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THE FORMATION AND MOLECULAR STRUCTURE OF BIS(η^5-CYCLOPENTADIENYL)BIS(PENTAFLUOROPHENYL)-VINYLENEVANADIUM: AN ACETYLENE DERIVATIVE OF VANADOCENE

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Summary

A reaction between vanadocene and bis(pentafluorophenyl)acetylene in benzene solution has produced the title compound, $(\eta^5\text{-}C_5H_5)_2V[\eta^2\text{-}C_2(C_6F_5)_2]$, in 66% yield. The product has been characterized by infrared, mass spectral, and electron spin resonance data, as well as by a single crystal X-ray diffraction study. The compound crystallizes in the monoclinic space group $C2/c$ with a = 11.961(6), b = 10.010(5), c = 16.670(8) Å, β = 98.42(5)°, and ρ_{calc} = 1.81 g cm^{-3} for Z = 4. Least-squares refinement based on 984 observed reflections led to an R value of 0.039. The molecule resides on a crystallographic two-fold axis. The V—C(η^2) bond length is 2.077(5) Å, while the V—C(η^5) distances range from 2.268(6) to 2.291(5) Å and average 2.282(8) Å. Within the acetylenic ligand the C≡C length is 1.269(9) Å, and the C≡C—C(C$_6$F$_5$) angle is 142.3(4)°.

Introduction

The isolation and study of stable acetylene derivatives of early transition metal (Groups IVB and VB) metallocenes has been a topic of increasing interest in recent years, since such species could provide important information concerning catalytic polymerization, cyclotrimerization, hydrogenation and insertion reactions of these metals [1—7]. Although acetylene adducts of vanadocene have been known since 1965 [1], only two detailed X-ray crystallographic investigations * have been reported in this area, one involving a niobocene- [7] and the other a titanocene [6] alkyne interaction.

In our continuing joint studies concerning the formation and structures of early transition metal organometallic compounds, we now report on the synthesis, spectral properties and molecular structure of bis(η^5-cyclopentadienyl)-bis(pentafluorophenyl)vinylenevanadium (I), an acetylene derivative of vanadocene.

Results and discussion

Complex I has been prepared in 66% yield by the direct reaction of vanadocene and bis(pentafluorophenyl)acetylene in benzene solution at 55°C. The product is air-stable in the crystalline state, in contrast to the previously reported dimethylacetylenedicarboxylate and hexafluoro-2-butyne analogs [1]. Solutions of I in organic solvents, however, are air-sensitive. Complex I is likewise thermally stable to its melting point of 231°C. The enhanced stabilities of bis(pentafluorophenyl)acetylene complexes of transition metals have been demonstrated previously [10—12].

Complex I has been characterized by elemental analysis and by spectroscopic techniques. The mass spectrum of I exhibited a molecular ion at m/e 539 as well as characteristic fragmentation peaks, whereas the infrared spectrum contained a coordinated acetylenic stretching frequency at 1750 cm^{-1} as well as bands due to cyclopentadienyl and perfluoroaromatic substituents. Complex I is paramagnetic and shows an ESR spectrum at room temperature typical of a d^1 vanadium compound, consisting of eight lines with a g value of 1.9983 and hyperfine isotropic splitting (^{51}V, 99.76%, $I = 7/2$) of 44.6 G (Figure 1). This splitting constant is appreciably lower than in other vanadocene d^1 compounds (A_{iso} = 64.0, 74.3, 60.3 and 76.1 G for $Cp_2V(CH_3)_2$ [11], Cp_2VCl_2 [14], $Cp_2V(CN)_2$ [14], and $Cp_2V(NCO)_2$ [14], respectively) indicating enhanced unpaired electron delocalization onto the perfluorinated ligand.

Since no crystallographic structural information has been reported for this type of complex, and since the coordination of an acetylene to vanadocene might be expected to significantly alter cyclopentadienyl—metal bond distances and angles, a single-crystal X-ray diffraction study of I was undertaken.

The molecular structure and atom numbering scheme are shown in Figure 2, and a stereoscopic view of the unit cell packing is presented in Figure 3. The $C_2(C_6F_5)_2$ ligand is symmetrically bonded to the vanadium atom since the molecule resides on a crystallographic two-fold axis. Although there are few compounds available for comparison, the short V—C(η^2) bond length of 2.077(5) Å has precedent. Vanadium—carbon(carbonyl) distances cluster about 1.93 Å [15,16], and the V—C(sp) length in $[\eta^5\text{-}C_5(CH_3)_4(C_2H_5)]_2VC{\equiv}CC_6H_2(CH_3)_3$ is 2.03(1) Å [17]. In the compounds most closely related to I, $(\eta^5\text{-}C_5H_5)_2V(SC_2)$ and $[(\eta^5\text{-}C_5H_5)_2VSCS(CH_3)]$ $[I_3]$, [18], the V—C(sp^2) separations are 2.08 Å.

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* Two others, $(\eta^5\text{-}C_5H_5)Nb(CO)[\eta^2\text{-}C_2(C_6H_5)_2][(\eta^4\text{-}C_4(C_6H_5)_4]$ and $(\eta^5\text{-}C_5H_5)Nb(CO)$-$[\eta^2\text{-}C_2(C_6H_5)_2]_2$, are in the literature [8,9], but unfortunately are of limited accuracy.

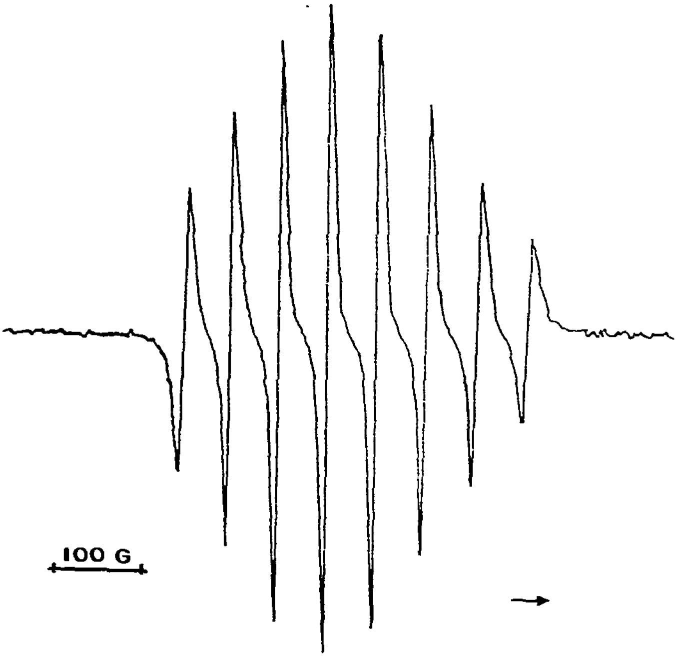

Fig. 1. Solution ESR spectrum of $(\eta^5\text{-}C_5H_5)_2V[\eta^2\text{-}C_2(C_6F_5)_2]$ recorded at room temperature.

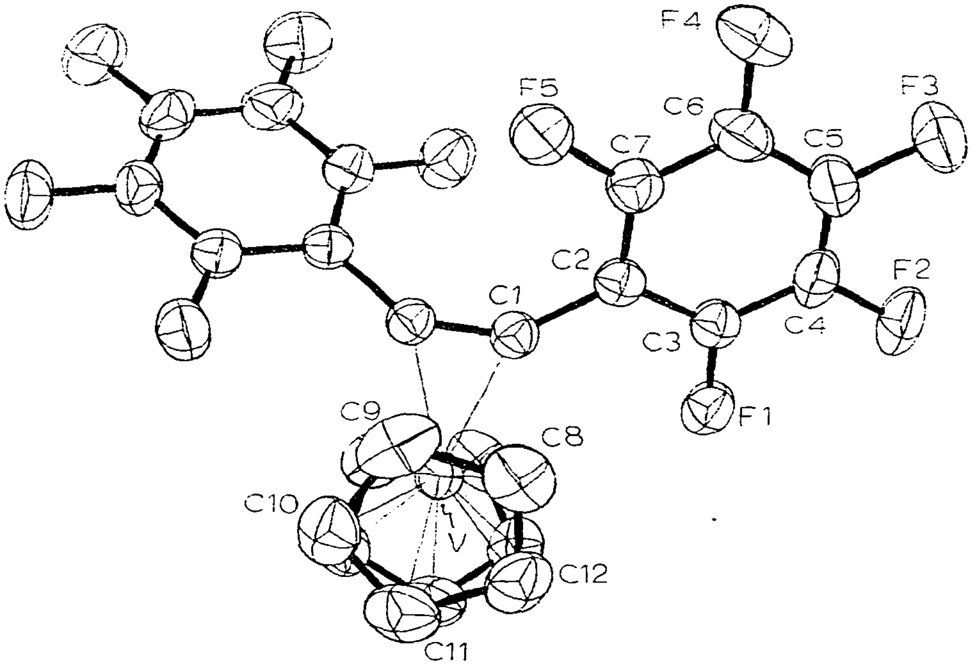

Fig. 2. Molecular structure and atom numbering scheme for $(\eta^5\text{-}C_5H_5)_2V[\eta^2\text{-}C_2(C_6F_5)_2]$ (I) with the atoms represented by their 40% probability ellipsoids for thermal motion.

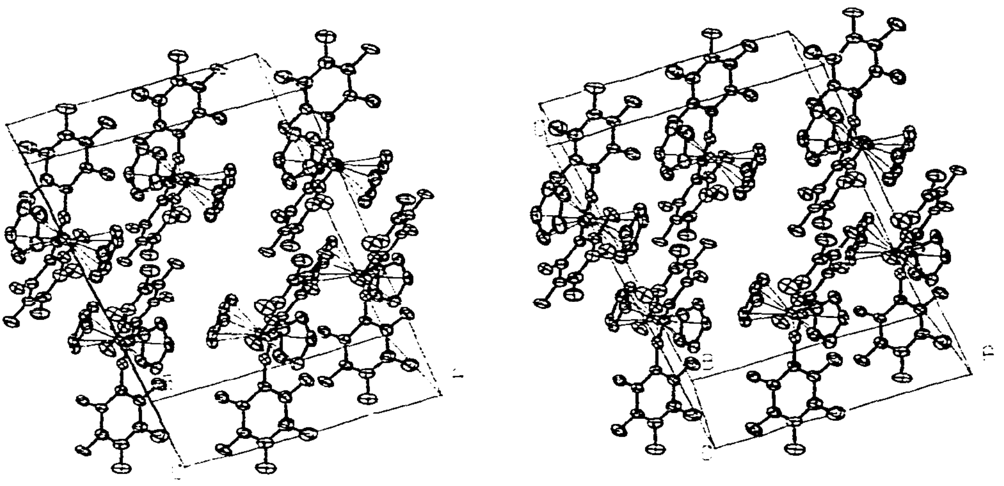

Fig. 3. Stereoscopic view of the unit cell packing for I.

The C≡C bond length, 1.269(9) Å, and the C≡C—C(C_6F_5) angle, 142.3(4)°, are typical for compounds exhibiting η^2-coordination of an acetylene [6,19,20]. For example, the corresponding values are 1.285(10) Å and 138.8(7)° in $(\eta^5\text{-}C_5H_5)_2Ti(CO)[\eta^2\text{-}C_2(C_6H_5)_2]$ [6]. Similarly, the C≡C stretch at 1750 cm^{-1} agrees well with the 1780 cm^{-1} value in $(\eta^5\text{-}C_5H_5)_2Ti(CO)$-$[\eta^2\text{-}C_2(C_6H_5)_2]$ and with those given for related compounds [6]. These features are consistent with the formulation of the title compound as a metallocyclopropene.

The V—C(η^5) bond distances range from 2.268(6) to 2.291(5) Å, and average 2.282(8) Å. This compares well with typical values in related compounds: 2.274(2) Å in $(\eta^5\text{-}C_5H_5)_2V(SCS)$ [18], 2.271(1) Å in $[(\eta^5\text{-}C_5H_5)_2VSCS(CH_3)]$-$[I_3]$ [18], and 2.305 Å in $(\eta^5\text{-}C_5H_5)_2V(SC_6H_5)_2$ [21].

The $C_2(C_6F_5)_2$ ligand is bisected by a two-fold axis, and consists of two halves each of which is planar to within 0.05 Å. The two symmetry related portions are twisted with respect to each other such that the C(2)—C(1)—C(1)′—C(2)′ torsion angle is 22°. In addition the phenyl groups are rotated about the C(1)—C(2) bond vector as evidenced by the C(1)′—C(1)—C(2)—C(7) torsion angle of 26°.

A stereoscopic view of the unit cell packing is shown in Figure 3. No unusually short intermolecular contacts are noted.

Experimental

All manipulations of air-sensitive compounds were carried out under a purified argon atmosphere using Schlenk techniques. The argon was dried with H_2SO_4 and P_2O_5, and trace oxygen was removed using BTS catalyst. Hexane, benzene and pentane were dried over calcium hydride and freshly distilled under argon. Ethyl ether and THF were predried over sodium and then distilled under argon from sodium/benzophenone. Column chromatography was performed under argon using Fischer silica gel (100—200 mesh). The silica gel was heated with mixing under vacuum for 2 hours and stored under argon. Melting points were performed under an argon atmosphere. Vanadocene [22] and bis(pentafluorophenyl)acetylene [23] were prepared by literature methods. IR spectra were taken on a Perkin-Elmer 2378 or a Beckman IR-10 spectrometer. The ESR spectrum was recorded on a Varian E-12 spectrometer. The mass spectrum was obtained on a Perkin-Elmer-Hitachi RMU-6L instrument at 70 eV.

Preparation of bis(η^5-cyclopentadienyl)bis(pentafluorophenyl)vinylenevanadium

Vanadocene (0.51 g, 2.8 mmol) and bis(pentafluorophenyl)acetylene (1.01 g, 2.8 mmol) were dissolved in 75 ml of benzene. The violet solution immediately began to turn to a yellow-green color. The mixture was heated to 55°C and stirred for 2 hours. The solvent was removed from the air-sensitive solution under vacuum, leaving a green solid which was dissolved in 20 ml of ethyl ether. Silica gel (3 g) was added, and the stirring slurry was evaporated under vacuum to a solid. This residue was added to an argon-filled chromatography column (1.5 × 30 cm) packed with silica gel. The column was eluted with hexane, benzene, and ethyl ether. Copious amounts of THF eluted a dark green air-sensitive band which was collected. Removal of the solvent by vacuum yielded 1.00 g (66%) of air-stable green crystals, m.p. 231—231.5°C. The compound was recrystallized from 10 : 1 ethyl ether/pentane at —20°C to produce green crystals (Found: C, 53.46; H, 1.81; V, 9.5. $C_{24}H_{10}F_{10}V$ calcd.: C, 53.45; H, 1.87; V, 9.45%). The infrared spectrum (KBr) exhibited typical peaks for cyclopentadienyl and fluorinated aromatic substituents (3040w, 1475s, 1260m, 1100m, 975s, 900m, 800s, 725m, 680 cm^{-1}) as well as a coordinated acetylenic stretch at 1750 cm^{-1}. The mass spectrum exhibited the following major peaks: *m/e* 539 (M^+), 358 ($C_6F_5C_2C_6F_5^+$), 181 ($C_{10}H_{10}V^+$), 116 ($C_5H_5V^+$).

X-ray data collection, solution and refinement of the structure

Crystals for the X-ray study were sealed in thin-walled glass capillaries. The final unit cell constants, obtained from a least-squares refinement of the angular settings of 14 accurately centered reflections, are given in Table 1. The

TABLE 1

CRYSTAL DATA [a] FOR $(\eta^5\text{-}C_5H_5)_2V[\eta^2\text{-}C_2(C_6F_5)_2]$ (I)

Mol. wt.		539.3
Linear abs. coeff. μ (cm^{-1})		6.46
Calcd. density (g cm^{-1})		1.81
Max. crystal dimenions (mm)		0.32 × 0.28 × 0.22
Space group		*C*2/*c*
Molecules/unit cell		4
Cell constants	*a* (Å)	11.961(6)
	b (Å)	10.010(5)
	c (Å)	16.670(8)
	β (°)	98.42(3)
Cell volume (Å^3)		1974.4

[a] Mo-K_α radiation, λ 0.71069 Å, ambient temperature of 20 ± 1°C.

diffracted intensities were collected on an Enraf-Nonius CAD-4 diffractometer by the θ—2θ scan technique. The scan rate was variable and was determined by a fast 20° min^{-1} prescan. Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 7 to 0.2° min^{-1}. Moving-crystal moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation, scan range = A + B tan θ, where A = 0.9° and B = 0.20°. Other diffractometer parameters and the method of estimation of standard deviations have been described previously [24]. As a check on the stability of the instrument and crystal, three reflections were measured after every 50 reflections; only a random variation of ±2% was noted.

One independent quadrant of data was measured out to $2\theta = 50°$; a slow scan was performed on a total of 1311 out of 1869 possible unique reflections. Since these data were scanned at a speed which would yield a net count of 3000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 5 was obtained in the prescan. Based on these considerations, the data set of 984 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted of those for which $I > \sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but not for absorption (the crystal was quite symmetrical and had $\mu = 6.46\ \text{cm}^{-1}$).

The full-matrix least-squares refinement was carried out using the SHELX [25] routine. Neutral atom scattering factors were generated from the analytic function coefficients given by Cromer and Waber [26] for V. Those for F, C, and H were used as presented in SHELX.

TABLE 2

ATOMIC POSITIONS IN FRACTIONAL COORDINATES FOR $(\eta^5\text{-}C_5H_5)_2V[\eta^2\text{-}C_2(C_6F_5)_2]$

Atom	*x/a*	*y/b*	*z/c*
V	0.0000	0.1086(1)	0.7500
F(1)	0.2460(2)	0.2490(3)	0.8775(2)
F(2)	0.3363(3)	0.3989(4)	1.0018(2)
F(3)	0.2291(3)	0.6209(4)	1.0431(2)
F(4)	0.0317(3)	0.6952(4)	0.9532(2)
F(5)	−0.0583(3)	0.5496(3)	0.8261(2)
C(1)	0.0355(4)	0.3061(5)	0.7823(3)
C(2)	0.0897(4)	0.3918(5)	0.8464(3)
C(3)	0.1905(4)	0.3587(5)	0.8949(3)
C(4)	0.2378(5)	0.4345(6)	0.9584(3)
C(5)	0.1852(5)	0.5464(6)	0.9792(3)
C(6)	0.0857(5)	0.5860(6)	0.9341(3)
C(7)	0.0404(4)	0.5089(6)	0.8684(3)
C(8)	−0.0811(5)	0.1177(7)	0.8658(3)
C(9)	−0.1168(5)	0.1370(6)	0.8002(4)
C(10)	−0.1753(5)	0.0214(9)	0.7540(4)
C(11)	−0.0974(5)	−0.0701(6)	0.7897(4)
C(12)	−0.0381(5)	−0.0104(7)	0.8586(4)
H(1)	−0.0528	0.1907	0.9141
H(2)	−0.2187(	0.2281	0.7873
H(3)	−0.2352	0.0066	0.6977
H(4)	−0.0849	−0.1718	0.7666
H(5)	0.0308	−0.0565	0.9003

TABLE 3

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $(\eta^5\text{-}C_5H_5)_2V[\eta^2\text{-}C_2(C_6F_5)_2]$ (I)

V—C(1)	2.077(5)	V—C(10)	2.279(5)
V—C(8)	2.286(5)	V—C(11)	2.285(6)
V—C(9)	2.291(5)	V—C(12)	2.268(6)
C(8)—C(9)	1.398(8)	C(12)—C(8)—C(9)	107.3(6)
C(9)—C(10)	1.389(8)	C(8)—C(9)—C(10)	108.0(5)
C(10)—C(11)	1.381(8)	C(9)—C(10)—C(11)	108.6(5)
C(11)—C(12)	1.393(8)	C(10)—C(11)—C(12)	107.7(6)
C(12)—C(8)	1.393(9)	C(11)—C(12)—C(8)	108.5(5)
C(1)—C(1)′ [a]	1.269(9)	C(7)—C(2)	1.386(7)
C(1)—C(2)	1.448(6)	C(3)—F(1)	1.337(5)
C(2)—C(3)	1.390(6)	C(4)—F(2)	1.338(6)
C(3)—C(4)	1.357(7)	C(5)—F(3)	1.343(6)
C(4)—C(5)	1.355(8)	C(6)—F(4)	1.332(6)
C(5)—C(6)	1.369(8)	C(7)—F(5)	1.347(6)
C(6)—C(7)	1.384(7)		
V—C(1)—C(2)	144.6(4)	C(4)—C(5)—F(3)	121.3(5)
C(2)—C(1)—C(1)′	142.3(4)	C(4)—C(5)—C(6)	119.9(5)
C(1)—C(2)—C(3)	123.0(5)	F(3)—C(5)—C(6)	118.9(6)
C(2)—C(3)—F(1)	119.1(4)	C(5)—C(6)—F(4)	121.3(5)
C(2)—C(3)—C(4)	123.2(5)	C(5)—C(6)—C(7)	118.7(5)
F(1)—C(3)—C(4)	117.7(5)	F(4)—C(6)—C(7)	119.9(5)
C(3)—C(4)—F(2)	120.4(5)	C(6)—C(7)—F(5)	117.3(5)
C(3)—C(4)—C(5)	120.4(5)	C(6)—C(7)—C(2)	123.3(5)
F(2)—C(4)—C(5)	119.2(5)	C(7)—C(2)—C(1)	122.3(4)
C(1)—V—C(1)′	35.6(2)	F(5)—C(7)—C(2)	119.4(5)
Cent—V—Cent′	138.3		

[a] Primed atoms are related to those in Table 2 by the two-fold axis.

The structure was solved with the aid of the direct methods program MULTAN [27]. Several cycles of least-squares refinement with isotropic thermal parameters led to $R_1 = [\Sigma(|F_0| - |F_c|)/\Sigma|F_0|] = 0.121$. Conversion to anisotropic temperature factors and further refinement produced an R_1 value of 0.050. Placement of the hydrogen atoms in calculated positions followed by more least-squares cycles on the nonhydrogen atoms led to final values of $R_1 = 0.039$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2} = 0.041$. Unit weights were used at all stages and unobserved reflections were not included. The standard deviation of an observation of unit weight was 2.04. The largest parameter shifts in the last cycle of refinement were less than 0.01 of their estimated standard deviations. The final values of the positional parameters are given in Table 2 *. Bond distances and bond angles are given in Table 3.

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* The tables of structure factors, best plane results, and thermal parameters have been deposited as NAPS Document, No. 03687, with National Auxilliary Publications Service, c/o Microfiche Publications, 440 Park Ave. So., New York, New York 10016. A copy may be secured by citing the document and remitting $ 3.00 for microfiche or $ 5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

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