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Preparation and structure of half-open vanadocene, $V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)CO$

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Abstract

The half-open vanadocene, $V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)CO$, was obtained by the reaction of $V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)PMe_3$ with CO in petroleum ether at room temperature. Its crystal structure was determined by X-ray diffraction technique. The crystal was monoclinic with space group $P2_1/n$, $a = 16.614(3)$, $b = 7.636(1)$, $c = 19.128(6)$ Å, $\beta = 99.92(2)°$, $V = 2390.5(9)$ Å^3, and $Z = 8$. The final R value was 0.043. The V(1)–C_{PD}(1) (half) (PD = $2,4\text{-}(CH_3)_2C_5H_5$) bonds were shorter (0.038 Å) than the V(1)–C_{CP}(1) (half) (CP = C_5H_5) bonds, averaging 2.224(4) *versus* 2.262(4) Å, respectively. $V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)CO$ has been characterized by IR and EPR methods.

Introduction

Cyclopentadienyl ligands have proven to be invaluable in the field of organometallic chemistry, largely due to their robust binding to metals, which allows them to function as superb "stabilizing ligand" [1]. The open pentadienyl ligands have become important because these open ligands can be both more strongly bound and more reactive than their cyclic counterparts [2]. Although the open metallocenes have provided some very interesting comparisons with the metallocenes, it is clear that direct comparisons between open metallocene and metallocene are, in various aspects, not possible due to their different steric and symmetry environments, and further complications may result from differing spin configurations. In order to circumvent such problems, and to allow for more direct comparisons, a series of half-open metallocenes have been synthesized [3–6]. In half-open metallocenes, one pentadienyl and one cyclopentadienyl ligand are both present. In such complexes, the steric, symmetry, and spin complications men-

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tioned above are eliminated, so that only relative ligand sizes and orbital energies remain as likely differentiating parameters. Additional experimental and theoretical studies are necessary to gain further insight into half-open metallocenes. The preparation and structural characterization are reported here.

Experimental

All operations involving organometallic syntheses and crystallization were carried out under an atmosphere of prepurified nitrogen in the Schlenk apparatus or in a glovebox. Non-aqueous solvents were thoroughly dried and deoxygenated by Na/K and benzophenone, and were distilled under nitrogen immediately prior to use. IR spectra were measured with a Nicolet 7199 spectrophotometer. EPR spectra were measured with a ER-200D spectrometer.

Preparation of $V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)CO$

$V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)CO$ was prepared as described in the literature [3]. A solution containing 10 mmol $[(C_5H_5)VClPMe_3]_2$ [7] in 100 ml THF (−20°C) and 10 mmol $K[2,4\text{-}(CH_3)_2C_5H_5]$ in 50 ml THF was added dropwise with stirring. The mixture was allowed to warm to room temperature and stirred overnight to give a golden-brown solution. After the solvent was removed *in vacuo*, the product was extracted with three 30 ml portions of petroleum ether. The combined golden extracts were filtered under nitrogen. Bubbling CO through the golden solution led to the formation of a deep-green solution. The deep-green solution was filtered, concentrated to 30 ml *in vacuo* and cooled to −75°C, yielding a green, air-sensitive crystalline product. Anal. Found: C, 64.76; H, 6.99. $C_{13}H_{16}OV$ calc.: C, 65.27; H, 6.74%.

Determination of crystal structure

A suitable crystal ($3 \times 5 \times 8$ mm^3) was selected and wedged into a thin walled glass capillary and sealed under nitrogen. It was mounted on a Nicolet XRD R3 four-circle diffractometer to collect the intensity data at room temperature; 4060 unique intensity data within the range of $3° \leq 2\theta \leq 50°$ were collected with graphite-monochromated Mo-K_α radiation and ω scan mode; 2584 reflections with $I \geq 2.5\sigma(I)$ were considered to be observed. The intensity data were corrected and reduced by applying the LP factor and empirical absorption. The structure was solved using the heavy atom method. The coordinates of the V atom derived from the Patterson analysis were used to calculate the Fourier map. Successive Fourier syntheses gave the positions of all atoms (including hydrogen atoms). Several cycles of block-diagonal least-squares refinement led to a final value of $R = 0.043$. All calculations were performed using the SHELXTL programs.

Results and discussion

Crystal structure

The molecular structure and atom numbering scheme of $V[2,4\text{-}(CH_3)_2C_5H_5]$-$(C_5H_5)CO$ is given in Fig. 1 and the packing of the molecules in the unit cell is shown in Fig. 2. The crystallographic data are given in Table 1 and the atomic coordinates and equivalent isotopic temperature factors for non-hydrogen atoms in

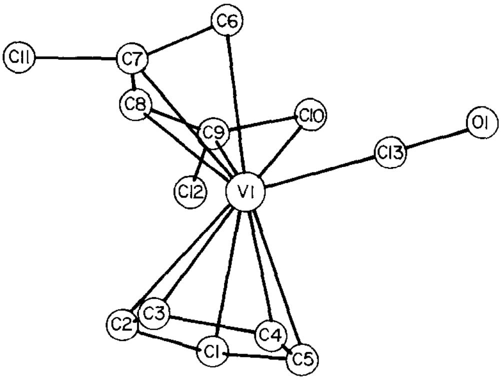

Fig. 1. Perspective view.

Table 2. Bond distances and angles are summarized in Table 3 and Table 4, respectively.

The results of the X-ray diffraction study revealed the apparent pentahapto mode (η^5) of bonding of the PD and CP ligands to the V^{II} cation, and the presence of a half-open sandwich configuration expected for the complex (Fig. 1).

Table 5 shows the data of the least-squares planes. Plane I is defined by the C(1), C(2), C(3), C(4), C(5) atom positions of the CP ligand and plane II by the C(6), C(7), C(8), C(9), C(10) atom positions of the PD ligand. It can be observed that the carbon atoms of the two ligands, CP and PD, deviate far less from the two given planes, respectively, except the two carbon atoms of the methyl groups attached to the PD ligand. The dihedral angle between planes I and II is 17.9°. The molecule of $V[2,4\text{-}(CH_3)_2C_5H_5](C_5H_5)CO$ is divided by the plane defined by the V(1), C(8) and C(2) atom positions. The C(8) atom of the PD ligand projects

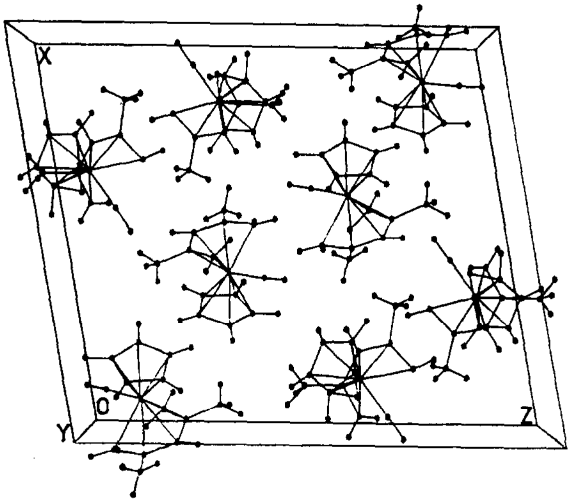

Fig. 2. Unit cell.

Table 1

Crystallography parameters

Chemical formula	$V(C_7H_{11})(C_5H_5)CO$
Molecular weight	239.21
Crystal system	Monoclinic
Space group	$P2_1/n$
Absorption factor (cm^{-1})	$\mu(Mo\text{-}K_\alpha) = 7.11$
$F(000)$	924
Crystal cell parameters	
a (Å)	16.614(3)
b (Å)	7.636(1)
c (Å)	19.128(6)
β (°)	99.92(2)
V (Å^3)	2390.5(9)
Z	8

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å$^2 \times 10^3$)

	x	y	z	U
V(1)	980(1)	8279(1)	1409(1)	41(1)
V(2)	6532(1)	6327(1)	1041(1)	43(1)
O(1)	1194(2)	5687(4)	219(2)	93(1)
O(2)	5042(2)	7094(4)	1750(2)	87(1)
C(1)	2073(2)	9201(5)	2190(2)	64(2)
C(2)	1557(2)	10640(5)	2019(2)	63(2)
C(3)	1508(3)	10998(5)	1302(2)	63(2)
C(4)	1984(2)	9787(5)	1022(2)	62(2)
C(5)	2343(3)	8661(6)	1571(2)	62(2)
C(6)	−251(2)	8163(5)	701(2)	58(2)
C(7)	−305(2)	9110(5)	1321(2)	47(1)
C(8)	−33(2)	8470(5)	2014(2)	48(1)
C(9)	426(2)	6945(5)	2232(2)	52(1)
C(10)	605(2)	5632(5)	1764(2)	62(2)
C(11)	−586(3)	10996(5)	1260(2)	69(2)
C(12)	796(4)	6801(9)	3008(3)	81(2)
C(13)	1122(2)	6683(5)	663(2)	61(2)
C(14)	6619(4)	9240(6)	971(3)	86(2)
C(15)	6106(3)	8610(6)	340(3)	84(2)
C(16)	6586(3)	7615(6)	−10(2)	79(2)
C(17)	7364(3)	7623(6)	378(3)	83(2)
C(18)	7372(3)	8623(6)	970(2)	89(2)
C(19)	6851(2)	5254(5)	2146(2)	59(2)
C(20)	7451(2)	4750(5)	1738(2)	51(1)
C(21)	7268(2)	3917(5)	1067(2)	52(2)
C(22)	6509(2)	3640(4)	627(2)	52(2)
C(23)	5748(3)	3925(5)	853(2)	62(2)
C(24)	8329(3)	5270(6)	1992(2)	72(2)
C(25)	6510(3)	3174(5)	−133(2)	73(2)
C(26)	5596(3)	6823(5)	1479(2)	58(2)

Table 3

Bond lengths (Å)

Molecular A		Molecular B	
V(1)–C(1)	2.256(4)	V(2)–C(16)	2.254(4)
V(1)–C(2)	2.268(4)	V(2)–C(17)	2.259(5)
V(1)–C(3)	2.277(4)	V(2)–C(18)	2.259(5)
V(1)–C(4)	2.255(4)	V(2)–C(14)	2.235(4)
V(1)–C(5)	2.252(4)	V(2)–C(15)	2.239(5)
V(1)–C(6)	2.251(4)	V(2)–C(19)	2.243(4)
V(1)–C(7)	2.205(4)	V(2)–C(20)	2.203(4)
V(1)–C(8)	2.205(4)	V(2)–C(21)	2.205(4)
V(1)–C(9)	2.204(4)	V(2)–C(22)	2.197(4)
V(1)–C(10)	2.254(4)	V(2)–C(23)	2.243(4)
V(1)–C(13)	1.922(4)	V(2)–C(26)	1.928(4)
O(1)–C(13)	1.161(5)	O(2)–C(26)	1.150(5)
C(1)–C(2)	1.398(6)	C(16)–C(17)	1.375(7)
C(2)–C(3)	1.385(6)	C(17)–C(18)	1.365(6)
C(3)–C(4)	1.384(6)	C(14)–C(18)	1.338(8)
C(4)–C(5)	1.408(6)	C(14)–C(15)	1.436(7)
C(1)–C(5)	1.399(6)	C(15)–C(16)	1.358(8)
C(6)–C(7)	1.405(5)	C(19)–C(20)	1.422(6)
C(7)–C(8)	1.413(5)	C(20)–C(21)	1.418(5)
C(8)–C(9)	1.414(5)	C(21)–C(22)	1.405(5)
C(9)–C(10)	1.410(6)	C(22)–C(23)	1.422(6)
C(7)–C(11)	1.513(6)	C(20)–C(24)	1.508(5)
C(9)–C(12)	1.510(6)	C(22)–C(25)	1.498(6)

about the C(2) atom of the CP ligand (eclipsed). The carbonyl ligand is situated at the open edge of the PD ligand. The V(1)–C(13)–O(1) bond angle is nearly linear (178.1(4)°). The linear V(1)–C(13)–O(1) is parallel to the PD ligand plane and the linear V(1)–C(13)–O(1) makes an angle of 18° with the perpendicular CP ligand plane.

The average V–C bond distances can be seen to be V–C(6,10) = 2.253(4), V–C(7,8,9) = 2.205(4) Å. The bond distances between V and the "external" C atoms of PD are dramatically longer than the bond distances between V and the "internal" C atoms of PD. The average bond distance of V–C(6), V–C(7), V–C(8), V–C(9) and V–C(10) is $V-C_{PD}$(half) = 2.224(4) Å, and the average bond distance of V–C(1), V–C(2), V–C(3), V–C(4) and V–C(5) is $V-C_{CP}$(half) = 2.262(4) Å. In $V[2,4-(CH_3)_2C_5H_5]_2CO$ and $V(C_5H_5)_2CO$, the average V–C bond distances are $V-C_{PD}$(open) = 2.277(4) [8] and $V-C_{CP}$(closed) = 2.280(5) Å [10], respectively. The $V-C_{PD}$(half) bonds are shorter than the $V-C_{PD}$(open) bonds. The $V-C_{CP}$(half) bonds are shorter than the $V-C_{CP}$(closed) bonds. In $V[2,4-(CH_3)_2C_5H_5](C_5H_5)CO$, the $V-C_{PD}$(half) bonds are dramatically shorter (0.038 Å) than the $V-C_{CP}$(half) bonds. In $Ti[2,4-(CH_3)_2C_5H_5](C_5H_5)PEt_3$ [6], the average Ti–C bond distances are 2.346(4) Å for the C_5H_5 ligand and 2.240(3) Å for the $2,4-(CH_3)_2C_5H_5$ ligand, yielding a difference of 0.106(5) Å. The structure of half-open vanadocene $V(C_5H_7)(C_5H_5)PEt_3$ [2], revealed very similar patterns, with average V–C distances of 2.207(4) Å for the C_5H_7 ligand and 2.299(4) Å for the C_5H_5 ligand. It can be noted that for titanium and vanadium, the metal–pentadienyl bonding appears stronger than the metal–cyclopentadienyl bonding.

Table 4

Bond angles (°)

Molecular A		Molecular B	
C(1)–V(1)–C(2)	36.0(1)	C(16)–V(2)–C(17)	35.5(2)
C(2)–V(1)–C(3)	35.5(2)	C(17)–V(2)–C(18)	35.2(2)
C(3)–V(1)–C(4)	35.6(2)	C(14)–V(2)–C(18)	34.6(2)
C(4)–V(1)–C(5)	36.4(2)	C(14)–V(2)–C(15)	37.4(2)
C(1)–V(1)–C(5)	36.2(2)	C(15)–V(2)–C(16)	35.2(2)
C(6)–V(1)–C(7)	36.7(1)	C(19)–V(2)–C(20)	37.3(2)
C(7)–V(1)–C(8)	37.4(1)	C(20)–V(2)–C(21)	37.5(2)
C(8)–V(1)–C(9)	37.4(1)	C(21)–V(2)–C(22)	37.2(1)
C(9)–V(1)–C(10)	36.9(1)	C(22)–V(2)–C(23)	37.3(2)
C(6)–V(1)–C(10)	82.9(1)	C(19)–V(2)–C(23)	83.6(1)
C(5)–V(1)–C(10)	113.5(2)	C(15)–V(2)–C(23)	115.2(2)
C(1)–V(1)–C(9)	93.4(1)	C(16)–V(2)–C(22)	95.0(2)
C(2)–V(1)–C(8)	88.3(1)	C(17)–V(2)–C(21)	89.3(2)
C(3)–V(1)–C(7)	96.5(1)	C(18)–V(2)–C(20)	95.1(1)
C(4)–V(1)–C(6)	118.0(1)	C(14)–V(2)–C(19)	114.4(2)
C(2)–C(1)–C(5)	107.9(4)	C(15)–C(16)–C(17)	108.0(4)
C(1)–C(2)–C(3)	108.4(4)	C(16)–C(17)–C(18)	109.0(4)
C(2)–C(3)–C(4)	108.1(3)	C(14)–C(18)–C(17)	108.8(4)
C(3)–C(4)–C(5)	108.4(4)	C(15)–C(14)–C(18)	107.5(5)
C(1)–C(5)–C(4)	107.1(4)	C(14)–C(15)–C(16)	106.8(4)
C(6)–C(7)–C(8)	123.9(3)	C(19)–C(20)–C(21)	123.8(3)
C(7)–C(8)–C(9)	129.1(3)	C(20)–C(21)–C(22)	129.8(4)
C(8)–C(9)–C(10)	124.1(3)	C(21)–C(22)–C(23)	123.4(4)
V(1)–C(13)–O(1)	178.1(4)	V(2)–C(26)–O(2)	178.6(3)

The carbon–carbon bond distances within the PD ligand are nearly equal. The average "external" bond distance (formed between the C(6)–C(7) and C(9)–C(10) positions) is 1.408(5) Å and the average "internal" bond distance (formed between

Table 5

Deviations of atoms from least-squares planes

	Plane I	Plane II	Plane III
V(1)	−1.9250	1.5980	0.0000 [a]
O(1)	−3.0380	1.4189	0.0912
C(13)	−2.5990	1.5081	0.0658
C(1)	0.0005 [a]	3.2622	1.1937
C(2)	−0.0021 [a]	3.0663	0.0000 [a]
C(3)	0.0029 [a]	3.7301	−1.0528
C(4)	−0.0026 [a]	3.7442	−0.5297
C(5)	0.0013 [a]	3.6867	0.8725
C(6)	−3.6356	−0.0086 [a]	−1.5652
C(7)	−3.1727	0.0277 [a]	−1.2957
C(8)	−3.0308	−0.0381 [a]	0.0000 [a]
C(9)	−3.1344	0.0270 [a]	1.2528
C(10)	−3.5907	−0.0081 [a]	1.4118
C(11)	−2.6518	0.2977	−2.4165
C(12)	−2.6248	0.2505	2.4797

[a] Atoms used to define a given plane. Equations of planes: (I) $12.647x + 4.690y + 1.411z = 7.246$; (II) $14.741x + 3.514y - 3.492z = 2.263$; (III) $6.278x - 4.520y + 11.959z = -1.525$.

Table 6

C–O stretching frequencies and EPR parameters for (η^5-L)^{2}VCO complexes [a]

	Pd$_2$VCO	PD$_2$'VCO	CP(PD)VCO	CP(PD')VCO	CP$_2$VCO	CP$_2$'VCO
ν(CO) (cm^{-1})	1950	1942	1937	1934	1881	1852
A_{iso} (G)	73.6	79.1	58.6	61.7	26.8	17.3

[a] PD = C_5H_7, PD' = 2,4-$(CH_3)_2C_5H_5$, CP = C_5H_5, CP' = $(CH_3)_5C_5$.

C(7)–C(8) and C(8)–C(9) positions) is 1.413(5) Å. The interior C–C–C bond angles in PD ligand are observed to fall into two sets, 129.1(3)° around the C(8) atom, 124.0(3)° around the C(7, 9) atoms. Those positions, with an attached methyl group, clearly have smaller interior C–C–C bond angles. The average interior C–C–C bond angle in the CP ligand is 108.0(4)°. The distances of V(1) with the CP and PD ligand planes are 1.925 and 1.598 Å, respectively.

In spite of the fact that the substance crystallized with two independent molecules (A and B) in the asymmetric unit, they have almost identical molecular parameters and conformation. This is readily shown by consideration of bond lengths and angles given in Table 3 and Table 4. The V–C_{CP}(half), V–C_{PD}(half) and $(C–C)_{PD}$(half) distances in both molecules are the same within experiment error (approximately 0.013 Å for V–C_{CP}(half), 0.006 Å for V–C_{PD}(half) and 0.006 Å for $(C–C)_{PD}$(half)). Similarly, the corresponding $(C–C–C)_{CP}$, $(C–C–C)_{PD}$ and V–C–O angles are essentially identical for both molecules. In fact, the only discernible difference is the slightly shorter (average 0.020(6) Å) $(C–C)_{CP}$(half) distance in molecule B. In molecule A, five $(C–C)_{CP}$(A) bond distances are similar, and in molecule B, five $(C–C)_{CP}$(B) bond distances are dramatically different. In molecule B, the CP ligand is distorted.

IR and EPR spectroscopic studies

Table 6 shows the C–O stretching frequencies and EPR parameters for (η^5-L)$_2$VCO complexes [3,9,11]. The observed carbonyl IR stretching frequencies are 1942, 1932 and 1881 cm^{-1} in V[2,4-$(CH_3)_2C_5H_5$]$_2$CO, V[2,4-$(CH_3)_2C_5H_5$]-(C_5H_5)CO and V(C_5H_5)$_2$CO, respectively. The results suggest greater V → CO back-bonding in V(C_5H_5)$_2$CO. The strength of V → CO back-bonding in V[2,4-$(CH_3)_2C_5H_5$](C_5H_5)CO lies between V[2,4-$(CH_3)_2C_5H_5$]$_2$CO and V(C_5H_5)$_2$CO, and tends to V[2,4-$(CH_3)_2C_5H_5$]$_2$CO. The EPR parameters, A_{iso}, of V[2,4-$(CH_3)_2C_5H_5$]$_2$CO, V[2,4-$CH_3)_2C_5H_5$](C_5H_5)CO and V(C_5H_5)$_2$CO are 79.0, 61.7 and 26.8 G, respectively. The delocalization of the unpaired electron in V(C_5H_5)$_2$CO is greater than that in V[2,4-$(CH_3)_2C_5H_5$]$_2$CO. The delocalization of the unpaired electron in V[2,4-$(CH_3)C_5H_5$](C_5H_5)CO lies between V[2,4-$(CH_3)_2C_5H_5$]$_2$CO and V(C_5H_5)$_2$CO, and tends to V[2,4-$(CH_3)_2C_5H_5$]$_2$CO. From the discussions above, we can come to the conclusion that the properties of half-open vanadocene lie between open vanadocene and vanadocene, and tend to open vanadocene. Vanadium–pentadienyl bonding is stronger than vanadium–cyclopentadienyl bonding. The properties of half-open vanadocene are more affected by the pentadienyl ligand than by the cyclopentadienyl ligand.

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