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Nonparameterized Molecular Orbital Calculations and Photoelectron Spectroscopy of Open- and Closed-Shell M(IV) M(η^5-C_5H_5)$_2$L$_2$ Complexes[1]

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Abstract: Nonparameterized (Fenske-Hall)-type molecular orbital calculations have been performed on several d^0, d^1, and d^2 M(IV) M(η^5-C_5H_5)$_2$L$_2$ molecules, and the results have been found to be completely compatible with the interpretations obtained from the electron paramagnetic resonance and photoelectron spectral measurements as well as from the crystallographically acquired bond-length and bond-angle data. The MO calculations reveal that the LUMO for the d^0 Ti(IV) complexes and the HOMO for the d^1 and nonhydridic d^2 M(IV) complexes possess analogous orbital characters principally associated with the metal d_{z^2} and $d_{x^2-y^2}$ AO's with considerable contributions from the 3p AO's of the sulfur or chlorine L ligands. The *relative* metal orbital compositions of the HOMO's in the open-shell d^1 V(IV) complexes are in remarkable agreement with those obtained from our previously reported dilute single-crystal EPR studies on V(η^5-C_5H_5)$_2$S$_5$ and V(η^5-$C_5H_4CH_3$)$_2$Cl$_2$. For V(η^5-C_5H_5)$_2$S$_5$ the per cent character ratio of $3d_{z^2}/3d_{x^2-y^2} = 12.7/1$ (EPR) vs. 7.7/1 (MO), while the corresponding ratio of 20.0/1 from the EPR data on V(η^5-$C_5H_4CH_3$)$_2$Cl$_2$ compares with that of 20.5/1 from the MO computations. Additional information concerning the electronic structure of M(η^5-C_5H_5)$_2$L$_2$ complexes has been obtained from photoelectron spectroscopy. The PE spectra of M(η^5-C_5H_5)$_2$Cl$_2$ and M(η^5-$C_5H_4CH_3$)$_2$Cl$_2$ (where M = Ti, V) are presented and interpreted with the aid of the approximate MO calculations.

Dilute single-crystal EPR studies of V(η^5-C_5H_5)$_2$S$_5$[2] and V(η^5-$C_5H_4CH_3$)$_2$Cl$_2$[3] have provided a *quantitative* determination of the relative metal orbital character for the unpaired electron in these d^1 V(IV) molecules. Although the d^1 electron occupies a molecular orbital of predominately metal character,[2,3] there is appreciable evidence which indicates that the composition of the highest occupied molecular orbital (HOMO) is not restricted solely to the $3d_{z^2}$ and $3d_{x^2-y^2}$ metal AO's but contains a significant orbital contribution from the L ligands. The presumed antibonding effect of the unpaired electron on the V-L bond length (rationalized from a bond-length comparison between the corresponding d^0 Ti(IV) and d^1 V(IV) pentasulfide and chloride complexes), the variation of 60-75 G in the ^{51}V isotropic hyperfine coupling constant for different V(η^5-C_5H_5)$_2$L$_2$ complexes, and the noticeably larger line widths for the hyperfine lines of V(η^5-$C_5H_4CH_3$)$_2$Cl$_2$ in comparison to those of V(η^5-C_5H_5)$_2$S$_5$ are all reasonable indications of partial delocalization of the unpaired electron onto the L ligands.

The fact that approximate molecular orbital calculations coupled with photoelectron spectroscopy were successfully utilized[4] in a characterization of the electronic structure and bonding in a number of transition metal carbonyl complexes prompted us to apply these methods to representative M(η^5-C_5H_5)$_2$L$_2$ complexes. The Fenske-Hall MO procedure[5] does not involve the use of empirical or variable parameters; the final results, which are invariant to a rotation of the local coordinate system on each atom, depend only upon the choice of basis functions and the interatomic distances.[6,7] This MO method applied to M(η^5-C_5H_5)$_2$S$_5$, M(η^5-C_5H_5)$_2$(SC$_6$H$_5$)$_2$, M′(η^5-C_5H_5)$_2$Cl$_2$ (M = Ti, V; M′ = Ti, V, Cr, Mo), and Mo(η^5-C_5H_5)$_2$H$_2$ has made possible a comparison of the calculated per cent metal orbital characters for the HOMO in the d^1 V(IV) molecules with those experimentally determined from the dilute single-crystal EPR studies. Our main goals were: (1) to estimate the degree of delocalization of the unpaired electron on the ligands (which cannot be directly determined in the absence of ligand hyperfine interaction from the EPR data) from the calculated orbital character of the ligand atoms in the HOMO; and (2) to determine to what extent the composition of the HOMO is affected as the population in the HOMO is varied from 0 to 2 electrons.

Additional experimental information about the electronic structure of M(η^5-C_5H_5)$_2$L$_2$ complexes has been obtained by means of photoelectron spectroscopy. The PE spectra of M(η^5-C_5H_5)$_2$Cl$_2$ and M(η^5-$C_5H_4CH_3$)$_2$Cl$_2$ (M = Ti, V) are presented and interpreted with the aid of the results from the (Fenske-Hall)-type molecular orbital calculations.

Experimental Section

Photoelectron Spectral Characterization. The photoelectron spectra were measured with a Varian IEE-15 electron spectrometer in the uv configuration. The helium source was pure to 0.0001%. Simultaneous observation of a number of reference gas ionization peaks indicated the energy scale to be linear within less than 0.01 eV over a range of binding energies from 9 to 17 eV. Argon was used as a single *internal* standard (15.76 eV peak) in order to check the spectrometer's resolution as well as its sensitivity. Because of the nature of the compounds used, the samples had to be heated to at least 150° in order to attain sufficient sample vapor pressure in the spectrometer. The samples were heated slowly until reasonable counting rates were reached. Before a sample was introduced into the spectrometer, however, the thermal stability of the compound was checked by vacuum sublimation of the compound at 150°. PE spectra for Ti(η^5-C_5H_5)$_2$S$_5$ and Ti(η^5-C_5H_5)$_2$(SC$_6$H$_5$)$_2$ were not obtained because of thermal decompo-

Table I. Average Bond Lengths and Angles Used for Nonparameterized (Fenske–Hall)-Type MO Calculations

Idealized symmetry	Molecule	Reference structure	Ref	Distance (Å)		Angles (deg)	
				M–R[a]	M–L[a]	R–M–R	L–M–L
C_s	$Ti(\eta^5\text{-}C_5H_5)_2S_5$	Same	14a–c	2.066	2.430	132.7	95.0
C_s	$V(\eta^5\text{-}C_5H_5)_2S_5$	Same	14a,c	1.966	2.455	134.1	89.5
C_2	$Ti(\eta^5\text{-}C_5H_5)_2(SH)_2$	$Ti(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$	14d,e	2.070	2.422	132.4	99.8
C_2	$V(\eta^5\text{-}C_5H_5)_2(SH)_2$	$V(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$	14a,e	1.970	2.460	134.6	94.1
C_{2v}	$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$	$Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$	3,14f	2.067	2.361	130.1	93.1
C_{2v}	$V(\eta^5\text{-}C_5H_5)_2Cl_2$	$V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$	3,14f	1.990	2.398	133.4	87.1
C_{2v}	$Cr(\eta^5\text{-}C_5H_5)_2Cl_2$	----		(1.910)[b]	(2.420)[b]	(136.0)[b]	(84.6)[b]
C_{2v}	$Mo(\eta^5\text{-}C_5H_5)_2Cl_2$	Same	14g	1.990	2.471	132.0	81.6
C_{2v}	$Mo(\eta^5\text{-}C_5H_5)_2H_2$	Same	14h	1.945	(1.75)[b,c]	152.0	(82.0)[b,c]
				1.945	(1.96)[c]	152.0	(82.0)[c]
				1.945	(1.96)[c]	152.0	(100.0)[c]

[a] R = Centroid of cyclopentadienyl ring; L = S, Cl, H. [b] Values in parentheses were assumed from stereochemical considerations. [c] See ref 17.

sition of these compounds. No changes in any of the spectra were observed once the surface conditions of the analyzer had equilibrated. All displayed spectra, obtained with an electron analyzer energy of 2 eV and reproduced by the instrument's recorder, represented a time-averaged sum of at least 20 100-second scans through the binding energy range. This technique not only reduced the time required for data collection but also generally increased peak resolution in that a much greater improvement in the signal-to-noise ratio was obtained without doubt being raised concerning peak positions, relative peak intensities, transient behavior, etc. The reported ionization potentials correspond to the peak maxima.

Molecular Orbital Characterization. (a) Utilized Functions and Molecular Parameters. The basis functions used are Hartree-Fock-Roothaan for the free atoms or ions generally chosen[8,9] to be consistent with the Mulliken gross charge and configuration of each atom in the calculation. The basis set included the 3d, 4s, and 4p AO's as valence orbitals for the first-row transition metals and the 4d, 5s, and 5p AO's as valence orbitals for molybdenum with all inner AO's taken as "frozen" atomic core orbitals. Similarly, for each of the ligand atoms the outermost s and p AO's were employed as valence orbitals with the inner ones frozen to their atomic form. The hydrogen and carbon functions were obtained from Clementi[10a] with the 1s H and the 1s and 2s C AO's being curve fit to reduce the number of exponents from two to one. The "best atom" functions of Clementi and Raimondi[10b] were used for sulfur and chlorine. The 1s through 3d functions for titanium, vanadium, and chromium (with a +1 charge for the 3d) were taken from Richardson et al.,[11] and the 4s and 4p metal functions from Radtke.[9] The 1s through 5p functions for molybdenum were taken from the results of Richardson et al.;[12] the 4d function corresponds to a $4d^5$ configuration of Mo^+, while the 5s and 5p functions were constructed[8] to maximize their overlap with the ligand valence orbitals. These wave functions, which in all cases were Schmidt orthogonalized (starting with the 1s function), are analogous with those used previously.[4,6,13] They are given elsewhere.[14]

The average bond lengths and angles (Table I) used for the molecular orbital calculations were based upon crystallographic data.[15-18] To simplify the calculations for $M(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$ (where M = Ti, V), the two phenyl rings were replaced by hydrogen atoms at distances of 1.34 Å from the metal-bonded sulfur atoms along the S-C directions. For $M(\eta^5\text{-}C_5H_5)_2S_5$ the atomic coordinates were idealized to C_s-m geometry with S-S distances of 2.06 Å, while for $M(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$ the atomic coordinates were idealized to C_2-2 geometry. For the chloride and the hydride molecules the atomic coordinates were idealized to C_{2v}-$2mm$ geometry. The cyclopentadienyl rings were constrained to D_{5h} symmetry[19] with C-C and C-H distances of 1.405 and 1.09 Å, respectively. Since in these complexes the variation of the M-C distances in a given unsubstituted cyclopentadienyl ring was less than 0.05 Å, equal M-C distances were assumed for each particular complex. The idealized atomic coordinates, calculated with the aid of the computer program MIRAGE,[20] are given elsewhere.[14]

Each cyclopentadienyl ring was calculated separately as a free ligand to determine the eigenvalues and eigenvectors to be used (after self-consistency was reached in the MO calculation of the metal cyclopentadienyl complex) to transform the orbitals from a basis of free-atom orbitals to a basis of free-ligand orbitals. In these calculations the first three of the ten low-energy, occupied cyclopentadienyl ring σ-type valence orbitals (constructed from the 2s C, 2p C, and 1s H AO's) were frozen as ligand core orbitals and thereby were deleted (along with the ten virtual, antibonding σ-type valence ring orbitals of higher energy than the virtual π-type e_2 level) from the SCF solution. This treatment of the cyclopentadienyl rings is identical with that performed on other first-row transition metal cyclopentadienyl complexes by Lichtenberger and Fenske[13d,e] who found that this procedure substantially reduced the time for solution of the SCF equations without introducing serious errors into the results. Calculations with the cyclopentadienyl ligand treated either as a radical (open-shell) or monoanion (closed-shell) were made without noticeably affecting the orbital character; those involving the $C_5H_5^-$ monoanion were used to be consistent with the formal oxidation state of IV for the central metal atom.

The idealized atomic coordinates for all of the molecules were calculated such that the x direction of the master coordinate system originating on the central metal atom bisects the L-M-L bond angle, the y direction is normal to the ML_2 plane, and the z direction is normal to the plane which bisects the L-M-L angle. This coordinate system is coincident with the principal directions obtained for the hyperfine tensor in $V(\eta^5\text{-}C_5H_5)_2S_5$[2] and for the magnetic tensors (**g** and **T**) in $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$.[3] Although the computational method is rotationally invariant to the local coordinate system on the metal, this particular coordinate system was selected to simplify a comparison between the molecular orbital calculations and the dilute single-crystal EPR results. The z direction of the local Cartesian coordinate system located on each carbon atom of a given cyclopentadienyl ring was directed perpendicular to the $C_5H_5^-$ plane toward the central metal atom. The z direction of the local coordinate system on each ligand L points toward the metal atom along the internuclear bond.

(b) Open-Shell Calculations. The presence of an unpaired electron in the V(IV) molecules greatly complicates the application of the Hartree-Fock SCF theory.[21] For the (Fenske-Hall)-type method, which essentially involves a restricted Hartree-Fock approach, the unpaired electron was replaced by two half-electrons of opposite spin. This "half-electron method" was originally proposed by Diercksen,[22] who maintained that the electronic structure of a radical can be approximated by a closed-shell structure in which the HOMO contains two half-electrons of opposite spin. The total energy of the system was obtained by the subtraction of an electron repulsion term between these two electrons from the closed-shell energy. For systems in which this term is negligible with respect to the total energy, the eigenvalue calculated for the HOMO by the "half-electron method" should reasonably agree with that calculated from a more rigorous method, such as an unrestricted Hartree-Fock SCF calculation which allows different spins to occupy different orbitals. Further, this method assumes that the corresponding coefficients of the AO's, which are related to the orbital character in the HOMO, are not greatly perturbed.

Although the "half-electron method" may not be a suitable choice for many open-shell calculations, this approach appears to give entirely reasonable results for the d^1 V(IV) $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes as evidenced by the similar orbital compositions of the LUMO for the analogous closed-shell d^0 Ti(IV) complexes and of the HOMO for the open-shell d^1 and closed-shell d^2 M(IV) complexes. From crystallographic data obtained for a considerable

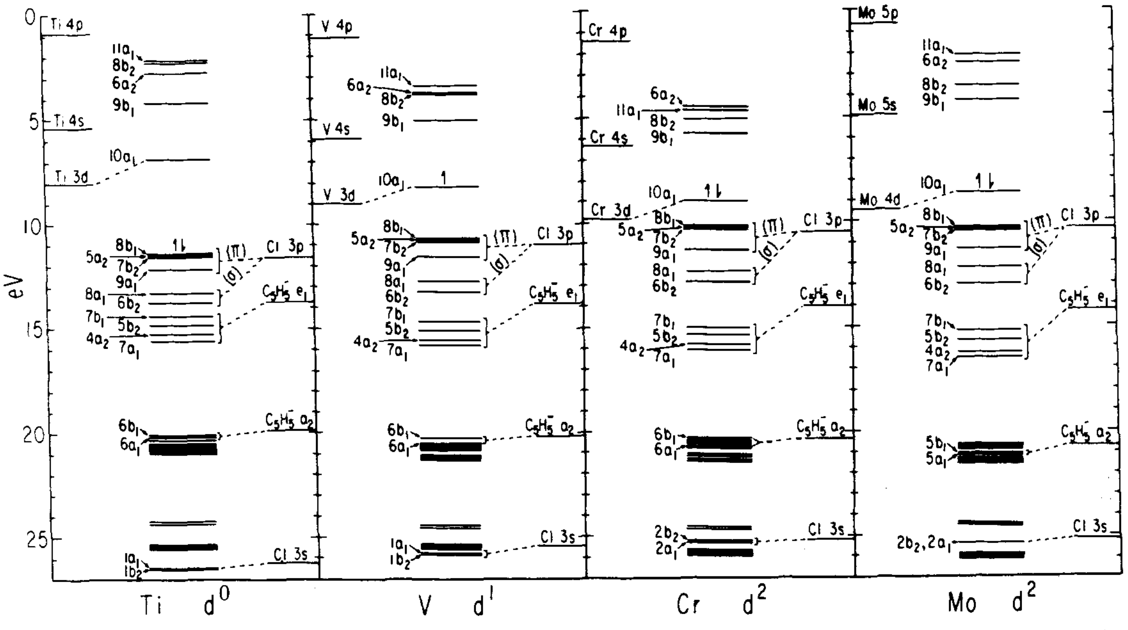


Figure 1. Molecular orbital energy-level diagrams for $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (M = Ti, V, Cr, Mo). Half-arrows designate the number of electrons in the highest occupied molecular orbital.

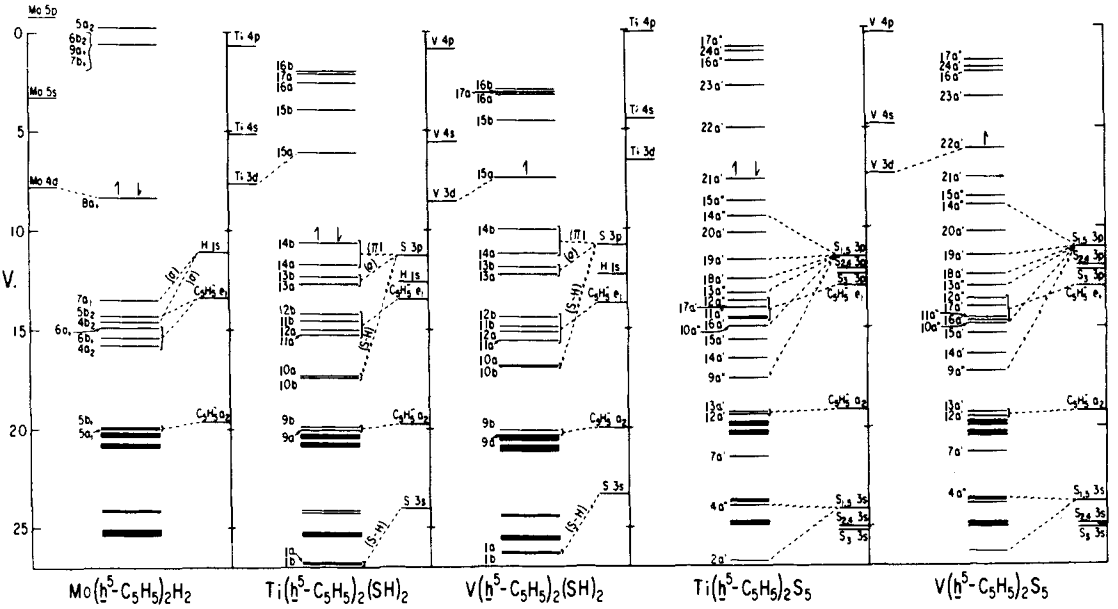


Figure 2. Molecular orbital energy-level diagrams for $Mo(\eta^5\text{-}C_5H_5)_2H_2$, $M(\eta^5\text{-}C_5H_5)_2(SH)_2$, and $M(\eta^5\text{-}C_5H_5)_2S_5$ (M = Ti, V).

number of $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes, a correlation was found[15c,e,g,16,23,24] to exist between the number of d^n electrons occupying the HOMO (i.e., or LUMO when $n = 0$) and the L-M-L bond angle. As the number of electrons which occupy this orbital is increased from 0 to 1 to 2, a continual decrease of ca. 6° occurs in the L-M-L bond angle (e.g., from 93.1° for the d^0 Ti(IV) $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ to 87.1° for the d^1 V(IV) $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ to 81.6° for the d^2 Mo(IV) $Mo(\eta^5\text{-}C_5H_5)_2Cl_2$). This correlation strongly suggests that the orbital character of the HOMO is not appreciably different for the open- and closed-shell configurations. Dewar et al.[25] have also used the "half-electron method" for semiempirical calculations of several radical species and have obtained good agreement between the calculated and observed heats of formation of hydrocarbon radicals.

Results and Discussion

Molecular Orbital Calculations and Resulting Stereochemical Implications. The calculated one-electron MO energy diagrams for $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (M = Ti, V, Cr, and Mo) and for $Mo(\eta^5\text{-}C_5H_5)_2H_2$, $M(\eta^5\text{-}C_5H_5)_2(SH)_2$, and $M(\eta^5\text{-}C_5H_5)_2S_5$ (M = Ti, V) are shown in Figures 1 and 2, respectively. The irreducible representation of each MO is consistent with the idealized geometry for each molecule. The $C_5H_5^-$ levels are labeled with their appropriate localized symmetries prior to bonding in the complex. The HOMO in each case is designated by the half-arrows which represent the number of electrons in the orbital; the dashed line is used to designate the primary contributor to the MO. Table II presents the energies and per cent orbital characters of the HOMO's for the vanadium, chromium, and molybdenum complexes and corresponding LUMO's for the titanium complexes. The eigenvalues, eigenvectors, and per cent characters of these and the other molecular orbitals which are important to the description of the bonding in each of these complexes are tabulated elsewhere[14] along with the calculated Mulliken gross atomic charges.

A qualitative understanding of the bonding in these complexes can be formulated from a close inspection of the MO diagrams. Each of the $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes with L =

Table II. Per Cent Character of the HOMO[a] in $M(\eta^5\text{-}C_5H_5)_2L_2$ where M = V, Cr, Mo and Corresponding LUMO[a] in $Ti(\eta^5\text{-}C_5H_5)_2L_2$[b-d]

Configuration	Molecular symmetry	Molecule	% metal d_{z^2}	% metal $d_{x^2-y^2}$	% ligand $3p_\pi$ (L)	% ligand e_2 (C_5H_5)	Energy (eV)	Ratio % d_{z^2}/% $d_{x^2-y^2}$
d^0 LUMO (22a′)	C_s	$Ti(\eta^5\text{-}C_5H_5)_2S_5$	57.9	8.2	16.1	4.6	−4.99	7.1
d^0 LUMO (15a)	C_2	$Ti(\eta^5\text{-}C_5H_5)_2(SH)_2$	65.7	7.6	16.9	5.1	−6.15	8.6
d^0 LUMO ($10a_1$)	C_{2v}	$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$	69.5	4.9	16.1	6.1	−6.88	14.1
d^1 HOMO (22a′)	C_s	$V(\eta^5\text{-}C_5H_5)_2S_5$	50.1	6.6	20.7	3.1	−6.12	7.7
d^1 HOMO (15a)	C_2	$V(\eta^5\text{-}C_5H_5)_2(SH)_2$	64.7	5.5	22.5	3.9	−7.45	11.7
d^1 HOMO ($10a_1$)	C_{2v}	$V(\eta^5\text{-}C_5H_5)_2Cl_2$	67.6	3.3	22.3	4.4	−8.19	20.5
d^2 HOMO ($10a_1$)	C_{2v}	$Cr(\eta^5\text{-}C_5H_5)_2Cl_2$	53.0	2.4	40.0	1.6	−9.03	22.4
d^2 HOMO ($10a_1$)	C_{2v}	$Mo(\eta^5\text{-}C_5H_5)_2Cl_2$	54.0	1.3	37.0	5.6	−8.64	40.9
d^2 HOMO ($8a_1$)	C_{2v}	$Mo(\eta^5\text{-}C_5H_5)_2H_2$	(a)[e] 80.7	5.5	–	11.1	−8.32	14.6
			(b) 81.1	5.4	–	10.8	−8.66	15.1
			(c) 60.7	20.8	–	10.4	−8.50	2.9

[a] LUMO = lowest unoccupied molecular orbital; HOMO = highest occupied molecular orbital. [b] In these molecules, the Ti 4s and 4p characters were ≤ 0.3 and $\leq 1.7\%$, respectively; the V 4s and 4p characters ≤ 0.1 and $\leq 1.1\%$, respectively; the Cr 4s and 4p characters 0.1 and 0.3%, respectively; and the Mo 5s and 5p characters <0.5 and $<0.7\%$, respectively. [c] Per cent $3p_\pi$ (L) ligand character is the sum of the characters from both pairs of $3p_\pi$ ligand L orbitals (L = Cl, S^-). Per cent e_2 (C_5H_5) ligand character is the sum of the characters from each e_2 localized symmetry orbital on the cyclopentadienyl ligands. [d] For the molecules with M = Ti, V, Cr, Mo the 3s Cl (or ls H) ligand characters were 0.0% and the $3p_\sigma$ Cl ligand characters were of 0.7–0.9% range. For M = Ti, V the 3s and $3p_\sigma$ sulfur ligand characters were ≤ 0.5 and $\leq 0.4\%$, respectively, for the mercaptide complexes and ≤ 0.1 and $\leq 1.3\%$, respectively, for the pentasulfide complexes (i.e., for only the two metal-attached sulfur atoms). [e] Based on the following three sets of assumed molecular parameters (see Table I): (a) Mo–H, 1.75 Å; H–Mo–H, 82.0°; (b) Mo–H, 1.96 Å; H–Mo–H, 82.0°; (c) Mo–H, 1.96 Å; H–Mo–H, 100.0°.

Cl or S^- has 14 *occupied* metal-ligand MO's of predominately ligand orbital character, viz., two of primarily L 3s, two of primarily localized $C_5H_5^-$ a_2, four of primarily localized $C_5H_5^-$ e_1, two of primarily L $3p_\sigma$, and four of primarily L $3p_\pi$; in the case of $Mo(\eta^5\text{-}C_5H_5)_2H_2$ there are eight *occupied* metal–ligand MO's of mainly ligand orbital character, viz., two of primarily localized $C_5H_5^-$ a_2, four of primarily localized $C_5H_5^-$ e_1, and two of primarily H 1s. For each of these complexes there are five well-separated *higher-energy* MO's principally associated with the metal d orbitals, the *lowest* one being either the LUMO for the d^0 Ti(IV) or the HOMO for the d^1 and d^2 M(IV).[26]

Of these latter five MO's which are substantially metallic in nature (50–85%), the least destabilized and only one occupied in each of the d^1 and d^2 M(IV) $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes is comprised of mainly the d_{z^2} AO.[26] This particular orbital character can be rationalized from a consideration of the directional and bonding characteristics of the other *four* metal d AO's. The d_{xz} orbital, which is directed toward the two L ligands (Cl, S^-, or H), interacts mainly with the ligand $3p_z$ AO's (or 1s AO's for H) to give a bonding combination of representation $6b_2$ for $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (C_{2v}), $4b_2$ for $Mo(\eta^5\text{-}C_5H_5)_2H_2$ (C_{2v}), 13b for $M(\eta^5\text{-}C_5H_5)_2(SH)_2$ (C_2), and 15a″ for $M(\eta^5\text{-}C_5H_5)_2S_5$ (C_s); its antibonding counterparts are $8b_2$, $6b_2$, 16b, and 17a″, respectively. The d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{xy} metal AO's are also involved to some degree in bonding with the localized e_1 orbitals of the $C_5H_5^-$ rings. Since the metal d_{xy} and d_{yz} AO's are directed more toward the $C_5H_5^-$ rings than the metal $d_{x^2-y^2}$ and d_{xz} AO's, their interactions with the carbon p_π orbitals are expectedly somewhat greater. The consequence of the greater stabilization for the bonding MO's of these four metal d AO's with the ligands is a greater destabilization of their four corresponding antibonding MO's. In each of the MO diagrams, this destabilization effectively pushes these four antibonding levels above the HOMO for the d^1 and d^2 (or LUMO for d^0) M(IV), thereby leaving it as the lowest in energy of the five predominately metal MO's.[26]

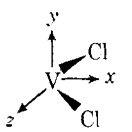
The MO diagrams for $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (where M = Ti, V, Cr, and Mo) illustrate that the MO's arising primarily from the two 3s and four $3p_\pi$ chlorine AO's are essentially nonbonding, which is consistent with the localization of three lone electron pairs on each of the two Cl atoms. The two MO's with localized $C_5H_5^-$ a_2 character are also essentially nonbonding. The two *principal* metal-ligand bonding modes stem from the interaction of the metal d_{xz} AO with the $3p_z$ Cl AO's and from the interactions of the four above-mentioned metal d AO's with the localized e_1 orbitals on the $C_5H_5^-$ rings. The bonding picture for $M(\eta^5\text{-}C_5H_5)_2(SH)_2$ (M = Ti, V) is nearly the same except for the stabilization of the 3s and one of the two p_π AO's on each of the S atoms due to the S-H bonding interactions. The energy levels for $M(\eta^5\text{-}C_5H_5)_2S_5$ (M = Ti, V) are considerably complicated by the additional sulfur atoms in the bidentate S_5^{2-} ligand which lowers the symmetry of the idealized geometry to C_s thereby allowing the possibility of greater mixing among the metal AO's; nevertheless, a comparison of these correlation diagrams and eigenvectors with those for the other $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes reveals analogous energies and similar metal orbital contributions for the corresponding levels in the titanium and vanadium pentasulfide molecules.[27]

The MO calculations on $Mo(\eta^5\text{-}C_5H_5)_2H_2$, carried out under C_{2v} symmetry with three different sets of assumed values for the average Mo-H bond length and the H-Mo-H bond angle (see Table I),[17] give rise to essentially identical energy-level diagrams with the completely occupied HOMO being predominately metal-like in character with contributions from mainly the $4d_{z^2}$ and $4d_{x^2-y^2}$ Mo AO's. An examination of the ratio of the per cent characters of the $4d_{z^2}$ to the $4d_{x^2-y^2}$ for each calculation (viz. (a) 80.7/5.5 = 14.6/1; (b) 81.1/5.4 = 15.1/1; (c) 60.7/20.8 = 2.9/1) reveals that this ratio remains relatively constant for the expected H-Mo-H bond angle of 82° to the 0.2 Å variation from 1.75 to 1.96 Å in the assumed Mo-H distances. However, a considerable decrease in this ratio is observed as the value of the H-Mo-H bond angle used in the MO calculations was increased from 82 to 100°, in accord with a larger H-Mo-H bond angle producing more electron density along the x direction bisecting the H-Mo-H bond angle and concomitantly less density along the perpendicular z direction in the MoH_2 plane. It is apparent from these calculations that the directional properties of the HOMO are strongly dependent upon the magnitude of the L-M-L bond angle.

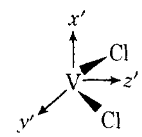
The results of prime interest are the per cent orbital character of the HOMO in each of the vanadium, chromium, and molybdenum complexes and the per cent character of the LUMO in each titanium complex. Table II summarizes the calculated composition of these particular molecular orbitals (of a_1 representation under C_{2v} molecular symmetry and of a or a′ representation under C_2 or C_s symmetry, respectively). To a first approximation, the composition of the HOMO (or the LUMO) in all cases is reasonably insensitive to the assumed molecular symmetry and to the change in the ligand L. The electron(s) in the HOMO reside(s) in an orbital of ***high*** metal character, primarily composed of d_{z^2} with a much smaller but still significant amount of $d_{x^2-y^2}$ and virtually no s or p.[27] Each HOMO also possesses considerable ligand p_π orbital character. Table II reveals an indicated trend of markedly increasing p_π(L) character for L = Cl, S^- with increased orbital occupancy (i.e., from 0 to 1 to 2 electrons); it is also noteworthy that the contribution of the $C_5H_5^-$ ring character in the HOMO (or corresponding LUMO) is much smaller than the p_π(L) character for these nonhydridic complexes.

The particular nature of the relative metal orbital character of the HOMO calculated for the vanadium complexes is in excellent agreement with that determined from the dilute single-crystal EPR studies of $V(\eta^5\text{-}C_5H_5)_2S_5$ and $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$. This accordance is illustrated from a comparison of the ratio of the per cent character of $3d_{z^2}$ to the per cent character of $3d_{x^2-y^2}$. For $V(\eta^5\text{-}C_5H_5)_2S_5$ this ratio of 7.7/1 from the HOMO corresponds with that of $(-0.963)^2/(0.270)^2$ = 12.7/1 calculated from the EPR data, while the ratio of 20.5/1 from the HOMO for $V(\eta^5\text{-}C_5H_5)_2Cl_2$ corresponds with that of $(-0.976)^2/(0.218)^2$ = 20.0/1 obtained from the EPR data for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$. Hence, the (Fenske-Hall)-type MO treatment of these one-electron open-shell systems further confirms the interpretation of the EPR data.

Although the relative per cent orbital character of the metal orbitals from the MO calculations agrees exceptionally well with that obtained from the EPR results, the calculated Mulliken per cent orbital characters can be misleading with respect to a clear understanding of the spatial distribution of the unpaired electron. To illustrate this point, the eigenvectors for the metal orbitals calculated for $V(\eta^5\text{-}C_5H_5)_2Cl_2$ were transformed[28] to another right-handed Cartesian coordinate system with the z' direction bisecting the Cl-V-Cl bond angle, as illustrated below. The per cent orbital character and corresponding eigenvector (given in parentheses) for the $d_{z'^2}$ and $d_{x'^2-y'^2}$ orbitals are 32.4% (0.588) and 38.8% (0.638), respectively, compared to 67.0% (−0.845) and 3.3% (0.190) for the d_{z^2} and $d_{x^2-y^2}$ orbitals. Since the electron density for a particular MO is invariant to the choice of the master coordinate system, the electron-density contour diagrams provide a more satisfactory means for understanding the spatial distribution of the unpaired electron about the metal atom. Figure 3 represents the respective electron-density contour diagrams[29] for the *xz*, *xy*, and *yz* planes computed from the wave function of the HOMO for $V(\eta^5\text{-}C_5H_5)_2Cl_2$. These plots are quite similar to the corresponding contour diagrams (see Figure 9 in ref 3) representing the *metal* orbital character of the unpaired electron determined for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ from the single-crystal EPR data. Figure 3a is especially interesting with regard to the nature of the distribution of the unpaired electron. Rather than being delocalized on the Cl ligands along the V-Cl directions, the unpaired electron apparently is delocalized on the Cl ligands through a mechanism involving the Cl p_π orbitals in the VCl_2 molecular plane. Furthermore, Figure 3a shows that the largest electron density of the unpaired electron is localized along the *z* direction.



original coordinate system



new coordinate system

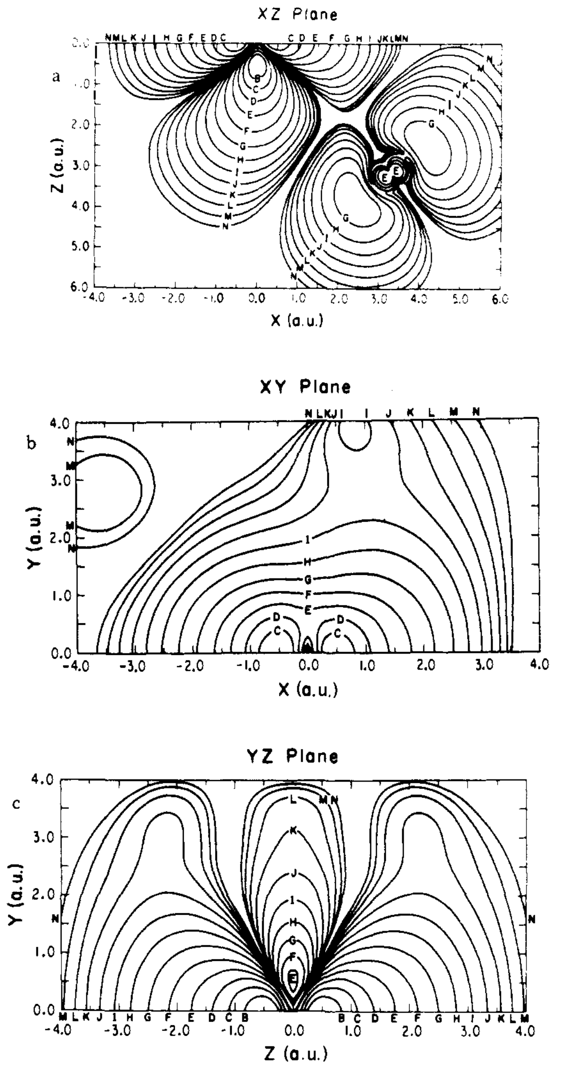


Figure 3. Electron-density contour maps of the HOMO for $V(\eta^5\text{-}C_5H_5)_2Cl_2$ in the (a) *xz* plane, (b) *xy* plane, and (c) *yz* plane. These three principal sections show the anisotropy of the calculated density distribution of the unpaired electron over the entire molecule in $V(\eta^5\text{-}C_5H_5)_2Cl_2$. The coordinates in atomic units for the vanadium atom are 0, 0, 0 and for the two chlorine atoms are 3.28, 0.00, ±3.12. The density conforms to the assumed C_{2v} molecular symmetry with the twofold axis along the *x* direction and the normals of the mirror planes along the *y* and *z* directions. Based on the assumption that the ground state contains one electron in the HOMO, the scale (in units of $e^-/(au)^3$) for the contour lines on each map decreases by a factor of 2 for each successive line from a maximum value of 0.250 for B to 0.610×10^{-4} for N.

From the MO diagrams it is further evident that the HOMO in the d^1 and d^2 M(IV) complexes (except for $Mo(\eta^5\text{-}C_5H_5)_2H_2$) is antibonding with respect to the metal atomic d orbitals. A calculation of the overlap population[30] with only the major components of the HOMO (i.e., M(IV) d_{z^2}, $d_{x^2-y^2}$ and L $3p_x$, $3p_y$, $3p_z$) gives a negative value for this orbital, viz., $V(\eta^5\text{-}C_5H_5)_2Cl_2$, −0.098; $Cr(\eta^5\text{-}C_5H_5)_2Cl_2$, −0.174; $Mo(\eta^5\text{-}C_5H_5)_2Cl_2$, −0.214; $V(\eta^5\text{-}C_5H_5)_2(SH)_2$, −0.095; $V(\eta^5\text{-}C_5H_5)_2S_5$, −0.092. This small but significant antibonding contribution to the M-L bonds in each complex is consistent with the crystallographic results which showed (in contradistinction to the difference in metal radii) that the V-L bond distance in these d^1 systems is significantly *longer* than the Ti-L bond distance in the analogous d^0 systems.[31]

Photoelectron Spectra and Resulting Stereochemical Implications. The photoelectron spectra of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $V(\eta^5\text{-}C_5H_5)_2Cl_2$ are shown in Figure 4. The band posi-

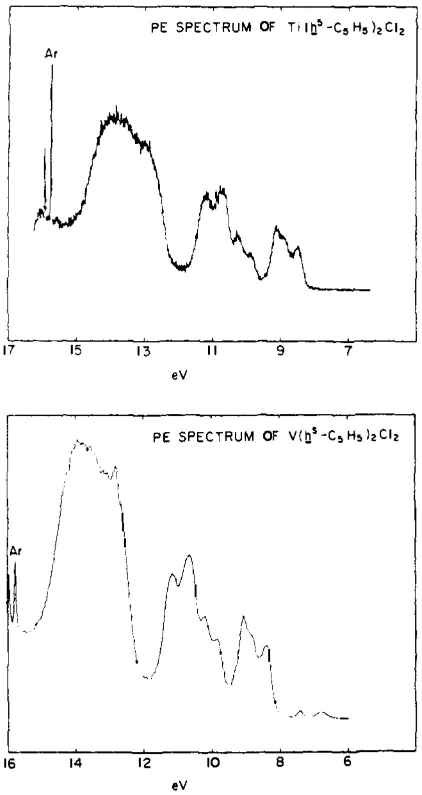


Figure 4. Photoelectron spectra of $Ti(\eta^5-C_5H_5)_2Cl_2$ and $V(\eta^5-C_5H_5)_2Cl_2$. Binding energy increases from right to left.

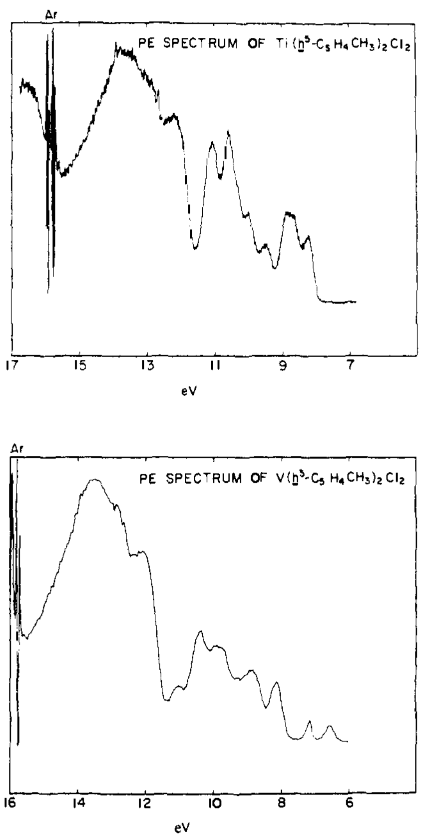


Figure 5. Photoelectron spectra of $Ti(\eta^5-C_5H_4CH_3)_2Cl_2$ and $V(\eta^5-C_5H_4CH_3)_2Cl_2$.

tions and spectral features for both molecules are quite similar except for two additional weakly resolved, low-energy ionizations obtained for the paramagnetic molecule. Since it was necessary to heat the compounds to at least 150° in order to attain sufficient sample vapor pressure in the PE spectrometer, the thermal stability of these compounds must be considered. Under vacuum sublimation, $Ti(\eta^5-C_5H_5)_2Cl_2$ readily sublimes at ca. 150° while $V(\eta^5-C_5H_5)_2Cl_2$ appears to undergo thermal decomposition to a blue-green substance, possibly $V(\eta^5-C_5H_5)_2Cl$ or $V(\eta^5-C_5H_5)_2$, which exhibits a solution EPR spectrum different from that of the starting material. Consequently, this information raises a question with regard to whether the spectrum shown in Figure 4 is actually that for $V(\eta^5-C_5H_5)_2Cl_2$, some other species, or a combination of both.

Based on the work at Oxford which showed that the substitution of a methyl group on each of the cyclopentadienyl rings in the corresponding niobium dichloride molecule increased markedly the volatility of the resulting complex,[32] the methylcyclopentadienyl derivatives of the titanium and vanadium dichlorides were prepared with the hope that the volatility of the vanadium complex would likewise be sufficiently improved to eliminate the thermal decomposition problem encountered with $V(\eta^5-C_5H_5)_2Cl_2$. Preliminary vacuum sublimation of either $Ti(\eta^5-C_5H_4CH_3)_2Cl_2$ or $V(\eta^5-C_5H_4CH_3)_2Cl_2$ gave no indication of thermal decomposition at 150°, which was substantiated for the latter compound by identical solution EPR spectra for the original and sublimed material. The mass spectra for $Ti(\eta^5-C_5H_4CH_3)_2Cl_2$ and $V(\eta^5-C_5H_4CH_3)_2Cl_2$ each indicated the presence of a weak parent ion peak with the m/e values for the molecular ions $M(C_5H_5)_2Cl^+$, $M(C_5H_5)_2^+$, and Cl^+ being considerably more intense. The subsequent photoelectron spectra for $Ti(\eta^5-C_5H_4CH_3)_2Cl_2$ and $V(\eta^5-C_5H_4CH_3)_2Cl_2$ are shown in Figure 5. A comparison of the PE spectra of $V(\eta^5-C_5H_5)_2Cl_2$ and $V(\eta^5-C_5H_4CH_3)_2Cl_2$ indicates the intensity of the two low-energy ionizations is enhanced for the methylcyclopentadienyl compound.

Our interpretation of the PES shown in Figures 4 and 5 is based upon the approximate (Fenske-Hall)-type molecular orbital calculations performed on $Ti(\eta^5-C_5H_5)_2Cl_2$ and $V(\eta^5-C_5H_5)_2Cl_2$. Since the band structures in the PE spectra of the two titanium complexes are nearly identical, MO calculations for the methylcyclopentadienyl molecules were not carried out.

Of particular interest are the ionizations that occur at less than 12 eV. For $Ti(\eta^5-C_5H_5)_2Cl_2$ the approximate MO calculations predict that these bands arise from the ionization of the lone pairs on the chlorine ligands, the σ-bonding orbitals between the chlorine ligands and the metal, and the bonding orbitals between the e_1 localized orbitals on each cyclopentadienyl ring and the metal. Since several of these orbitals with analogous energies possess similar orbital character, the probability of resolving the individual bands due to ionization of these ten orbitals is quite small. Nevertheless, a closer look at the ionization region of interest for the titanium complexes reveals considerable band structure. Although seven bands can be readily recognized, the intensities of the individual bands vary considerably. Because of the complexity of the band structure in these PE spectra and the sensitivity of the ordering of individual Cl ligand orbitals to the choice of basis set, no attempt has been made to assign a symmetry type to a particular ionization band. However, the approximate MO calculations and photoelectron spectroscopy experiments previously performed for $Fe(\eta^5-C_5H_5)_2(CO)_2X$ (where X = Cl, Br, I) and $Mn(\eta^5-C_5H_5)(CO)_3$[13d,e] have shown that the cyclopentadienyl ring levels are located below the halogen and metal levels. Furthermore, for a set of well-resolved photoelectron spectra of the series $Mn(CO)_5X$ (where X = Cl, Br, I), Lichtenberger, Sarapu, and Fenske[4a] assigned the lowest ionization potentials (IP's) in the range of 8-10 eV to the different

Table III. Assignment of Orbital Type for Experimental Ionization Potentials (eV) of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$

Calcd	$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ Exptl	$Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ Exptl	Orbital type
−11.36	8.45	8.22	p_x,p_y Cl
−11.40	8.90	8.65	p_x,p_y Cl
−11.54	9.12	8.88	p_x,p_y Cl
−12.15			
−13.27	9.83	9.46	p_σ Cl
−13.79	10.22	10.03	p_σ Cl
−14.39	10.72	10.60	e_1 C_5H_5
−14.88	11.20	11.06	e_1 C_5H_5
−15.34			
−15.61			

halogen orbitals, with the two halide p_π orbitals above the p_σ. On the basis of these results, the three bands (8–9 eV) are tentatively assigned to the four chlorine p_π molecular orbitals, the two weak bands (9–10 eV) to the chlorine σ-bonding orbitals with the metal, and the two strong bands (10–12 eV) to the ring interaction with the metal through the bonding e_1 orbitals on the ring. Table III summarizes the assignment of the orbital types to the ionization potentials. Although the calculated eigenvalues for the ground state of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ differ somewhat from the experimental IP's due (in addition to errors inherent in the calculated procedure) to the intrinsic uncertainty in Koopmans' theorem,[33-35] the assignments appear entirely reasonable.

This qualitative analysis of the PE spectra of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ has provided a basis from which the PE spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ can be interpreted. Since $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ has one more occupied orbital than $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, its PE spectrum should contain at least one additional ionization.[36] Besides a band at 6.60 eV, which is most likely associated with the ionization of the unpaired electron (shown by EPR and approximate MO calculations to occupy a MO of a_1 representation primarily localized on the vanadium), an inspection of the photoelectron spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ reveals a second low-energy band at 7.20 eV. Furthermore, the valence IP region for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ is more complex and diffuse than that of $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$. This is in accord with the greater complexity of the PE spectrum of VCl_4 compared to that of $TiCl_4$.[37] For an open-shell configuration, ionization of an inner-filled MO can lead to more than one state of the resulting ion. For a nondegenerate orbital two possible spin states (i.e., a triplet and singlet) are generated due to coupling of the spin of the inner ionized orbital with the spin of the unpaired electron in the HOMO. The exchange splitting between these two states is simply $\Delta E_{ex} = 2K$,[38] where K is the average exchange integral between the two molecular orbitals involved. Weak exchange interactions of this type normally appear as line-broadening effects.[39] However, when K is sufficiently large, two distinct peaks may be observed with the higher spin state located at the lower binding energy. Since the relative probability of ionization to these spin states is the ratio of their spin degeneracies, the relative intensities of the triplet:singlet peaks is 3:1. The triplet band is displaced by $K/2$ above while the singlet band is shifted by $3K/2$ below the energy of the inner-filled MO prior to ionization, which to a first approximation is equal to the weighted mean of the energies of the two spin states.[40]

To determine the feasibility of extra bands occurring in the PE spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ due to an exchange interaction, the exchange integral of the HOMO with each of the other occupied molecular orbitals was calculated[41] from the relationship

$$K = \langle \psi_1\psi_2 | \psi_1\psi_2 \rangle = \sum_i \sum_j \sum_k \sum_l C_{i1}C_{j2}C_{k1}C_{l2}\langle \phi_i\phi_j | \phi_k\phi_l \rangle$$

where the wave function for a molecular orbital, i, is represented by a linear combination of atomic orbitals, $\psi_i = \Sigma_j C_j \phi_j$. From the eigenvectors and integrals calculated for the approximate molecular orbital calculations, the exchange integrals for two of the ligand MO's ($9a_1$ and $7b_2$) with the HOMO ($10a_1$) are 2.1 and 1.0 eV, respectively. The $9a_1$ orbital is the bonding counterpart to the $10a_1$ orbital, while the $7b_2$ orbital is essentially p_π in character. The exchange integrals calculated for the other MO's are essentially zero.

In order for an exchange interaction between the unpaired electron in the HOMO and an electron from the $7b_2$ orbital to account for the ionization band at 7.20 eV in the PE spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, the $7b_2$ orbital without exchange splitting would have to be located near 7.7 eV. Since the energy of the nonbonding $7b_2$ orbital is similar for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, its location can be approximated from the PE spectrum of $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$. Because the lowest IP in the titanium spectrum is at 8.22 eV, it is concluded that the exchange integral K ($7b_2$, $10a_1$) is probably too small to account for the 7.20 eV ionization band. However, this spin-exchange interaction is large enough to contribute to the diffuse nature of the band structure in the PE spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$. On the other hand, the magnitude of the exchange integral for the $9a_1$ orbital, K ($9a_1$, $10a_1$), is of the right order of magnitude to explain the origin of this ionization peak. If one takes into consideration that the error in K ($9a_1$, $10a_1$) may be as much as 20%, the $9a_1$ orbital prior to ionization is placed somewhere in the region between 8.0 and 8.6 eV. Since the ionization bands at 8.22 and 8.15 eV in the PE spectrum of $Ti(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ and $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, respectively, are quite similar in shape and magnitude, the $9a_1$ orbital in $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ is most likely located in the region from 8.2 to 9.0 eV. The diffuse structure of the PE spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ prevents an unambiguous assignment of the location of the singlet band.

Since the calculated exchange integral contains a substantial contribution from the Cl p_π orbitals, the magnitude of the observed exchange splitting in the case of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$ is related to the amount of Cl p_π character in the HOMO. Although the rationalization that has been used to explain the origin of the ionization peak at 7.20 eV is semiquantitative, at best, it is apparent that the Cl p_π character in the HOMO is of the order of 20%. Not only is this result compatible with the results of the EPR studies and the approximate molecular orbital calculations but it provides experimental evidence for ligand p_π character in the HOMO in these $M(\eta^5\text{-}C_5H_5)_2L_2$ systems.

Conclusions

Table IV summarizes some of the important information obtained from the X-ray structure determinations, the electron paramagnetic resonance studies, and the nonparameterized (Fenske-Hall)-type molecular orbital calculations performed on $M(\eta^5\text{-}C_5H_5)_2S_5$ and $M(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, where M = Ti, V. An examination of these data shows an internal consistency with regard to the orbital character of the unpaired electron in the HOMO of the d^1 V(IV) complexes.

The consequence of adding an electron to the LUMO of each d^0 Ti(IV) complex by a transmutation to the V(IV) analog is demonstrated by a dramatic decrease in the L–M–L bond angle. The fact that the L–V–L bond angle is ca. 6° less than the corresponding L–Ti–L bond angle led to

Table IV. Summary of X-Ray, EPR, and MO Results

	$M(\eta^5\text{-}C_5H_5)_2S_5$		$M(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$	
	Ti	V	Ti	V
L–M–L (deg)	95	89	93	87
M–L (Å)	2.43 (av)	2.46 (av)	2.36 (av)	2.40
	$\Delta = +0.03$ Å		$\Delta = +0.04$ Å	
$M-C_5H_5$ (cent) (Å)	2.06	1.97	2.07	1.99
M–C (Å)	2.38 (av)	2.30 (av)	2.37 (av)	2.32 (av)
	$\Delta = -0.08$ Å		$\Delta = -0.05$ Å	
A_{iso}		(–)64.8 G		(–)74.5 G
$3d_{z^2}/3d_{x^2-y^2}$ (EPR)		$(-0.963)^2/(0.270)^2 = 12.7$		$(-0.976)^2/(0.218)^2 = 20.0$
$3d_{z^2}/3d_{x^2-y^2}$ (MO)		$(0.501)/(0.066) = 7.7$		$(0.676)/(0.033) = 20.5$
% metal character[a]		58.2		71.7
% ligand L character[b]		37.4		23.1
% C_5H_5 character[c]		4.4		4.9

[a] The sum of vanadium 3d, 4s, and 4p characters for the HOMO. [b] The sum of the 3s and 3p characters for the HOMO from either the five sulfur atoms of the pentasulfide ligand or the two chlorine atoms. [c] The sum of the characters for the HOMO from the localized a_2, e_1, and e_2 orbitals on the cyclopentadienyl ligands.

our initial rejection[15a,23] of the Ballhausen-Dahl bonding model[42] for $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes. From covalent radii considerations (viz., Ti, 1.32 Å vs. V, 1.22 Å)[43] the V-L and V-C distances would be expected to be nearly 0.1 Å *shorter* than the corresponding Ti-L and Ti-C distances. Although the M-C bond lengths follow this trend, the V-L bond lengths instead are 0.03-0.04 Å longer than their Ti-L counterparts. Hence, the crystallographic data indicate that the unpaired electron in each vanadium complex occupies a MO which has significant *antibonding* L ligand character but relatively little cyclopentadienyl character. This evidence is substantiated by the MO calculations which for the HOMO estimate the per cent cyclopentadienyl ligand character of each vanadium complex to be only ca. 5% compared to substantial L ligand character of 37.4% for the entire pentasulfide group and 23.1% for the two chlorine atoms; furthermore, the major components of the HOMO in each molecule give via an overlap-population analysis a small but highly significant antibonding contribution to the M-L bonds. The greater ligand character for $V(\eta^5\text{-}C_5H_5)_2S_5$ is in harmony with the lower ^{51}V isotropic coupling constant of (–)64.8 G for the solution EPR spectrum of $V(\eta^5\text{-}C_5H_5)_2S_5$ compared to that of (–)74.5 G for the solution EPR spectrum of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$.

The electron-density contour maps of the *xy* and *yz* planes (Figures 3b and 3c) also support the structural data that the unpaired electron must be primarily associated with the ML_2 fragment. The unpaired electron density lies mainly along the *z* direction (i.e., normal to the plane bisecting the L-V-L angle). This density distribution is compatible from electron-electron repulsion arguments with the observed decrease of the L-M-L bond angle as the number of d electrons in the HOMO is increased from 0 to 1 to 2. The remarkable agreement for each vanadium complex between the ratio of the relative per cent $3d_{z^2}$ to $3d_{x^2-y^2}$ metal orbital character obtained from the EPR data and the corresponding ratio determined from the MO calculation provides convincing evidence for the validity of the results.

A delocalization of the unpaired electron onto the L ligands was further indicated from the interpretation of photoelectron spectra obtained for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, which possesses *two* low-energy ionization bands rather than only one due to the unpaired electron. These additional bands arise from the ionization of a nondegenerate filled orbital, which leads to additional ion states through a spin-exchange interaction. The magnitude of the exchange splitting is related directly, in the case of $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$, to the amount of Cl p_π character in the HOMO. Since the magnitude of the calculated exchange integral K ($9a_1$, $10a_1$), which was computed to be ca. 2.1 eV, is in reasonable agreement with the observed splitting, the per cent ligand Cl p_π character is of the order of 20% for $V(\eta^5\text{-}C_5H_4CH_3)_2Cl_2$.

The consistency of the approximate (Fenske-Hall)-type MO calculations with the EPR and PES interpretations is most gratifying, especially when one considers the difficulties which would confront other approximate methods in their treatment of such transition metal complexes. The confidence gained in this method has provided the opportunity to extend our understanding of the bonding in $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes beyond that of the metal orbital character in the HOMO of the V(IV) complexes. Not only have these calculations allowed us to estimate the amount of the ligand character in the HOMO but also they have provided a sound theoretical foundation from which to correlate the experimental data.

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Supplementary Material Available. The wave functions and the atomic coordinates used in the molecular orbital calculations and their results will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to the code number JACS-75-6433.

References and Notes

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(17) For $Mo(\eta^5\text{-}C_5H_5)_2H_2$ the MO calculations, based on the molecular parameters from a photographic X-ray diffraction study[15h] which furnished the coordinates of only the nonhydrogen atoms, were performed with three different sets of values for the average Mo–H bond distance and the H–Mo–H bond angle in that the position of the two hydrogen atoms coordinated to the Mo atom were not determined by neutron diffraction prior to our original MO calculations. From stereochemical considerations, we initially carried out a calculation based upon: (a) a Mo–H distance of 1.75 Å and a H–Mo–H bond angle of 82°. However, a subsequent report[18] detailing large-scale syntheses of both the molybdenum and tungsten cyclopentadienyl dihydrides cited a Mo–H distance of 1.96 ± 0.1 Å from the preliminary (unpublished) results by A. K. Cheetham of a neutron powder diffraction investigation of $Mo(\eta^5\text{-}C_5H_5)_2D_2$. Although an earlier ir study (H. P. Fritz, Y. Hristidu, H. Hummel, and R. Schneider, *Z. Naturforsch., Teil B*, **15**, 419 (1960)) of both the molybdenum and tungsten cyclopentadienyl dihydride molecules and their protonated species led to an estimation of 100–115° for the H–Mo–H bond angle, the L–M–L bond angles typically found by later crystallographic analyses for d^2 M(IV) $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes with two identical nonhydridic L ligands ranged from only 80 to 83°. Hence, in order to investigate the sensitivity of the Mo–H bond distance and the H–Mo–H bond angle on the calculated metal orbital composition of the HOMO, we repeated the calculations with the following two pairs of molecular parameters: (b) Mo–H, 1.96 Å; H–Mo–H, 82°; and (c) Mo–H, 1.96 Å; H–Mo–H, 100°. We later found that a recent publication by Prout and coworkers[15g] on the crystallographic data of a large number of $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes cites the structural analysis of $Mo(\eta^5\text{-}C_5H_5)_2D_2$ by Cheetham with both a Mo–D distance of 1.96 Å and a D–Mo–D angle of 83.2° being given. A single-crystal neutron diffraction study of either the hydride or deuteride molecule is deemed highly desirable in order to obtain more precise molecular parameters.

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(27) The contributions from the other d orbitals to the HOMO for the molecules with less than C_{2v}-2*mm* symmetry are negligible.

(28) The necessary transformations for the d_{z^2} and $d_{x^2-y^2}$ orbitals are $d_{z'^2} = -0.500d_{z^2} + 0.866d_{x^2-y^2}$ and $d_{x'^2-y'^2} = -0.866d_{z^2} - 0.500\,d_{x^2-y^2}$.

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(30) The following relationship was used to calculate the overlap population between two atoms i and j in the mth molecular orbital containing N_m electrons:

$$\mathrm{OP} = 2N_m \sum_i \sum_j C_{im} C_{jm} S_{ij}$$

where i refers to metal atomic d orbital (i), j refers to ligand atomic p orbital (j), m refers to the molecular orbital of interest, C_{im} is the coefficient of the ith AO in the mth MO, and S_{ij} is the overlap between i and j.

(31) This same crystallographic bond-length trend in M–L distances was observed by Prout and coworkers[15g] for a large number of second-row transition metal $M(\eta^5\text{-}C_5H_5)_2L_2$ complexes and was attributed by them to steric repulsions. One striking example is between the parent d^2 Mo(IV) $Mo(\eta^5\text{-}C_5H_5)_2Cl_2$ molecule and its d^1 Mo(IV) monocation, for which the Mo–Cl bond length of the monocation is 0.1 Å shorter whereas the Mo–C_5H_5 bond lengths remain unchanged.[15g]

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