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THE CRYSTAL STRUCTURE OF DICYCLOPENTADIENYLVANADIUM MONOCHLORIDE AND ITS IMPLICATIONS FOR THE STRUCTURES OF OTHER d^2 DICYCLOPENTADIENYL COMPOUNDS

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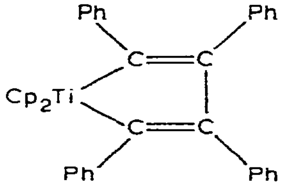
Summary

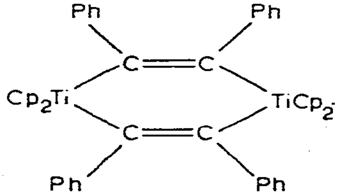
The crystal structure of dicyclopentadienylvanadium(III) monochloride, $(\eta^5\text{-}C_5H_5)_2VCl$, has been solved by the X-ray diffraction heavy atom method. The compound crystallizes in the orthorhombic space group $Ama2$ with cell parameters a 9.134(8), b 13.522(10), and c 7.484(6) Å; ρ_{obs} 1.55(1) g/cm^3, ρ_{calc} 1.56 g/cm^3 for $Z = 4$. Full matrix least squares refinement based on 760 reflections lead to agreement factors of $R = 0.054$ and $R_w = 0.069$. The structure confirms that $(\eta^5\text{-}C_5H_5)_2VCl$ is monomeric in contrast to $[(\eta^5\text{-}C_5H_5)_2ScCl]_2$ and $[\eta^5\text{-}C_5H_5)_2TiCl]_2$, which are dimeric. In the solid state the molecule possesses a crystallographic mirror plane of symmetry. The chlorine atom resides symmetrically in the open face of the $(\eta^5\text{-}C_5H_5)_2V^+$ group with a V—Cl bond distance of 2.390(4) Å. The average vanadium to carbon interatomic distance is 2.28(2) Å. The structure is discussed in terms of the electronic properties of d^2 compounds with structures $(\eta^5\text{-}C_5H_5)_2VX$ and $[\eta^5\text{-}C_5H_5)_2VY_2]^+$.

Introduction

There are a number of striking differences in the structural and chemical behavior of the dicyclopentadienyl compounds of vanadium and titanium. Vanadocene is a stable chemical species in the absence of oxygen and water, while the C—H bonds of the cyclopentadienyl groups of titanocene are much more susceptible to oxidative addition [1]. Titanium(II) compounds react with diphenylacetylene to give a metallocycle (I) [2,3] and, under different conditions to give a dimeric complex, probably the cyclic compound II [4], while vanadocene [5] forms a π adduct III.



(I)



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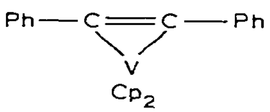

(III)

where Cp is the cyclopentadienyl anion ($C_5H_5^-$). The synthetic work of De Liefde Meijer, Teuben, and coworkers showed that, unlike titanium which readily forms compounds of the composition $(\eta^5\text{-}C_5H_5)_2TiR_2$, where R is one of many alkyl or aryl groups, vanadium prefers stable 16 electron products of the type $(\eta^5\text{-}C_5H_5)_2VR$ as shown below [6—8]:

$$(\eta^5\text{-}C_5H_5)_2TiCl_2 + (2\ LiR\ \text{or}\ 2\ NaR\ \text{or}\ 2\ MgRX) \rightarrow (\eta^5\text{-}C_5H_5)_2TiR_2$$

$$(\eta^5\text{-}C_5H_5)_2VCl + (LiR\ \text{or}\ MgRX) \rightarrow (\eta^5\text{-}C_5H_5)_2VR$$

$$(\eta^5\text{-}C_5H_5)_2VCl_2 + (2\ LiR\ \text{or}\ 2\ MgRX) \rightarrow (\eta^5\text{-}C_5H_5)_2VR$$

Several investigations have indicated that $(\eta^5\text{-}C_5H_5)_2VCl$ (Fig. 1) is not isostructural with $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ and $[(\eta^5\text{-}C_5H_5)_2ScCl]_2$, which are dimeric with bridging chlorine atoms as shown in Fig. 2 [9,10]. For example, Fischer et al. have demonstrated by means of cryoscopic molecular weight studies that $(\eta^5\text{-}C_5H_5)_2VCl$ is monomeric in a benzene solution [11]. An understanding of the structural and bonding details of low valent titanium and vanadium compounds could provide insights into these chemical differences.

One factor that has been considered important in explaining the variations between the chemistry of titanium and vanadium is that vanadium has a 10% smaller atomic radius. It has been proposed that $(\eta^5\text{-}C_5H_5)_2TiR_2$ is stable, but that the smaller vanadium atom can accommodate only one R group as in $(\eta^5\text{-}C_5H_5)_2VR$. The smaller size of vanadium relative to titanium may be important in determining the difference in chemical properties in the above examples, but the report that complexes such as $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]Cl$, $[\eta^5\text{-}C_5H_5)_2V(CO)(PBu_3)]Cl$, $[(\eta^5\text{-}C_5H_5)_2V(CNC_6H_{11})_2]BPh_4$ and $[(\eta^5\text{-}C_5H_5)_2$-

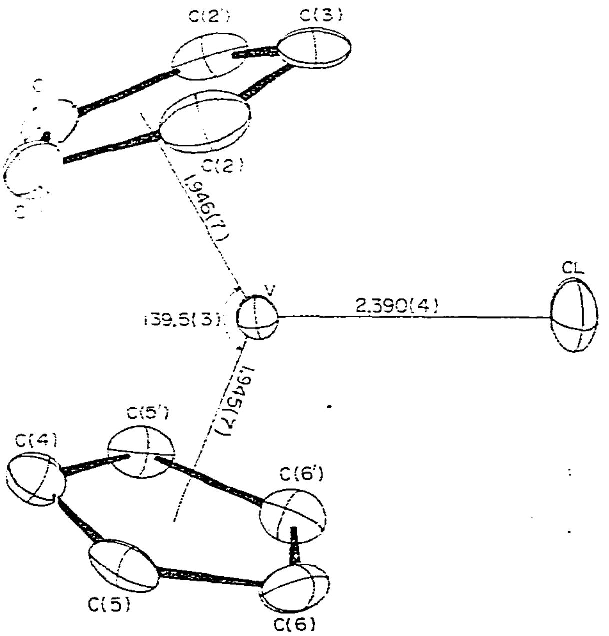

Fig. 1. Drawing of the structure of $(\eta^5\text{-}C_5H_5)_2VCl$.

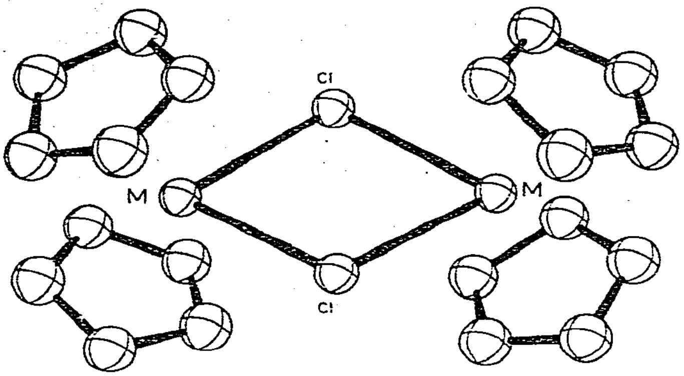

Fig. 2. The dimeric structure for $[(\eta^5\text{-}C_5H_5)_2ScCl]_2$ and $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$.

$V(Ph_2PCH_2CH_2PPh_2)]BPh_4$ exist and are isolable from solution is surprising in view of the bulkiness of the ligands in these compounds compared to Cl [13].

We have recently studied the electronic and structural properties of $(\eta^5\text{-}C_5H_5)_2$Ti(azobenzene) and $(\eta^5\text{-}C_5H_5)_2VY$ where Y is PhC≡CPh and PhN=NPh [14]. We also have examined in detail the magnetic and structural properties of $[(\eta^5\text{-}C_5H_5)_2TiX]_2$ (X = Cl or Br) [10a] and $[(\eta^5\text{-}C_5H_5)_2Ti]_2MCl_4$ (M = Be, Mn, and Zn) [10b, c]. As part of our continuing investigations into the stereochemistry and electronic properties of early transition metal organometallic compounds and the relative contributions of steric vs. electronic effects in dicyclopentadienylmetal derivatives, we report here the structural properties of $(\eta^5\text{-}C_5H_5)_2VCl$.

Experimental

Synthetic work with $(\eta^5\text{-}C_5H_5)_2VCl$ was carried out in a Vacuum Atmospheres dry box in a helium atmosphere. Solvents were distilled under a nitrogen atmosphere from sodium and benzophenone. Thallium(I) cyclopentadienide was prepared by the method of Cotton and Reynolds [15]. Vanadium trichloride was prepared by the method outlined by Brauer [16]. Commercial VCl_3 (Alfa) was sufficiently contaminated with VCl_2 to produce large quantities of vanadocene which greatly reduced the yield of the desired $(\eta^5\text{-}C_5H_5)_2VCl$. The University of Illinois Chemistry Microanalytical Laboratory performed all elemental analyses. Magnetic susceptibilities were run by the Faraday method using a balance described by Evans [17]. Diamagnetic corrections were based on published values [18]. Computer calculations were performed using the Sigma 5 Computer at the Materials Research Laboratory at the University of Illinois.

$(\eta^5\text{-}C_5H_5)_2VCl$ was synthesized by a modification of Manzer's procedure [19]. Ten grams (63.5 mmol) of VCl_3 were stirred with 35.0 g (130 mmol) of freshly sublimed thallium(I) cyclopentadienide in 250 ml of THF for 5 h at 55°C in a dry box. The blue solution was filtered, first through a coarse filter frit, and then through a medium frit to remove all thallium(I) chloride. The volume of the solution was reduced to 25 ml at reduced pressure, and the solution was heated to reflux. Upon slow cooling, lustrous blue plates of oxygen sensitive $(\eta^5\text{-}C_5H_5)VCl$ formed. The solution was filtered and the plates were washed with heptane. The filtered solution of approximately 15 ml of THF and 5 ml heptane was heated to reflux and slowly cooled. Dark blue prisms were obtained from the solution over a period of four days, and were used for the structure determination. (Found: C, 55.34; H, 4.61; Cl, 16.32. $C_{10}H_{10}VCl$ calcd.: C, 55.46; H, 4.65; Cl, 16.37%.) The total yield was 93%. The magnetic moment was measured by the Faraday technique [18] and found to be 2.80(5) BM on a powdered sample.

Twelve of the dark blue crystals were mounted in thin-walled capillary tubes and sealed under helium. Most of these crystals were examined by X-ray diffraction and an irregularly shaped crystal with dimensions, 0.48 × 0.35 × 0.54 mm was chosen for the structural analysis. Preliminary precession photographs indicated that the crystal was orthorhombic and systematic absences narrowed the possible space groups to either $Cmc2_1$, $Ama2$, or $Cmcm$ [20]. An N(Z) test [21] indicated that the structure is non-centrosymmetric, eliminating the space group $Cmcm$. The final structural solution was solved using the space group $Ama2$ (see below). The systematic extinctions were hkl, $k + l = 2n + 1$ and $h0l$, $h = 2n + 1$. The density was determined by flotation in a carbon tetrachloride/chloroform solution to be 1.55(1) g/cm^3, in good agreement with the calculated value of 1.556 g/cm^3, and requires 4 molecules per unit cell. Intensity data were collected on a Picker four circle diffractometer using Mo-K_α radiation. The crystal was mounted with its [001] axis parallel to the axis of the capillary. Reflections were scanned at 2°/min with a take-off angle of 1.6°. Three standard peaks were monitored every 100 reflections. During the course of data collection, the standards remained within 2.5% of the average with no apparent trend in the variations. The cell parameters were determined from a least squares refinement of 22 hand-centered reflections. A total of 760 reflections was collected with a 2θ angle between 2 and 55 degrees. Of the 760 reflections used in the refinement, 729 were considered observed using the criteria $I_{obs} > 3\ \sigma_c(I)$. The absorption ($\mu = 13.50$ cm^{-1}) was small enough so that no absorption corrections were considered necessary. The maximum error in the intensity data due to the neglect of the absorption correction was estimated to be ±8%.

The structure was solved by the standard heavy atom method. A Patterson map was calculated and found to be consistent only with the space group, $Ama2$. After placement of the vanadium and chlorine atoms, a Fourier map showed the positions of the carbon atoms *. With all atoms in place and using isotropic temperature factors, the discrepancy factors were $R_w = 0.21$ and $R = 0.32$. When all the carbon positions were refined anisotropically by repeated least squares, R was lowered slowly to 0.098 and R_w to 0.10 [22]. The positions of the hydrogen atoms were calculated and each hydrogen atom was given an isotropic temperature factor one unit larger than that of the isotropically refined carbon atom to which it was attached. After two cycles of refinement of the non-hydrogen atoms, new hydrogen atom positions were calculated and further refinement showed no positional changes. The final R factor was 0.054 and R_w was 0.069. The final difference Fourier map showed that the largest residual peak was 0.42 e/Å^3. The standard deviation in the atomic positions and temperature factors

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* $R = \Sigma[|F_0| - |F_c|]/\Sigma|F_0|]$ and $R_w = [\Sigma w||F_0| - |F_c||^2\ \Sigma w|F_0|^2]^{1/2}$. Least-squares refinements were based on the minimization of $\Sigma w||F_0| - |F_c||^2$.

were calculated using the program ORFEE [23] and the structure was drawn using the program ORTEP [24].

Results and discussion

The crystal structure determination is the first for a dicyclopentadienylvanadium(III) compound and confirms that $(\eta^5\text{-}C_5H_5)_2VCl$ is monomeric. The chlorine atom resides symmetrically in the open face created by the tilting cyclopentadienyl rings as shown in Fig. 1.

Crystal data, bond distances, bond angles and parameters of $(\eta^5\text{-}C_5H_5)_2VCl$ are given in Tables 1—6. The vanadium atom is located on a crystallographic mirror plane which contains the vanadium, chlorine, carbon(3), and carbon(4) atoms. The cyclopentadienyl rings are staggered and show no disorder. The average V—C distance is 2.28(2) Å with a range from 2.26(1) to 2.30(1) Å. The cyclopentadienyl groups shown no deviation from planarity with a Cp—V—Cp angle of 139.5(3)°, where Cp is the cyclopentadienyl anion. The V—Cl distance is 2.390(4) Å and compares favorably with similar metal—chlorine bond distances shown in Table 7.

The similarity of the V—Cl bond distance in $(\eta^5\text{-}C_5H_5)_2VCl$ (2.390(4) Å) with that in $(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$ (2.398(2) Å) provides an example of the interplay between electronic and steric factors in bonding *. In contrast to the general trend of dicyclopentadienylmetal compounds where the metal—ligand distance increases significantly as the number of *d* electrons at the metal center increases [25—27,36], there is very little difference between the above two bond lengths. The bond shortening effects due to decreased coordination number of $(\eta^5\text{-}C_5H_5)_2VCl$ ** offsets the bond lengthening factor of the increased antibonding contribution in the V^{III}—Cl bond vs. the V^{IV}—Cl bond.

The structural results can be readily understood in terms of the molecular orbitals of the $(\eta^5\text{-}C_5H_5)M^{n+}$ fragment where M is the metal atom overlapping with appropriate ligand orbitals. This approach of looking at the bonding in key metal and ligand orbitals has been used successfully by Hoffmann in the study of several trends in dicyclopentadienylmetal compounds [26]. Figure 3 shows the shapes of the important bonding orbitals with the lowest energy orbital being the $1a_1$ according to Hoffmann's calculations. A qualitative energy diagram is presented in Fig. 4. The more detailed calculations and photoelectron spectroscopy work of Dahl, Fenske, and coworkers [25,27] are in agreement with the ordering of energy levels. From the experimental magnetic moment of 2.80(5) BM, it is apparent that dicyclopentadienylvanadium monochloride has two unpaired electrons which occupy the $1a_1$ and b_2 orbitals as shown in Fig. 4. The observed structure is fully consistent with this molecular orbital interpretation. The chlorine atom resides between the occupied lobes of the b_2

(continued on p. 50)

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* We note that the substitution of methylcyclopentadiene for cyclopentadiene has only a minor effect on the M—Cl interatomic distance. (See Table 7, for examples.)

** Recently authors have shown renewed interest in the empirical relationship proposed by Pauling for relating bond distance to coordination number for complexes with the same metal and ligands. The formula $R_{II}/R_I = (CN_{II}/CN_I)^{1/9}$, where R_I and CN_I are the bond length and coordination of the first complex and R_{II} and CN_{II} are those for the second, quantifies the general trend that bond distance decreases with decreasing coordination number [39].

TABLE 1

CRYSTAL DATA FOR $(\eta^5\text{-}C_5H_5)_2VCl$

Compound $(\eta^5\text{-}C_5H_5)_2VCl$
Crystal system orthorhombic
Space group *Ama*2 (non-centrosymmetric)
$R = 0.054$; $R_w = 0.069$
Cell parameters *a* 9.134(8), *b* 13.522(10), *c* 7.484(6) Å
$Z = 4$ molecules/unit cell
Density observed 1.55(1) g/cm^3; calculated 1.556 g/cm^3
Wavelength 0.71069 Å (Mo-K_α)
Reflections 760 of which 729 were observed ($I_{obs} > 3\ \sigma(I)$)
Linear absorbtivity $\mu = 13.5$ cm^{-1}

TABLE 2

INTERATOMIC BOND DISTANCES FOR $(\eta^5\text{-}C_5H_5)_2VCl$

Atoms	Distances (Å)	Atoms	Distances (Å)
V—Cl	2.390(4)	C(1)—C(1′)	1.384(16)
V—C(1)	2.266(7)	C(1)—C(2)	1.379(12)
V—C(2)	2.270(8)	C(2)—C(3)	1.390(12)
V—C(3)	2.296(10)	C(4)—C(5)	1.402(11)
V—C(4)	2.261(11)	C(5)—C(6)	1.408(11)
V—C(5)	2.293(7)	C(6)—C(6′)	1.404(15)
V—C(6)	2.285(7)	average C—C	1.394(12)
average V—C	2.278(15)		

TABLE 3

INTERATOMIC BOND ANGLES

Angles	Angle (degrees)
Cp—V—Cp	139.5(3)
C(1′)—C(1)—C(2)	107.9(6)
C(1)—C(2)—C(3)	108.7(9)
C(2)—C(3)—C(2′)	106.8(9)
C(5)—C(4)—C(5′)	111.2(9)
C(4)—C(5)—C(6)	105.6(7)
C(5)—C(6)—C(6′)	108.9(5)

TABLE 4

DEVIATION OF CYCLOPENTADIENE RINGS FROM PLANAR

Atom	Distance (Å)	Atom	Distance (Å)
C(1)	−0.002	C(4)	−0.001
C(1′)	−0.002	C(5)	0.001
C(2)	−0.005	C(5′)	0.001
C(2′)	−0.005	C(6)	0.000
C(3)	0.006	C(6′)	0.000

TABLE 5

POSITIONAL PARAMETERS FOR ATOMS IN $(\eta^5\text{-}C_5H_5)_2VCl$

Atom	x	y	z
V	0.2500	0.2621(1)	0.0000
Cl	0.2500	0.2543(2)	0.3191(4)
C(1)	0.1743(9)	0.1579(5)	−0.2182(11)
C(2)	0.1279(10)	0.1194(11)	−0.0572(13)
C(3)	0.2500	0.0940(7)	0.0435(20)
C(4)	0.2500	0.3751(7)	−0.2226(18)
C(5)	0.1233(8)	0.3922(5)	−0.1213(13)
C(6)	0.1732(8)	0.4206(5)	0.0492(12)
H(1)	0.1131	0.1805	−0.3125
H(2)	0.0284	0.1114	−0.0209
H(3)	0.2500	0.0650	0.1593
H(4)	0.2500	0.3549	−0.3443
H(5)	0.0248	0.3855	−0.1592
H(6)	0.1126	0.4377	0.1479

TABLE 6

ANISOTROPIC THERMAL PARAMETER FOR THE NONHYDROGEN ATOMS IN $(\eta^5\text{-}C_5H_5)_2VCl$

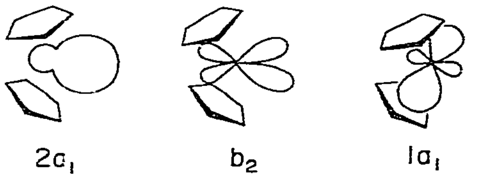
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	0.0097(2)	0.0028(1)	0.0082(3)	0.0000	0.0000	0.0001(3)
Cl	0.0241(7)	0.0076(3)	0.0086(6)	0.0000	0.0000	0.0001(3)
C(1)	0.0189(14)	0.0038(4)	0.0135(15)	−0.0014(6)	−0.0032(13)	−0.0016(7)
C(2)	0.0212(19)	0.0039(4)	0.0251(25)	−0.0025(7)	−0.0018(17)	−0.0025(8)
C(3)	0.0447(42)	0.0014(5)	0.0204(37)	0.0000	0.0000	0.0001(10)
C(4)	0.0205(22)	0.0036(6)	0.0163(25)	0.0000	0.0000	0.0026(10)
C(5)	0.0070(9)	0.0049(4)	0.0239(20)	0.0000(5)	−0.0094(14)	0.0028(8)
C(6)	0.0116(10)	0.0039(4)	0.0227(23)	0.0014(5)	0.0054(13)	−0.0007(7)

TABLE 7

SELECTED BOND DISTANCES AND ANGLES FOR RELATED COMPOUNDS

Compound	d electrons	M—Cl distance (Å) [a]	M—Cp distance (Å) [a]	Cl—Cl distance (Å) [a]	Cl—M—Cl distance angle [a]	Ref.
$(\eta^5\text{-}C_5H_5)_2TiCl_2$	d^0	2.364	2.06	3.47	94.53	35
$(\eta^5\text{-}C_5H_4CH_3)_2TiCl_2$	d^0	2.361	2.06	3.43	93.15	25
$[(\eta^5\text{-}C_5H_5)_2SeCl]_2$	d^0	2.584, 2.564	2.18	3.39, 3.31	82.0, 80.4	9
$[(\eta^5\text{-}C_5H_5)_2TiCl]_2$	d^1	2.545, 2.537	2.05	3.20, 3.16	78.40, 77.11	10
$[(\eta^5\text{-}C_5H_4CH_3)_2TiCl]_2$	d^1	2.547	2.06	3.25	79.19	10
$(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$	d^1	2.398	1.99	3.30	87.06	25
$(\eta^5\text{-}C_5H_5)_2VCl$	d^2	2.390	1.946			this work

[a] Indicates an average value if there is more than one value for this parameter. Rows with more than one entry for a compound indicates that two crystallographically unique species exist and they are reported independently.



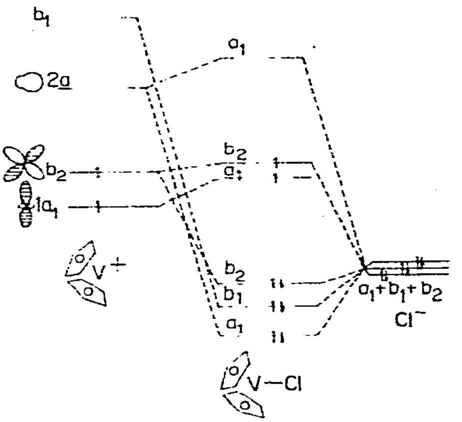
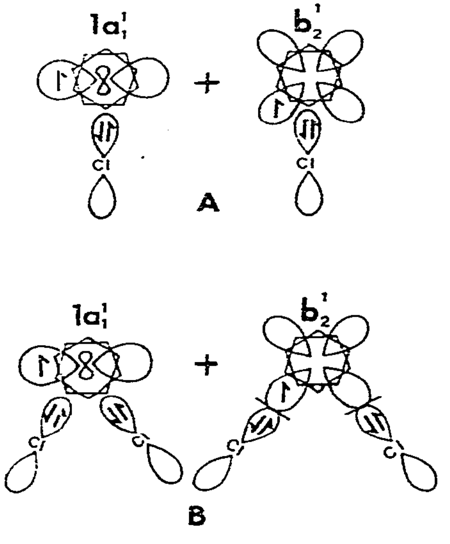


Fig. 3. The bonding orbitals for the fragment Cp_2M as determined by Hoffmann [26] placed in order of energy decreasing left to right.

Fig. 4. Proposed molecular orbital diagram for $(\eta^5\text{-}C_5H_5)_2VCl$.

orbital and minimizes antibonding π^* repulsion between the vanadium and chlorine atoms while maximizing σ orbital overlap with the metal $2a_1$ orbital (see Fig. 5A).

We may extend the diagram of d^2 high spin dicyclopentadienylmetal compounds to other metals and to other similar bonding ligands. Compounds such as



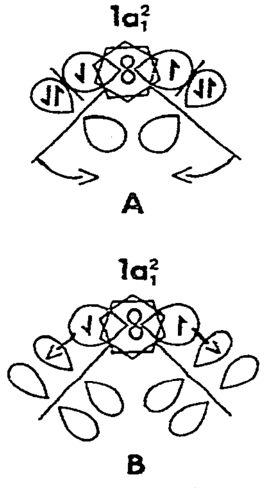


Fig. 5. Interaction of σ bonding ligands at two orientations with the occupied $1a_1$ and b_2 orbitals of dicyclopentadienylvanadium(III) as viewed looking down the axis of the cyclopentadiene rings. (A) The observed bonding arrangement in dicyclopentadienylvanadium monochloride which minimizes ligand interaction with metal d electrons. (B) The unfavorable orientation showing repulsion between the ligand orbitals and the occupied metal b_2 orbital.

Fig. 6. The interaction of weakly and strongly π-acceptor ligands with the filled $1a_1$ orbital of dicyclopentadienylvanadium(III). (A) The unstable configuration of non-π-acceptor ligands whose nonbonding electrons destabilize the metal $1a_1$ orbital. (B) The observed bonding of π-acceptor ligands delocalizing charge from the metal $1a_1$ orbital.

$[(\eta^5\text{-}C_5H_5)_2VX]BPh_4$, where X is pyridine or acetone, are paramagnetic and should be isostructural with the chlorine compound reported in this paper [13]. Derivatives with the basic formula $(\eta^5\text{-}C_5H_5)_2VR$, where R is an alkyl or aryl group may be assumed to be structurally and electronically analogous to dicyclopentadienylvanadium monochloride [6—8]. A similar molecular orbital description has been applied in the examination of the interesting isoelectronic d^2 dimer $[(\eta^5\text{-}C_5(CH_3)_5)_2Ti]_2N_2$, where the connecting group is a nitrogen molecule [28].

We have discussed bonding in dicyclopentadienyl compounds with one ligand symmetrically placed in the open face of the tilted rings; however, it is possible that more than one ligand may fit in the open face to permit formation of the dimer. It is clear from Fig. 5B why $(\eta^5\text{-}C_5H_5)_2$ VCl does not form a dimer analogous to those of $[(\eta^5\text{-}C_5H_5)_2ScCl]_2$ and $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ with two chlorine atoms attached to each metal [9,10]. When the dicyclopentadienylvanadium fragment is in the configuration $1a_1^1b_2^1$, any dimer with two bridging chlorine atoms would result in the overlap of filled chlorine orbitals with the occupied metal b_2 orbital shown in Fig. 5B. This interaction yields a high energy molecular arrangement that would be expected to have a net antibonding bond order.

If the high spin d^2 configuration $1a_1^1b_2^1$ of dicyclopentadienylvanadium monochloride makes dimer formation energetically unfavorable, why does the molecule not assume the low spin configuration $1a_1^2b_2^0$ shown in Fig. 6A as a dimer with two bridging chlorine atoms? One reason why the dimer $[(\eta^5\text{-}C_5H_5)_2VCl]_2$ cannot form, even with the pairing of the two electrons in the $1a_1$ orbital, is the expected decrease in the Cl—Cl contact distance for the dimer suggested by Table 7. As electrons are placed in the metal $1a_1^1$ orbital shown in Fig. 6A, they increase the metal $1a_1$ to chlorine nonbonding electron repulsion and contribute to a decrease in the Cl—M—Cl angle [26,27]. For the d^0 dimer $[(\eta^5\text{-}C_5H_5)_2ScCl]_2$, the average Cl—Cl separation is 3.31 and 3.39 Å for the two crystallographically unique dimers while those for the d^1 metal case, $1a_1^1$, of $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ are shortened to 3.16 and 3.20 Å. If the trend were to continue to the hypothetical diamagnetic d^2 species, $1a_1^2$, $[(\eta^5\text{-}C_5H_5)_2VCl]_2$, the repulsion between the filled metal $1a_1^2$ and the nonbonding chlorine electrons would reduce the Cl—Cl distance to a value much less than the Van der Waals diameter for the chlorine atom (3.4—3.8 Å) [31]. The resulting electronic repulsion shown in Fig. 6A would destabilize dimer formation.

Even though the d^2 dimer of dicyclopentadienylvanadium monochloride cannot form, compounds of the type $[(\eta^5\text{-}C_5H_5)_2VX_2]^+$ have been prepared where X is a π-acceptor ligand such as carbon monoxide, nitriles, or phosphines [13]. Isoelectronic d^2 compounds such as dicyclopentadienyltitanium dicarbonyl are also known [32,33]. All these diamagnetic vanadium(III) and titanium(II) complexes have the configuration $1a_1^2b_2^0$. These results have been explained by the calculations of Hoffmann, who showed that the electrons can pair on the $1a_1$ orbital if the metal is able to delocalize charge by donation into the π^* orbitals of the ligands as shown in Fig. 6B [26]. Because the metal b_2 ororbital is unoccupied, two ligands can σ bond to the metal atom and the vanadium atom $1a_1$ orbital can back donate by overlap with the empty ligand π^* orbitals which are of the correct energy and symmetry.

In Fig. 7 we have generalized from the structure of dicyclopentadienylvanadium(III) compounds and from an understanding of the shapes of the metal $1a_1$ and b_2 orbitals to show how π-acceptor ability and structure are related. With strong π-acceptor ligands diamagnetic, pseudotetrahedral complexes, with the metal in the $1a_1^2b_2^0$ configuration are formed. Weak π-acceptor ligands produce pseudotriangular, paramagnetic complexes with the metal in the high spin $1a_1^1b_2^1$ configuration. This systematic approach also is applicable to the few isoelectronic dicyclopentadienyltitanium(II) compounds that have been prepared [9,11].

The relationship between ligand π-acceptor ability and geometry presented above and in Fig. 7 does not appear to apply in the second and third row d^2 dicyclopentadienylmetal compounds. Both of the compounds $[(\eta^5\text{-}C_5(CH_3)_5)_2ZrN_2]N_2$ and $(\eta^5\text{-}C_5H_5)_2MoCl_2$ have pseudotetrahedral structures and are diamagnetic regardless of the π-acceptor ability of their ligands [36,37]. Such behavior is possible because the larger atomic radii of these metal atoms reduce the antibonding interactions of the $1a_1^2$ orbital with the occupied ligand orbitals as shown in Fig. 6A.

One compound that appears to violate the trends outlined in Fig. 7 is the diamagnetic complex $(\eta^5\text{-}C_5H_5)_2VBH_4$ [34]. This molecule is an example of two non-π-acceptor ligands forming with the cyclopentadienyl rings a pseudotetrahedral environment about the metal. The fluxional behavior of the molecule can be slowed to indicate the presence of MH_2BH_2 ligation, where M is dicyclopentadienylvanadium(III). Because there are no nonbonding electrons on the bridging hydrogen atoms, the interaction shown in Fig. 6A between the filled $1a_1$ metal orbital and the nonbonding electrons is not a factor in determining molecular geometry.

Mixed ligand complexes such as $[(\eta^5\text{-}C_5H_5)_2V(CO)(P(CH_2CH_3)_3)]BPh_4$ have been reported and are diamagnetic [29]. Compounds with two different ligands such as $[(\eta^5\text{-}C_5H_5)_2V(CO)(\text{pyridine})]BPh_4$ and $(\eta^5\text{-}C_5H_5)_2V(CO)I$ in which one ligand is a weaker π-acceptor appear to achieve enough delocalization of the metal charge onto carbon monoxide to exist and to form diamagnetic complexes [13,29]. When attempts are made to prepare the mixed ligand product $(\eta^5\text{-}C_5H_5)_2V(CO)(R)$ where R is a methyl or benzyl group by treating $(\eta^5\text{-}C_5H_5)_2VR$ with carbon monoxide, the insertion product $(\eta^5\text{-}C_5H_5)_2V(CO)$-

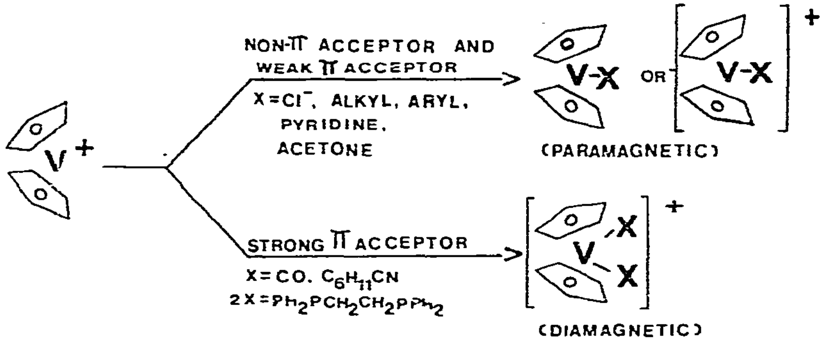
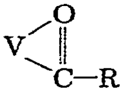


Fig. 7. Two types of ligand arrangement observed in dicyclopentadienylvanadium(III) compounds and their relation to ligand π-acceptor ability.

(COR) is recovered [38]. One factor that contributes to drive the insertion reaction is the expected instability of the intermediate $(\eta^5\text{-}C_5H_5)_2V(CO)(R)$. This reactivity arises from the non-existent π-acceptor ability of the R group and its inability to aid the carbon monoxide molecule in delocalizing electron density from the $1a_1^2$ orbital of the vanadium atom. The intermediate $(\eta^5\text{-}C_5H_5)_2V(CO)(R)$ can be stabilized by dissociation of a carbon monoxide molecule or by inserting the carbon monoxide molecule into the V—R bond. The acyl group is a π-acceptor ligand, and when another molecule of carbon monoxide is added to give a tetrahedral structure, the two π-acceptors greatly stabilize the product $(\eta^5\text{-}C_5H_5)_2V(CO)(COR)$. From the low frequency of the acyl CO stretch reported in the infrared spectra, 1605 cm^{-1} when R is methyl and 1615 cm^{-1} when R is benzyl, it is likely that the acyl group may enhance its π-acceptor ability by partially side-bonding to the vanadium atom so that there is some  interaction [38] *.

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