complexes are correctly represented by our results provided of course that the s.c.f. m.o. approximation itself is accurate enough for our purpose.

Investigation of Basis Set Effects

Free Atoms and Free Rings

The selection of an appropriate set of basis orbitals has been a major concern in the present work. Really good basis sets for transition metal complexes become necessarily very large and therefore impractical. This holds for Slater type orbitals as well as for the basis orbitals of the Gaussian type G.T.O.'s) which are used in this work.

The use of contracted basis functions significantly reduces the integral storage and processing problems but it does not affect the time necessary to calculate the integrals. It is therefore often imperative to represent the contracted functions by the smallest possible sets of primitive functions, for instance in the case of core electrons whose distribution should be fairly insensitive to the formation of chemical bonds.

Fairly large uncontracted or primitive basis sets of G.T.O.'s for the first row transition metals have been reported by Wachters [11]. These sets consist of 14 s-type, 9 p-type and 5 d-type functions for which we shall henceforth use the abbreviated notation (14, 9, 5). Basis sets of medium size (12, 6, 4) are given by Roos *et al.* [12]. For our calculations we adopted a (9, 5, 4) set with orbital exponents optimized by minimizing the ground state s.c.f. energies of the $3d^n4s^2$ neutral atom configurations. These basis sets were constructed from those of Roos *et al.* by a procedure which guarantees an optimal description of the valence orbitals. In the (12, 6, 4) sets we first deleted the three innermost s functions and reoptimized the exponents of the next three inner shell s functions. Then the innermost p function was discarded and the remaining 2p exponents were reoptimized. A final reoptimalisation round of all core exponents turned out to be of no significance. The resulting sets were then contracted to "double zeta" sets [8, 4, 2] and to mixed [4, 2, 2] sets *i.e.* "single zeta" for s and p, "double zeta" for 3d.

TABLE II. Total Energies and Orbital Energies for Ti, V and Cr for Different Basis Sets and Different Contractions.

	Basis Set		Ref.	Energy (in A.U.)	Orbital Energies (in A.U.)						
					1s	2s	3s	4s	2p	3p	3d
Ti(^{3}F)											
	14s, 9p, 5d	(a)	[11]	−848.389	−183.261	−21.4105	−2.86328	−.21822	−17.7792	−1.78613	−.43611
	12s, 6p, 4d	(a)	[12]	−848.200	−183.254	−21.4099	−2.86213	−.21732	−17.7640	−1.77866	−.42391
		(b)		−848.114	−183.232	−21.3908	−2.85641	−.21704	−17.7769	−1.77740	−.42491
		(c)		−846.597	−182.447	−20.7263	−2.71674	−.20586	−17.5176	−1.76061	−.41819
	9s, 5p, 4d	(a)		−845.262	−182.470	−21.3765	−2.85348	−.21684	−17.7351	−1.76911	−.42861
		(b)		−845.243	−182.476	−21.3757	−2.85305	−.21679	−17.7400	−1.76813	−.42883
		(c)		−842.925	−181.206	−20.8275	−2.73971	−.20606	−17.5549	−1.74568	−.41518
V(^{4}F)											
	14s, 9p, 5d	(a)	[11]	−942.862	−201.489	−23.8600	−3.17094	−.22756	−20.0083	−2.00831	−.50160
	12s, 6p, 4d	(a)	[12]	−942.646	−201.483	−23.8597	−3.16870	−.22640	−19.9923	−1.99914	−.48847
		(b)		−942.552	−201.461	−23.8394	−3.16218	−.22610	−20.0059	−1.99727	−.48948
		(c)		−940.847	−200.651	−23.1050	−2.99609	−.21068	−19.7384	−1.97263	−.47565
	9s, 5p, 4d	(a)		−939.428	−200.625	−23.8144	−3.15709	−.22582	−19.9555	−1.98704	−.49342
		(b)		−939.408	−200.630	−23.8139	−3.15660	−.22577	−19.9608	−1.98574	−.49366
		(c)		−936.737	−199.238	−23.2307	−3.03404	−.21447	−19.7852	−1.96411	−.48154
Cr(^{5}D)											
	14s, 9p, 5d	(a)	[11]	−1043.282	−220.576	−26.4225	−3.48486	−.23632	−22.3490	−2.23605	−.55859
	12s, 6p, 4d	(a)	[12]	−1043.037	−220.548	−26.4073	−3.47597	−.23439	−22.3171	−2.21963	−.54001
		(b)		−1042.937	−220.542	−26.3973	−3.47373	−.23446	−22.3433	−2.22226	−.54456
		(c)		−1041.045	−219.669	−25.5904	−3.29261	−.21870	−22.0491	−2.19760	−.53058
	9s, 5p, 4d	(a)		−1039.572	−219.618	−26.3638	−3.46720	−.23415	−22.2866	−2.21084	−.54831
		(b)		−1039.549	−219.625	−26.3624	−3.46650	−.23409	−22.2921	−2.20939	−.54852
		(c)		−1036.687	−218.152	−25.7119	−3.33064	−.22223	−22.0923	−2.18729	−.53615

[a] Uncontracted basis sets. [b] [8,4,2] contraction. [c] [4,2,2] contraction.

TABLE III. Total Energies and Orbital Energies for C and H for Different Basis Sets and Different Contractions.

	Basis Set		Energy (A.U.)	Orbital Energies (A.U.)		
				1s	2s	2p
$C(^3P)$						
	10s, 6p	(a)	−37.6873	−11.3252	−.70552	−.43305
		(b)	−37.6847	−11.3285	−.70437	−.43381
	8s, 4p	(a)	−37.6774	−11.3147	−.69976	−.42668
	6s, 3p	(a)	−37.6230	−11.3041	−.70098	−.42088
		(c)	−37.6217	−11.3065	−.70031	−.42102
		(d)	−37.5674	−11.2269	−.67538	−.41276
	5s, 3p	(a)	−37.4441	−11.2397	−.69707	−.42251
		(c)	−37.4432	−11.2414	−.69659	−.42263
		(d)	−37.3934	−11.1700	−.67115	−.41466
$H(^2S)$						
	5s	(e)	−.49981	−.49981		
	3s	(e)	−.49698	−.49698		

[a] Uncontracted basis set. [b–d] Contracted basis sets: [5,3] (b), [4,2] (c) and [2,1] (d). [e] Contraction of 1s basis functions does not change the energy.

These last sets were the largest ones we could afford in the molecular calculations. A comparison of the total energies and orbital energies obtained with the various basis sets is given in Table II. We see that the 4s orbital energies are only affected by the contraction from double zeta to single zeta. The 3d orbital energies are affected by the truncation of the primitive sets as well. The resulting energy shifts are, however, systematic and small (0.3–0.4 *eV*).

In molecular orbital calculations it is important to use balanced basis sets for the various atoms present. We have therefore determined (5,3) and (3) primitive sets for C and H respectively. These sets were then contracted to double zeta forms {4,2} and {2} and to single zeta forms {2,1} and {1}. Table III presents the atomic total energies and orbital energies calculated with these and other basis sets. Total energies and valence orbital energies calculated for the free, neutral and charged ring systems C_5H_5 and C_7H_7 with different primitive and contracted sets are reported in Table IV. It can be inferred from this table that the valence energy levels are only significantly influenced by increasing the contraction from {4,2/2} to {2,1/1}. The shifts are again fairly systematic but of opposite sign and of larger magnitude (1.3–2.6 *eV*) when compared with those of the metals. Significant changes also occur, not unexpectedly, in the population analysis results. This is illustrated by the gross orbital populations calculated for the neutral rings (Table V).

The Moieties $Ti(C_5H_5)$ *and* $Cr(C_5H_5)$

Calculations on the mixed sandwich molecules were feasible only by restricting ourselves to the smallest primitive sets (9,5,4/5,3/3) and the highest contracted sets {4,2,2/2,1/1} discussed above (Table VI). As we have seen the orbital energies of respectively the free metals and free rings respond rather differently to an increase in contraction. Also a significant redistribution of the population in the ring σ-orbitals was observed. The question then arises whether meaningful results can still be expected from calculations with such basis sets on the molecules. In order to investigate this matter a series of pilot calculations was carried out on the systems $Ti(C_5H_5)$ and $Cr(C_5H_5)$ using double zeta and nearly single zeta sets, *i.e.* the (9,5,4/5,3/3) set contracted to respectively {8,4,2/4,2/2} and {4,2,2/2,1/1}. The electronic states selected were the ^2E states arising from the configurations $4e_2)^3 10a_1)^0$ for $Ti(C_5H_5)$ and $4e_2)^3 10a_1)^2$ for $Cr(C_5H_5)$. These configurations correlate with the separated ion situations $Ti^+[3d\delta)^3]$ $(C_5H_5)^-$ and $Cr^+[3d\delta)^3 3d\sigma)^2](C_5H_5)^-$. The resulting total energies, valence m.o. energies, gross populations and gross charges are listed in Tables VIIa and VIIb. The changes in these quantities occurring when the contraction is increased are given in the columns labelled Δ_{Ti} and Δ_{Cr}. We note that the entries in these columns for corresponding orbitals in the two compounds are very similar so that the trends in the various quantities on going from Ti to Cr are hardly

TABLE IV. Total Energies (in A.U.) and Valence Molecular Orbital Energies (in eV) for the Neutral and Charged Rings C_5H_5 and C_7H_7 for Different Basis Sets and Different Contractions.

Symmetry	Basis Set	I	IIa	IIb	IIIa	IIIb	I	II-a	II-b	III-a	III-b
			(C_5H_5)					$(C_5H_5)^-$			
$4e_1$		−8.35	−8.25	−10.76	−8.28	−10.78	−1.87	−1.41	−3.48	−1.43	−3.50
$4a_1$		−13.56	−13.55	−15.93	−13.57	−15.95	−7.73	−7.39	−9.41	−7.40	−9.43
$3e_2$		−14.55	−14.36	−16.22	−14.38	−16.25	−8.15	−7.57	−9.17	−7.60	−9.19
$3e_1$		−15.18	−15.07	−16.93	−15.10	−16.95	−8.84	−8.34	−9.87	−8.35	−9.88
$3a_1$		−19.60	−19.46	−20.94	−19.47	−20.95	−13.31	−12.78	−13.97	−12.79	−13.98
$2e_2$		−20.26	−20.17	−21.52	−20.13	−21.47	−13.98	−13.53	−14.57	−13.49	−14.53
$2e_1$		−26.28	−26.33	−27.92	−26.24	−27.80	−19.82	−19.44	−20.62	−19.35	−20.50
$2a_1$		−32.30	−32.46	−34.35	−32.36	−34.23	−25.57	−25.21	−26.60	−25.11	−26.48
	Energy	−192.126	−191.767	−191.241	−190.884	−190.375	−192.165	−191.791	−191.346	−190.910	−190.481
			(C_7H_7)					$(C_7H_7)^+$			
$4e_2$			−5.12	−7.49	−5.13	−7.51		−4.11	−6.45	−4.13	−6.47
$4e_1$			−10.14	−12.55	−10.16	−12.57		−15.63	−18.26	−15.65	−18.28
$3e_2$			−13.28	−15.15	−13.30	−15.17		−19.16	−21.23	−19.19	−21.26
$4a_1$			−13.44	−15.73	−13.45	−15.74		−19.13	−21.62	−19.14	−21.64
$3e_3$			−14.82	−16.59	−14.84	−16.59		−20.69	−22.59	−20.70	−22.60
$3e_1$			−16.76	−18.36	−16.77	−18.38		−22.69	−24.50	−22.71	−24.53
$3a_1$			−19.26	−20.61	−19.27	−20.63		−25.19	−26.75	−25.20	−26.77
$2e_3$			−19.57	−21.20	−19.55	−21.18		−25.53	−27.42	−25.51	−27.40
$2e_2$			−24.36	−25.88	−24.29	−25.79		−30.35	−32.12	−30.28	−31.90
$2e_1$			−28.68	−30.27	−28.58	−30.14		−34.79	−36.67	−34.69	−36.54
$2a_1$			−31.10	−32.62	−30.99	−32.49		−37.29	−39.08	−37.18	−38.96
	Energy		−268.518	−267.773	−267.282	−266.561		−268.349	−267.517	−267.113	−266.305

I Contraction scheme (10,5/5) → [5,3/3]
II Contraction scheme (6,3/3) → a)[4,2/2] and b) [2,1/1]
III Contraction scheme (5,3/3) → a)[4,2/2] and b) [2,1/1]

TABLE V. Gross Orbital Populations for the Neutral Rings for Different Basis Sets and Contractions.

Basis Set	I	II-a	II-b	III-a	III-b	II-a	II-b	III-a	III-b
		(C_5H_5)					(C_7H_7)		
C 2s	1.107	1.246	1.086	1.233	1.076	1.195	1.075	1.182	1.065
$2p_\sigma$	2.068	2.025	2.136	2.030	2.140	2.060	2.147	2.065	2.151
$2p_\pi$	1.	1.	1.	1.	1.	1.	1.	1.	1.
Charge (e)	−.239	−.229	−.206	−.228	−.204	−.213	−.205	−.212	−.203
H 1s	.761	.771	.794	.772	.796	.787	.795	.788	.797
Charge (e)	.239	+.229	+.206	+.228	+.204	+.213	+.205	+.212	+.203

I Contraction scheme (10,5/5) → [5,3/3]
II Contraction scheme (6,3/3) → a)[4,2/2] and b)[2,1/1]
III Contraction scheme (5,3/3) → a)[4,2/2] and b)[2,1/1]

TABLE VI. Orbital Exponents (α) and Contraction Coefficients (c.c) for the Ti, V, Cr, C and H Basis Sets Used in This Work.

	Ti(^{3}F)		V(^{4}F)		Cr(^{5}D)			C(^{3}P)	
	α	c.c	α	c.c	α	c.c		α	c.c
s	2693.07	.05350	2993.14	.05258	3231.	.05306	s	132.030	.08322
	406.523	.32565	450.975	.32137	488.140	.32351		19.8349	.44104
	89.8547	.66524	99.7856	.66630	108.059	.66513		4.36231	.59501
	13.2356	.30341	14.8239	.29235	16.2072	.29829		.565720	.44512
	5.47417	.76138	6.09769	.77329	6.73669	.76759		.178954	.66475
	1.38870	.53797	1.57364	.54894	1.74645	.56135			
	.583370	.69214	.650938	.68952	.717674	.68129	p	4.19582	.11227
	.080663	.58630	.088861	.56807	.094109.	.58263		.856630	.46506
	.032828	.54988	.035435	.56507	.036848	.54702		.200293	.62363
p	109.656	.10995	120.805	.11607	135.774	.10755		H(^{2}S)	
	24.8168	.48086	27.3984	.48420	30.8749	.47722			
	7.13330	.54738	7.91458	.54370	8.97595	.54843	s	4.46834	.07098
	1.87140	.52389	2.10690	.53145	2.41609	.52441		.678538	.40872
	.596298	.61469	.674850	.60776	.766685	.61728		.151055	.64642
d	13.7482	.06268	15.9635	.06374	18.3628	.06424			
	3.50857	.27554	4.14185	.27932	4.79639	.28236			
	1.04080	.51573	1.23818	.51811	1.44225	.51847			
	.287729	1.	.343496	1.	.400287	1.			

influenced. A closer analysis reveals furthermore that the changes can to a large extent be associated with the earlier noted redistribution of the σ-populations already occurring in the free ring. The overall gross charge on the ring calculated with the two contraction schemes is therefore not very different ($|\Delta| < 0.03$).

On the basis of these results it is reasonable to assume that if calculations on the double sandwich molecules were carried out with the two basis sets the contraction effects would be very similar to the ones just discussed for the simpler moieties. In particular the properties calculated with the smaller basis set may be expected to display trends as a function of the metal that are essentially independent of the contraction.

Results for (C_5H_5)M(C_7H_7)

The calculated total energies, valence m.o. energies and valence m.o. compositions of the ground states of the compounds with M = Ti, V and Cr are given in Tables VIIIa, VIIIb and VIIIc. The established ground state electron configurations can be inferred from these tables. They agree with the generally accepted m.o. structure of these compounds. The non-degenerate (3dσ) character of the singly occupied orbital in (C_5H_5)V(C_7H_7) is experimentally established [9]. The m.o. compositions are expressed in terms of the ratios of a.o. gross populations and total m.o. population. The symmetry character of the m.o.'s is indicated by means of the irreducible representation symbols of the point group C_s as well as by those of

TABLE VIIa. Total Energies (A.U) and Valence Molecular Orbital Energies (eV) for the Moieties Ti(C_5H_5) and Cr(C_5H_5) for Different Basis Set Contractions.

Symmetry	Ti(C_5H_5)		Δ_{Ti}	Cr(C_5H_5)		Δ_{Cr}
	a	b		a	b	
$4e_2$	−4.17	−4.97	.80	−7.05	−7.70	.65
$10a_1$	–	–	–	−7.64	−8.42	.78
$6e_1$	−7.57	−9.56	1.99	−7.94	−9.92	1.98
$3e_2$	−12.80	−14.28	1.48	−13.13	−14.61	1.48
$9a_1$	−13.15	−15.12	1.97	−13.57	−15.51	1.94
$5e_1$	−13.69	−15.15	1.46	−14.03	−15.49	1.46
$8a_1$	−18.08	−19.23	1.15	−18.46	−19.60	1.14
$2e_2$	−18.67	−19.67	1.00	−18.99	−19.99	1.00
$4e_1$	−24.95	−26.17	1.22	−25.34	−26.56	1.22
$7a_1$	−31.09	−32.64	1.55	−31.56	−33.13	1.57
Total energy	−1036.040	−1033.277	2.763	−1230.307	−1226.989	3.318

[a]Contraction scheme (9,5,4/5,3/3) → [8,4,2/4,2/2]. [b]Contraction scheme (9,5,4/5,3/3) → [4,2,2/2,1/1].

TABLE VIIb. Gross Atomic Orbital Populations and Gross Atomic Charges for the Moieties Ti(C_5H_5) and Cr(C_5H_5) for Different Basis Set Contractions.

Basis Set	(C_5H_5)Ti			(C_5H_5)Cr		
	a	b	Δ_{Ti}	a	b	Δ_{Cr}
C 2s	1.239	1.055	.184	1.242	1.058	.184
2pσ	1.954	2.098	−.144	1.961	2.102	−.141
2pπ	1.195	1.197	−.002	1.181	1.186	−.005
Charge	−.388	−.349	−.039	−.385	−.346	−.039
H 1s	.815	.858	−.043	.807	.851	−.044
Charge	+.185	+.142	.043	+.193	+.149	.044
M 3d(a_1)	.028	.017	.011	1.869	1.895	−.026
3d(e_1)	.204	.201	.003	.189	.178	.011
3d(e_2)	2.726	2.768	−.042	2.806	2.857	−.051
4s	.110	.022	.088	.252	.121	.131
Charge	+1.014	+1.037	−.023	+.958	+.984	−.026

[a]Contraction scheme (9,5,4/5,3/3) → [8,4,2/4,2/2]. [b]Contraction scheme (9,5,4/5,3/3) → [4,2,2/2,1/1].

the axial groups C_5 and C_7. The axial symmetry can be seen to be generally well preserved except for the higher occupied e_2 m.o.'s originating from C_7H_7 in the vanadium and chromium compounds.

The valence a.o. gross populations found for the three compounds are summarized in Table IX, the valence metal–ligand overlap populations in Table X. In Table XI the resulting gross charges on the atoms and on the rings are displayed. Other results such as those concerning core and valence ionization energies will be presented when needed in the discussion to follow.

Discussion

The Role of the 4s Orbital

Before starting our discussion of the results a remark must be made concerning the contribution of the 4s basis orbital to the molecular charge distri-

TABLE VIIa. Total Energy, Orbital Energies and Orbital Composition of the Valence Molecular Orbitals of $(C_5H_5)Ti(C_7H_7)$.

Symmetry		Energy eV	Population Analysis (per cent)									
			Ti		C_5H_5				C_7H_7			
			3d	4s	C			H	C			H
					2s	$2p_\sigma$	$2p_\pi$	1s	2s	$2p_\sigma$	$2p_\pi$	1s
33a′ 20a″	($7e_2$)	−9.19	41		1		1			3	54	
32a′ 19a″	($10e_1$)	−11.83	8			1	89				1	
31a′ 18a″	($9e_1$)	−13.09	4							2	92	
30a′ 17a″	($6e_2$)	−15.45	1							66		33
29a′ 16a″	($5e_2$)	−16.30	1		2	74		22				
28a′	($13a_1$)	−16.34	1				21				76	
27a′ 15a″	($3e_3$)	−16.42				1			7	59		32
26a′ 14a″	($8e_1$)	−17.21				69		30				
25a′	($12a_1$)	−17.59		2			75				21	
24a′ 13a″	($7e_1$)	−19.11	2							69		27
23a′ 12a″	($2e_3$)	−21.12							16	70		13
22a′	($11a_1$)	−21.13			4	28		13	2	39		14
21a′	($10a_1$)	−21.27			6	33		16	2	32		11
20a′ 11a″	($4e_2$)	−21.69			25	53		21				
19a′ 10a″	($3e_2$)	−26.20	1						43	45		11
18a′ 9a″	($6e_1$)	−28.49			64	24	1	10				
17a′ 8a″	($5e_1$)	−30.97	1						71	19		7
16a′	($9a_1$)	−33.50		−5	2	1			82	11		6
15a′	($8a_1$)	−33.51		−6	71	23	1	5	4	1		

Total energy −1300.0694 A.U.

bution. The gross population of this orbital is small and negative. This is common for a basis orbital whose m.o. coefficients are small and of opposite sign compared to those of the dominating ligand orbitals while its overlap with these orbitals is large. The gross population will then be determined by the negative overlap population. The results for the moieties $M(C_5H_5)$ suggest that this somewhat undesirable feature would be reduced when a more flexible basis set on the rings were employed. The addition of a less diffuse 4s orbital would then probably remedy the situation completely. In retrospect the use of such a less diffuse 4s function alone might have been preferable [13]. Negative gross populations can of course be avoided altoghether by using a different rule then Mulliken's for distributing overlap charges. We have not bothered to do this because first of all the populations involving 4s are very similar in all

TABLE VIIIb. Total Energy, Orbital Energies and Orbital Composition of the Valence Molecular Orbitals of $(C_5H_5)V(C_7H_7)$.

Symmetry		Energy eV	Population Analysis (per cent)									
			V		C_5H_5				C_7H_7			
			3d	4s	C			H	C			H
					2s	$2p_\sigma$	$2p_\pi$	1s	2s	$2p_\sigma$	$2p_\pi$	1s
34a′	(14a$_1$)	−15.27	97									
20a″ 33a′	(7e$_2$)	−8.68 −10.47	25 64				1 2			2 4	71 29	
32a′ 19a″	(10e$_1$)	−11.56	8			1	90					
31a′ 18a″	(9e$_1$)	−13.99	3							1	94	
17a″ 30a′	(6e$_2$)	−15.43 −15.72	1 2			2				65 64		33 31
16a″ 29a′	(5e$_2$)	−16.04 −16.05			2 2	77 75		21 21		1		
28a′	(13a$_1$)	−16.17	1				45				53	
27a′ 15a″	(3e$_3$)	−16.57 −16.58							7 7	60 60		32 32
26a′ 14a″	(8e$_1$)	−16.97				69		30				
25a′	(12a$_1$)	−17.37		2			52				44	
24a′ 13a″	(7e$_1$)	−19.18	2							70		27
23a′	(11a$_1$)	−20.87			8	56		26		7		2
22a′ 12a″	(2e$_3$)	−21.20 −21.26				3		2	12 16	67 69		15 13
11a″ 21a′	(4e$_2$)	−21.43 −21.45			26 20	50 38		22 17	2	17		6
20a′	(10a$_1$)	−21.46			7	15		7	5	50		16
10a″ 19a′	(3e$_2$)	−26.26 −26.31							42 43	46 44		11 11
18a′ 9a″	(6e$_1$)	−28.08			64	23	1	10				
17a′ 8a″	(5e$_1$)	−31.05	1						71	19		7
16a′	(9a$_1$)	−33.58		−3	6	2			77	10		6
15a′	(8a$_1$)	−34.69		−7	68	20	1	5	9	2		2

Total energy −1393.8426 A.U.

three compounds. Secondly such a procedure tends to attaching a more literary significance to orbital populations than is warranted.

The Metal–Ring Bonds

We shall consider the overlap populations listed in Table X as the characteristic quantities in terms of which the covalent character of the metal to ring bonds can be discussed. The populations involving 4s will be disregarded for the reasons discussed above. Of the remaining populations those involving the $3d\pi$–$2p\pi$ and $3d\delta$–$2p\pi$ distributions are by far the most prominent ones. They show two salient features. First, the M–(C_5H_5) and M–(C_7H_7) bonds differ characteristically. The first one is almost exclusively a π-type bond, the second is dominantly a δ-type bond although its π-character is not negligible. The second feature is that the π-bonds to

TABLE VIIIc. Total Energy, Orbital Energies and Orbital Composition of the Valence Molecular Orbitals of $(C_5H_5)Cr(C_7H_7)$.

Symmetry	Energy eV	Population Analysis (per cent)									
		Cr		C_5H_5				C_7H_7			
		3d	4s	C			H	C			H
				$2p\pi$	$2p_\sigma$	$2p\pi$	1s	2s	$2p_\sigma$	$2p_\pi$	1s
20a″ $(7e_{2b})$	−8.71	19				1	1				
34a′ 19a″ $(10e_1)$	−11.52	8			1	90					
33a′ $(7e_{2a})$	−12.13	73			1	2			7	15	1
32a′ $(14a_1)$	−13.35	76			1	7	1	1	1	11	1
31a′ 18a′ $(9e_1)$	−14.01	2				1			1	95	
17a″ $(6e_{2b})$	−15.54	2							65		33
30a′ $(5e_2)$	−15.92			2	62		18		12		6
16a″	−15.95			2	74		23				
29a′ $(5e_{2a})$	−16.10	6			13		5		50		25
28a′ $(13a_1)$	−16.58	16			2	36			1	43	1
27a′ $(3e_3)$	−16.75				1			7	59		31
15a″	−16.77				2		1	7	59		30
14a″ $(8e_1)$	−16.87				66		30		2		
26a′	−16.88				67		30		1		
25a′ $(12a_1)$	−17.55		2			53				43	
24a′ $(7e_1)$	−19.30	1							71		27
13a″	−19.31	1							71		26
3a′ $(11a_1)$	−20.91	1		8	49		23	1	13		4
22a′ $(10a_1)$	−21.32	1		2	8		4	12	60		13
12a″ $(4e_2)$	−21.33			24	51		20	1	3		1
21a′	−21.37	1		24	49		20	1	4		1
11a″ $(2e_3)$	−21.40			1	2		1	16	66		13
20a′	−21.70	3		1	4		2	6	63		20
10a″ $(3e_2)$	−26.36	1						42	46		11
19a′	−26.44	1						44	43		11
9a″ $(6e_1)$ 18a′	−28.16	1		64	24	1	10				
17a′ 8a″ $(5e_1)$	−31.10	1						72	19		7
16a′ $(9a_1)$	−33.66		−4	4	1			81	10		6
15a′ $(8a_1)$	−35.08		−8	70	22	1	5	6	1		1

Total energy −1493.6840 A.U.

both rings weakly decrease in the sequence Ti–Cr, while the δ-bond to the seven membered ring decreases strongly in this sequence. These features corraborate the qualitative picture of the bonding mentioned in the introduction except for the decrease of the π-bonds in going from Ti to Cr. In addition the results suggest the C_7H_7 ring to be bound much stronger than C_5H_5 particularly in the titanium compound. In the latter compound this would even be true per metal–carbon bond, while in the chromium complex the metal–carbon bonds to both rings would be about equally strong. Experimentally the abnormally short Ti–(C_7H_7) distance has been considered as evidence for a very strong bond [1, 5]. Another characteristic difference in the series is shown by the overlap populations

TABLE IX. Orbital Gross Populations in $(C_5H_5)M(C_7H_7)$.

		$(C_5H_5)Ti(C_7H_7)$		$(C_5H_5)V(C_7H_7)$		$(C_5H_5)Cr(C_7H_7)$	
		C_5H_5	C_7H_7	C_5H_5	C_7H_7	C_5H_5	C_7H_7
C	2s	1.095	1.076	1.105	1.079	1.092	1.087
	$2p_\sigma$	2.132	2.150	2.114	2.153	2.125	2.151
	$2p_\pi$	1.121	1.139	1.133	1.121	1.141	1.106
H	1s	.805	.798	.812	.797	.815	.793
M	$3d(a_1)$	.052		1.003		1.966	
	$3d(e_1)$	.643		.565		.500	
	$3d(e_{2a})$	.860		1.354		1.636	
	$3d(e_{2b})$	.860		.535		.414	
	4s	−.145		−.138		−.154	

TABLE X. Metal–Ligand Overlap Populations in $(C_5H_5)M(C_7H_7)$.

M		C_5H_5			C_7H_7		
		2s	$2p_\sigma$	$2p_\pi$	2s	$2p_\sigma$	$2p_\pi$
Ti	4s	−.188	−.007	.047	−.292	−.030	.044
	$3d(a_1)$	−.009	.002	.031	−.002	.022	.015
	$3d(e_1)$	−.008	−.014	.362		.044	.186
	$3d(e_{2a})$	.001	−.008	.021	.015	−.042	.319
	$3d(e_{2b})$	.001	−.008	.021	.015	−.042	.319
V	4s	−.192	−.006	.059	−.292	−.034	.031
	$3d(a_1)$	−.014	−.018	.008	−.005	−.002	−.005
	$3d(e_1)$	.006	−.003	.315	.004	.036	.148
	$3d(e_{2a})$	.003	−.010	.031	.012	−.044	.233
	$3d(e_{2b})$	.001	−.003	.016	.014	−.014	.245
Cr	4s	−.204	−.008	.053	−.308	−.046	.007
	$3d(a_1)$	−.017	−.033	−.001	−.005	−.003	−.019
	$3d(e_1)$	.012	.002	.275	.009	.040	.114
	$3d(e_{2a})$	.003	−.010	.028	.009	−.040	.155
	$3d(e_{2b})$	.001	−.001	.013	.013	−.004	.198

TABLE XI. Gross Charges on Metal and Rings.

	$(C_5H_5)Ti(C_7H_7)$			$(C_5H_5)V(C_7H_7)$			$(C_5H_5)Cr(C_7H_7)$		
	C_nH_n	C	H	C_nH_n	C	H	C_nH_n	C	H
C_5H_5	− .702	−.335	+.195	−.752	−.339	+.188	−.803	−.345	+.185
C_7H_7	−1.054	−.352	+.202	−.957	−.340	+.203	−.865	−.330	+.207
M		+1.756			+1.709			+1.668	

associated with the metal 3dσ orbital. The change in bonding character from weakly bonding to weakly antibonding is a consequence of the fact that this orbital becomes occupied in the vanadium and chromium compounds.

An indication of decreasing bond strength in the series can also be found in the theoretical binding energies of the compounds with respect to the free radicals and the free metals. From the listed total energies one finds respectively 5.7 eV, 4.6 eV and

TABLE XII. Core Ionization Energies (eV) in $(C_5H_5)M(C_7H_7)$.

M	I^a_{2p}		I_{3s}	
	Exp^b	$-\epsilon^c + 27.1$	Exp^b	$-\epsilon^c + 18.2$
Ti	457.6	457.3	60.3	60.8
V	515.9	516.2	67.5	67.6
Cr	577.8	577.7	75.5	74.7

$^a1/3\ I_{2p1/2} + 2/3\ I_{2p3/2}$. ^{b}Ref. [7]. ^{c}Orbital Energies.

1.6 eV in the sequence Ti, V and Cr. Not too much significance should be attached to these numbers as such but the trend they show is consistent with that observed in the overlap populations. Experimentally it is only known that the thermal stability of the chromium compound is distinctly less than that of the titanium compound.

Gross Charges and Bonding Model

The calculated charges listed in Table XI show an appreciable negative charge on C_7H_7 which decreases in going from Ti to Cr. The charge on the metal also decreases in this order. These trends are in accord with the conclusions reached by Groenenboom *et al.* [5] referred to in the introduction to this paper. Differences exist, however, with regard to the charge on C_5H_5. Although this charge is indeed significantly less than that on C_7H_7 in the titanium compound, an increase rather than a decrease occurs in the series Ti, V, Cr. Furthermore, although our results exhibit a clear tendency towards equalization of the charges on both rings in this series, there is no indication that this actually happens in the vanadium compound. We note, however, that such a pivotal position may be assigned to the latter compound on the basis of the charge per C atom calculated for both rings. As mentioned earlier effective charges on the metals have been determined by linear interpolation of ESCA data on the 2p and 3s core ionisation in various compounds. The charges on Ti, V and Cr were found to be 1.1, 0.8 and 0.4 respectively. The calculated gross charges of 1.76, 1.71 and 1.67 not only are appreciably larger but they show much smaller differences as well. They also show, however, a good linear correlation with the measured ionisation energies to be discussed in the next section. The magnitudes of the empirical charges are rather arbitrary since they depend on the charge one chooses to assign to the metal in two members of a series of compounds *e.g.* 0 to Ti in Ti metal and +4 to Ti in TiO_2. The discrepancies between the two sets of charges are therefore only apparent. A convenient summary of our findings concerning the trends in bonding and gross charges can be given in terms of a simplified picture of the bonding process. To this end we start with the 6π-electron systems $(C_5H_5)^-$ and $(C_7H_7)^+$ and the neutral metal in a $d\delta)^4d\sigma)^x$ valence state. We then consider the metal at the same time as a "δ-donor" and a "π-acceptor" with the provision that the acceptor property can manifest itself only as a consequence of the δ-donation. The observed trends then follow from the fact that the d electrons become increasingly tighter bound in the sequence Ti, V, Cr.

Core Ionization Energies

Metal 2p and 3s ionization

The calculated orbital energies of the m.o.'s corresponding to the 2p and 3s core orbitals of the metals are listed in Table XII together with the measured ionisation energies [7]. For comparison purposes the calculated energies have been shifted by an amount such that their average coincides with the average of the measured values. The experimental findings are quite well reproduced by this procedure which demonstrates the correct trend displayed by the theoretical results. Since we have not carried out independent hole state calculations we shall not attempt to discuss the origin of the applied energy shifts.

Carbon 1s ionization

Experimentally only one 1s carbon peak is observed for each compound [5]. The position of this peak is nearly the same in all three compounds and corresponds to an ionization energy of 284.8 eV. The peak widths are about 1.3 eV which is slightly larger than the instrumental width of about 0.9 eV. No distinction can hence be made between the carbon atoms on the two rings. Lacking the results of hole state calculations we can theoretically only consider the behavior of the calculated 1s carbon orbital energies. For the C_5H_5 ring these are 308.0 eV, 307.8 eV and 307.5 eV in the sequence Ti, V, Cr. In contrast to the C_5H_5 ring the calculated energies for the C_7H_7 ring show a spread as a consequence of the slight loss of axial symmetry, the spread calculated for the free rings being an order of magnitude smaller. The spread increases from 0.3 eV in the titanium compound to 1.3 eV and 2.2 eV in the vanadium and chromium species. The average value is the same, 308.0 eV in all compounds. This value together with those given for C_5H_5 would be consistent with the fact that only one 1s peak is observed, if we could disregard the spread in energies for C_7H_7. This implies the assumption that the spreads would be substantially reduced if localised hole state calculations were carried out for the various 1s ionisations. The results on the e_2 valence ionisation of $(C_5H_5)Cr(C_7H_7)$ to be discussed in the next section suggest that such an assumption is not unreasonable.

TABLE XIII. Calculated and Experimental Ionization Energies (in eV). The configurations are labelled on the basis of axial symmetry, a and b indicate the e_2 components that are respectively symmetric and antisymmetric with respect to the molecular symmetry plane.

$(C_5H_5)M(C_7H_7)^+$	Configuration	$-\epsilon$[a]	ΔSCF[b]	I.P.[c]
Ti	$e_1)^4\, e_{2a})^1\, e_{2b})^2$	9.2	7.9	6.8
	$e_1)^4\, e_{2a})^2\, e_{2b})^1$		8.0	
	$e_1)^3\, e_2\,)^4$	11.8	10.5	8.7
V	$e_1)^4\, e_2\,)^4$	15.3	9.4	6.4
	$e_1)^4\, e_{2a})^1\, e_{2b})^2\, a_1)^1$	10.5	(7.6)[d]	6.9
	$e_1)^4\, e_{2a})^2\, e_{2b})^1\, a_1)^1$	8.7	(7.6)[d]	
	$e_1)^3 e_2\,)^4\, a_1)^1$	11.6	(10.5)[d]	8.7
Cr	$e_1)^4\, e_2\,)^4\, a_1\,)^1$	13.4	7.9	5.6
	$e_1)^4\, e_{2a})^1\, e_{2b})^2\, a_1)^2$	12.1	7.8	7.2
	$e_1)^4\, e_{2a})^2\, e_{2b})^1\, a_1)^2$	8.7	7.8	
	$e_1)^3\, e_2\,)^4\, a_1\,)^2$	11.5	10.5	8.7

[a] Orbital energy from groundstate. [b] Relaxed ionization energies. [c] Experimental ionization (ref. [6]). [d] Estimated energies (see text).

TABLE XIV. Orbital Gross Populations for $(C_5H_5)M(C_7H_7)^+$.

Molecule	Open Shell	Charge M	Gross Populations					(C_7H_7)	(C_5H_5)
			$3da_1$	$3de_{2a}$	$3de_{2b}$	$3de_{1a}$	$3de_{1b}$	$2p_\pi$	$2p_\pi$
$(C_5H_5)Ti(C_7H_7)$	–	+1.75	.052	.860	.860	.321	.321	7.97	5.60
$(C_5H_5)Ti(C_7H_7)^+$	e_{2a}	+1.80	.059	.774	.742	.394	.394	7.22	5.42
	e_{2b}	+1.80	.060	1.165	.332	.403	.403	7.23	5.40
$(C_5H_5)V(C_7H_7)$	a_1	+1.71	1.002	1.354	.535	.282	.283	7.85	5.66
$(C_5H_5)V(C_7H_7)^+$	–	+1.72	.058	1.517	1.004	.433	.433	7.16	5.38
$(C_5H_5)Cr(C_7H_7)$	–	+1.67	1.966	1.636	.414	.250	.250	7.74	5.71
$(C_5H_5)Cr(C_7H_7)^+$	a_1	+1.59	1.015	1.396	1.396	.394	.391	6.93	5.45
	e_{2a}	+1.70	1.968	.931	.910	.328	.330	6.97	5.52
	e_{2b}	+1.70	1.969	.907	.932	.330	.329	6.97	5.51
	e_{1b}	+1.50	1.968	1.213	1.144	.226	.147	7.33	4.94

Valence Orbital Ionization and Relaxation

Relaxation

It has become clear in recent years [13, 14] that in the case of transition metal compounds ionization processes cannot be adequately discussed in terms of orbitals and orbital energies obtained from ground state calculations. In particular when ionization from orbitals with a significant amount of d-character is considered the relaxation of the charge distribution with respect to the frozen orbital situation cannot be disregarded. For this reason we have carried out independent SCF calculations for a number of ionized states of the compounds at hand. The configurations considered are given in Table XIII together with the calculated relaxed and unrelaxed ionization energies and the corresponding experimental values [6]. For the vanadium compound only the a_1 ionization could be calculated because of program and computer memory limitations. The listed e_1 and e_2 ionization energies have been estimated from a plot of the calculated relaxation energies as a function of the percentage d-character of the groundstate orbitals involved (Fig. 1). We first discuss the relaxation behavior of the charge densities. To this end we display in Table XIV the metal 3d and ring 2p gross populations, and the net charges on the metals in the groundstates and a number of ionized states. A

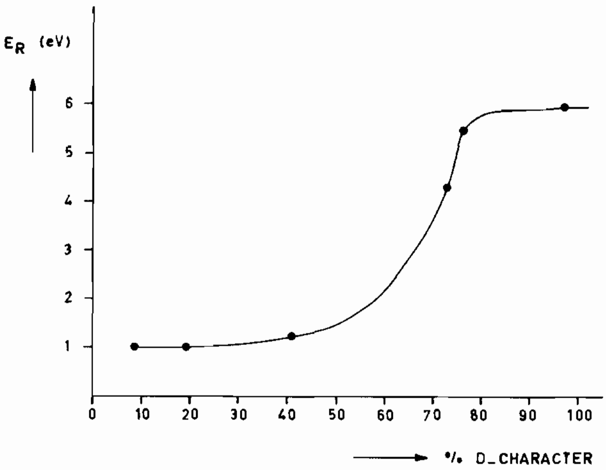

Figure 1. Electronic relaxation energy as a function of the d-character of the ground state m.o.'s.

general conclusion that can be drawn is that in all cases the ionized electron is essentially removed from the rings. The net charges on the metals show only minor changes with respect to those in the neutral systems even in the case of ionization from the $3d_{z^2}$ orbital. Another interesting aspect of these results is that they provide some insight into the possible physical consequences of the lack of complete axial symmetry. It was noted, earlier, that in the ground-state the degeneracy of the highest occupied e_2 orbital pair was preserved only in the case of the titanium compound. The significance of this observation can be assessed by looking at the results for the e_2 ionization where an electron has been removed alternatively from the symmetric (a) or the anti-symmetric (b) components of the e_2 or e_2-like orbitals.

These results are actually quite different from what might have been expected on the basis of a frozen orbital picture. In the titanium case the relaxed ionization energies are slightly different but, more importantly, the orbital structures of the symmetrical and antisymmetrical final states are so different that they cannot be considered as two components of one (nearly) degenerate $^2E_2$ state. In the symmetrical final state the open shell e_{2a} orbital has predominantly (77%) 3d character while the closed shell e_{2b} orbital is mainly (63%) a ring orbital. In the antisymmetrical final state the situation is reversed. The 3d character of the e_{2b} open shell orbital is now only 33% and that of the e_{2a} closed shell orbital 58%. In contrast to this the chromium compound presents a much more symmetrical picture. Both final states not only have the same energy but also the e_{2a} and e_{2b} open shell orbitals as well as the corresponding e_{2b} and e_{2a} closed shell orbitals now have virtually the same character: 93% 3d for the open shells, 46% 3d for the closed shells.

Unlike the e_2 ionization, the a_1 ionization in the vanadium and chromium compounds does not lead to a situation qualitatively different from that encountered in the ground state calculations. One may note, however, that the removal of an a_1 electron tends to restore the orbital symmetry.

Ionization energies

Comparison of the calculated ionization energies with the ground state orbital energies shows the expected strong dependence of the relaxation energies on the groundstate orbital characters (Fig. 1). In comparing the calculated energies with the experimental ionization potentials (Table XIII) we first look at the trends shown by these numbers as a function of the metal accepting the assignments given in reference [6]. The experimental values for the first three ionization energies show that on going from Ti to Cr, i) the e_1 ionization occurs at virtually the same energy for all three compounds, ii) the e_2 ionization energy increases slightly, iii) the a_1 ionization energy decreases markedly. The calculated energies display the same trends except for the e_2 ionization where a slight decrease in energy is seen. Whether this discrepancy is significant or not cannot be discussed at present. A basis set effect does not seem a likely explanation, however.

The actual values of the calculated ionization energies differ substantially from the measured values. This is to be expected. Errors due to the truncated basis sets and those inherent in the single configurational SCF model are all large enough to account in general for such discrepancies [14]. A conspicuous and somewhat disturbing discrepancy is the reversed order of the a_1 and e_2 ionization energies predicted by the calculations. A lowering of roughly 2.5 eV of the calculated a_1 energies with respect to the e_2 energies would be necessary to obtain consistency with the experimental assignments. Possible reasons for such a lowering are presently investigated. Basis set effects are not a likely explanation because these would tend to increase the discrepancies.

Conclusion

The main purpose of the calculations described in this work has been to provide a basis for a more objective and more detailed analysis of the bonding situation in mixed sandwich complexes than is possible on semi-empirical grounds. Rather severe limitations had to be put on the basis sets used as a consequence of the practical constraints one is still faced with when carrying out all electron calculations on molecules of this size. Calculations on smaller systems indicate, however, that basis effects will not essentially change the overall picture obtained concerning the charge distribution and its change as a function of the metal. This overall picture can be summarized in simple terms. We start with a reference state consisting of the 6 π-electron systems $(C_5H_5)^-$ and $(C_7H_7)^+$ and the neutral metals in the configuration $d_\delta)^4 d_\sigma)^X d_\pi)^0$. The metal then acts as a strong δ-donor ($\approx$2 electrons) towards the seven membered cation and simultaneously as a weak π-acceptor ($\approx$0.25 electron) with respect to the cyclopentadienyl anion. This leads to a strong bond in the Ti compound. This bond is progressively weakened in the V and Cr compounds on account of the decreasing donor tendency as well as on account of the occupation of the weakly antibonding d_σ-like orbtial.

The calculated ionization energies quantitatively leave much to be desired. Qualitatively, the dominant feature of the valence ionization results is the large final state relaxation. In all cases considered the net charge loss occurs on the rings, the net charge on the metal being approximately restored after ionization. The results also indicate that the fact that mixed sandwich complexes do not possess strict axial symmetry may have physical consequences. The question can be raised therefore as to whether the usual frozen orbital picture based on axial symmetry is entirely adequate to interprete the observed spectra.

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