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Synthesis and molecular structure of bis(tetraphenylcyclopentadienyl)tetrakis(μ-trifluoroacetato)-divanadium(III)

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Abstract

The reaction between V(η-C_5HPh_4)$_2$ and trifluoroacetic acid in benzene at 115–120 °C produces (η-C_5HPh_4)V(μ-O_2CCF_3)$_4$V(η-C_5HPh_4) (**I**). Recrystallization from THF yields **I**·2THF, which crystallizes in the space group $P\bar{1}$ with $a=12.048(8)$, $b=15.607(5)$, $c=9.689(6)$ Å, $\alpha=97.16(4)$, $\beta=108.62(5)$, $\gamma=68.01(3)°$, $V=1601(2)$ Å^3, and $Z=1$ at -110 °C. Refinement of 442 variables on 3772 reflections $I>3\sigma(I)$ converged to $R=0.060$ and $R_w=0.075$. The structure contains four bridging carboxylates, terminal η-C_5HPh_4 ligands staggered with respect to one another, and a non-bonding V–V separation of 3.752(1) Å. The structural data suggest the steric effect of the η-C_5HPh_4 ligand rivals that of η-C_5Me_5.

Introduction

Studies of M(η-C_5HPh_4)$_2$ (M = V, Cr, Fe, Co and Ni) and Ti(η-C_5HPh_4)$_2$Cl suggest that the η-C_5HPh_4 ligand has electron donor properties similar to the η-C_5H_5 group, but has a steric size that equals or exceeds that of η-C_5Me_5 [1, 2]. The reaction between $PhCO_2H$ and vanadocene under ambient conditions yields the benzoate bridged dimer, CpV(μ-O_2CPh)$_4$VCp [3]. An analogous reaction occurs between $PhCO_2H$ and V(C_5Me_5)$_2$. To see whether the bulky C_5HPh_4 ligand might be completely eliminated from the complex to allow formation of a divanadium tetracarboxylate, we examined the reaction between V(C_5HPh_4)$_2$ and carboxylic acids. If an analogous dimer formed as in the η-C_5Me_5 and η-C_5H_5 systems, we also sought to determine whether the bulky η-C_5HPh_4 significantly perturbed the structure between the V(III) centers.

Experimental

Synthesis of bis(tetraphenylcyclopentadienyl)tetrakis(μ-trifluoroacetato)divanadium(III)·2-(dichloromethane), (I·2CH_2Cl_2)

Trifluoroacetic acid (0.25 ml, 3.2 mmol) was added to a benzene solution of V(C_5HPh_4)$_2$ (0.50 g, 0.63 mmol in 20 ml), which was sealed in a heavy-wall glass tube under 3–4 atm N_2 [3]. The solution was heated to 115–120 °C for 40 h, followed by cooling to room temperature, and solvent removal *in vacuo*. The resulting light brown solid was dissolved in a minimum amount of boiling toluene (10 ml) and filtered rapidly through a frit. The solution was cooled to -45 °C giving dark brown microcrystals (0.31 g, 0.48 mmol) in 76% yield. Recrystallization from dichloromethane yielded the title complex. IR (THF): 1458 and 1707 cm^{-1} ($\nu(CO_2)$). *Anal.* Calc. for $C_{68}H_{46}Cl_4F_{12}O_8V_2$: C, 55.84; H, 3.17. Found: C, 56.48; H, 3.16%. Crystals for an X-ray structure determination were grown from hexane–THF and crystallized with 2 lattice THF, **I**·2THF. *Anal.* Calc. for $C_{74}H_{58}F_{12}O_{10}V_2$: C, 61.85; H, 4.07. Found: C, 62.67; H, 4.18%.

X-ray structure determination

Crystals of the dichloromethane solvate $C_{68}H_{46}Cl_4F_{12}O_8V_2$ were poorly formed and twinned. The THF solvated crystals grown proved suitable for X-ray diffraction studies. A red–brown plate-shaped crystal of $C_{74}H_{58}F_{12}O_{10}V_2$ having dimensions of 0.05 × 0.15 × 0.2 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer at -110 ± 1 °C with graphite monochromated Mo Kα radiation and a 12 kW rotating anode generator. Crystal, data collection and refinement parameters are given in Table 1.

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TABLE 1. Crystal data for $[(C_5HPh_4)V(O_2CCF_3)_2]_2 \cdot 2THF$

Empirical formula	$C_{74}H_{58}F_{12}O_{10}V_2$
Formula weight	1437.13
a (Å)	12.048(8)
b (Å)	15.607(5)
c (Å)	9.689(6)
α (°)	97.16(4)
β (°)	108.62(5)
γ (°)	68.01(3)
V (Å^3)	1601(2)
Space group	$P\bar{1}$
Z	1
ζ_{calc} (g/cm^3)	1.49
μ (Mo Kα) (cm^{-1})	4.15
T (°C)	−110
λ (Å)	0.71069
R	0.060
R_w	0.075

The structure was solved by direct methods [4]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d(C–H) = 0.95 Å), and were assigned isotropic thermal parameters 20% greater than the B_{eq} value of the atom bonded to them. The final cycle of full-matrix least-squares refinement was based on 3772 observed reflections ($I > 3.00\sigma(I)$) and 442 variable parameters*. It converged (largest parameter shift was 0.15 times its e.s.d.) with unweighted and weighted agreement factors of $R = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.60$ and $R_w = [(\Sigma w|F_o| - |F_c|)^2/\sigma w F_o^2)]^{1/2} = 0.075$.

The standard deviation of an observation of unit weight was 1.78**. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin σ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.63 and −0.67 e/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber [5]. Anomalous dispersion effects were included for all non-hydrogen atoms in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer [6, 7]. All calculations were performed on a VAX based TEXRAY [8] system. Atomic coordinate and isotropic thermal parameters are provided in Table 2.

1.27(4)

TABLE 2. Positional parameters and B_{eq} for $[(C_5HPh_4)V(O_2CCF_3)_2]_2 \cdot 2THF$

Atom	x	y	z	B_{eq}
V	0.45600(8)	0.12281(5)	0.06655(9)	1.27(4)
F1	0.2007(4)	0.1413(4)	−0.4224(5)	7.4(3)
F2	0.3300(7)	0.0225(3)	−0.4952(4)	10.3(4)
F3	0.3682(5)	0.1437(3)	−0.4348(4)	5.7(3)
F4	0.8361(3)	−0.0355(2)	−0.1617(4)	3.9(2)
F5	0.9005(3)	−0.0239(3)	0.0697(4)	4.3(2)
F6	0.8016(3)	0.0984(2)	−0.0595(4)	3.6(2)
O1	0.3772(4)	0.1224(2)	−0.1545(4)	2.9(2)
O2	0.4318(3)	−0.0258(2)	−0.2250(4)	2.3(2)
O3	0.6154(3)	0.0842(2)	0.0068(4)	2.3(2)
O4	0.6697(3)	−0.0642(2)	−0.0627(4)	2.5(2)
O5	0.779(10)	0.4932(7)	0.699(1)	13.0(8)
C1	0.4186(5)	0.2120(3)	0.2607(5)	1.6(2)
C2	0.5217(4)	0.2241(3)	0.2354(5)	1.5(2)
C3	0.4753(5)	0.2699(3)	0.0989(5)	1.3(2)
C4	0.3446(4)	0.2874(3)	0.0439(5)	1.5(2)
C5	0.3100(4)	0.2517(3)	0.1459(5)	1.4(2)
C6	0.6510(5)	0.1943(3)	0.3379(5)	1.6(2)
C7	0.7562(5)	0.1677(3)	0.2897(6)	2.0(2)
C8	0.8754(5)	0.1361(4)	0.3882(6)	2.6(3)
C9	0.8912(6)	0.1307(4)	0.5359(6)	3.2(3)
C10	0.7867(6)	0.1570(4)	0.5836(6)	3.1(3)
C11	0.6677(5)	0.1886(4)	0.4855(6)	2.4(3)
C12	0.5439(4)	0.3100(3)	0.0380(5)	1.5(2)
C13	0.5873(5)	0.3759(3)	0.1190(5)	1.9(2)
C14	0.6438(5)	0.4218(3)	0.0655(6)	2.3(3)
C15	0.6554(5)	0.4007(4)	−0.0737(6)	2.4(3)
C16	0.6133(4)	0.3350(4)	−0.1549(6)	2.3(3)
C17	0.5575(5)	0.2888(3)	−0.1009(6)	2.1(3)
C18	0.2548(4)	0.3505(3)	−0.0761(5)	1.5(2)
C19	0.1694(5)	0.4326(3)	−0.0402(5)	1.8(2)
C20	0.0852(5)	0.4967(3)	−0.1445(6)	2.2(3)
C21	0.0828(5)	0.4809(4)	−0.2880(6)	2.5(3)
C22	0.1663(6)	0.4000(4)	−0.3271(6)	2.7(3)
C23	0.2526(5)	0.3359(3)	−0.2220(6)	2.2(3)
C24	0.1832(4)	0.2550(3)	0.1357(5)	1.5(2)
C25	0.1510(5)	0.2618(3)	0.2642(6)	1.9(2)
C26	0.0351(5)	0.2627(3)	0.2606(6)	2.5(3)
C27	−0.0506(5)	0.2568(4)	0.1293(7)	2.7(3)
C28	−0.0208(5)	0.2502(4)	0.0013(6)	2.4(3)
C29	0.0956(5)	0.2499(3)	0.0045(5)	1.8(2)
C30	0.3818(5)	0.0585(3)	−0.2438(5)	2.0(3)
C31	0.3158(7)	0.0894(4)	−0.4039(6)	3.5(3)
C32	0.6841(5)	0.0110(3)	−0.0352(5)	1.7(2)
C33	0.8060(5)	0.0132(3)	−0.0494(6)	2.3(3)
C34	0.675(1)	0.5504(7)	0.596(1)	7.5(7)
C35	0.6527(9)	0.4911(6)	0.461(1)	6.7(6)
C36	0.777(1)	0.4073(6)	0.4913(9)	6.8(6)
C37	0.826(1)	0.4033(8)	0.649(1)	7.4(8)

Results and discussion

Synthesis

No reaction was observed between $V(C_5HPh_4)_2$ and $PhCO_2H$, even in refluxing toluene. However, the reaction between $V(C_5HPh_4)_2$ and the strong acid, CF_3CO_2H, (eqn.(1)) under forcing conditions (120 °C, 3.5 atm N_2, 40 h) yields a product of composition,

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*Least-squares function minimized: $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, $p = p$ factor.

**Standard deviation of an observation of unit weight: $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where: N_o = number of observations, N_v = number of variables.

$(C_5HPh_4)V(\mu\text{-}O_2CCF_3)_4V(C_5HPh_4)\cdot 2(\text{Solvent})$, after recrystallization from dichloromethane ($\mathbf{I}\cdot 2CH_2Cl_2$) or THF ($\mathbf{I}\cdot 2THF$).

$$V(C_5HPh_4)_2 + 2CF_3CO_2H \xrightarrow[120\ ^{\circ}C]{C_6H_6} (C_5HPh_4)V(\mu\text{-}O_2CCF_3)_4V(C_5HPh_4) \quad (1)$$

This reaction with trifluoroacetic acid may proceed, where the reaction with benzoic acid does not, because the strong acid protonates the tetraphenylcyclopentadienyl ring, followed by a ring slip, which allows room for attack by the $CF_3CO_2^-$ counter ion. An analogous cyclopentadienyl dimer has been prepared by the reaction between $CpV(CO)_4$ and CF_3CO_2H [9].

Molecular structure

The molecular structure of $\mathbf{I}\cdot 2THF$ is shown in Fig. 1. Bond distances and angles are given in Tables 3 and 4, respectively. Lattice THF molecules were observed; however their location suggests that there is no interaction with the vanadium atoms. The unsubstituted carbons on the C5 ring in the dimer are oriented 180° apart. This suggests there is a steric interaction between the C_5HPh_4 rings through the trifluoroacetate ligands, which causes staggering of the rings on opposite ends of the dimer. In contrast, the less hindered cyclopentadienyl analogue adopts an eclipsed ring structure; however, it should be noted that $[(\eta\text{-}C_5H_5)V(\mu\text{-}O_2CPh)_2]_2$ adopts a staggered ring geometry, while $[(\eta\text{-}C_5Me_5)V(\mu\text{-}O_2CPh)_2]_2$ is eclipsed [3, 9]. This suggests that crystal packing forces may contribute to the solid state conformational preference.

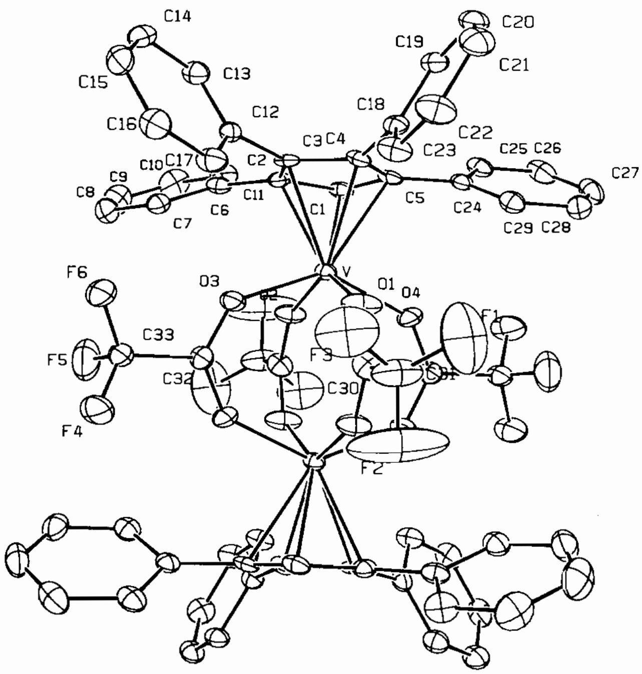

Fig. 1. ORTEP and atom numbering scheme for $[(C_5HPh_4)V(O_2CCF_3)_2]_2\cdot 2THF$.

TABLE 3. Selected intramolecular distances (Å) in $[(C_5HPh_4)V(O_2CCF_3)_2]_2\cdot 2THF^a$

V–V′	3.752(1)
V–O1	2.047(4)
V–O2	2.049(4)
V–O3	2.035(4)
V–O4	2.030(4)
V–C1	2.258(5)
V–C2	2.295(5)
V–C3	2.366(4)
V–C4	2.412(5)
V–C5	2.358(5)
V–CNT	1.997
O1–C30	1.234(6)
O2–C30	1.233(6)
O3–C32	1.244(6)
O4–C32	1.235(6)
O5–C37	1.39(1)
O5–C34	1.40(1)
C1–C5	1.403(7)
C1–C2	1.421(6)
C2–C3	1.427(6)
C3–C4	1.420(7)
C4–C5	1.427(6)
C2–C6	1.488(7)
C3–C12	1.488(6)
C4–C18	1.476(6)
C5–C24	1.481(7)

^{a}E.s.d.s in the least-significant figure are given in parentheses. CNT = centroid of cyclopentadienyl ring.

TABLE 4. Selected intramolecular bond angles (°) in $[(C_5HPh_4)V(O_2CCF_3)_2]_2\cdot 2THF^a$

O4–V–O3	136.1(1)
O4–V–O1	82.2(2)
O4–V–O2	81.7(2)
O3–V–O1	81.6(2)
O3–V–O2	82.6(2)
O1–V–O2	136.4(1)
C30–O1–V	131.4(3)
C30′–O2–V	141.9(3)
C32–O3–V	135.2(3)
C32′–O4–V	139.5(3)

^{a}E.s.d.s in the least-significant figure are given in parentheses. Primed atoms are related to the unprimed atoms by the crystallographic center.

The vanadium atoms in **I** lie 3.752(1) Å apart. This exceeds the sum of their covalent radii (2.45 Å) and suggests there is no direct bonding between the vanadium atoms [10]. The vanadium–vanadium separation significantly exceeds that found for others in the series $(C_5R_5)V(\mu\text{-}O_2CR')_4(C_5R_5)$ (R = H, R′ = CF_3, Ph, 2-furanyl; R = Me and R′ = Ph) (Table 5) [3, 9, 11]. As further evidence of steric crowding we note the V–C distance to the unsubstituted carbon (C1) of the C_5HPh_4 ring is shorter than the distances to the more hindered

TABLE 5. Structural data for tetra-μ-carboxylatobis(η-cyclopentadienyl)di-vanadium(III) complexes

Complex	V–V′ (Å)	Reference
$[CpV(\mu\text{-}O_2CCF_3)_2]_2$	3.70^a	9
$[C_5Me_5V(\mu\text{-}O_2CPh)_2]_2$	3.652(2)	9
$[CpV(\mu\text{-}O_2C\text{-}\alpha\text{-furan})_2]_2$	3.625	12
$[CpV(\mu\text{-}O_2CPh)_2]_2$	3.636(1)^a	3, 13
$[(C_5HPh_4)V(\mu\text{-}O_2CCF_3)_2]_2$	3.752(1)	this work

^{a}The structure of this trifluoroacetate complex, $R = 13.9\%$ for 750 observed reflections, was said to be of low accuracy.

C4 and C5 carbons. The O–V–V′–O torsion angles have been used as a measure of steric hindrance in $[(\eta\text{-}C_5H_5)V(\mu\text{-}O_2CPh)_2]$ (within ±2.8° of 0, 180, ±90°) versus $[(\eta\text{-}C_5Me_5)V(\mu\text{-}O_2CPh)_2]$ (within ±10.9° of 0, 180, ±90°) [3]. Little distortion is observed in the O–V–V′–O torsion angles for **I** (within ±10.9° of 0, 180, ±90°). These differences between compounds containing a Ph group on the C-5 ring and CF_3 groups on the carboxylate bridge versus CH_3 groups on the ring and Ph groups on the carboxylate bridge are interesting. Significant variation in the C–O–V angles 131–141° is observed (Table 4), which has the effect of slightly tilting the bridging trifluoroacetate groups so the CF_3 groups point away from the phenyl substituted C3 and C4 atoms of the tetraphenylcyclopentadienyl ring and toward the unsubstituted Cl atom. Since the phenyl rings on C3 and C4 make dihedral angles of 63.5 and 116.8° with the cyclopentadienyl C1–C5 ring, and the corresponding values for phenyl sbstituents on C2 and C5 are only 28.6 and 32.6°, we expect the phenyl rings on C3 and C4 to interact most severely with the bridging carboxylate. As we have noted previously, the conveniently prepared $C_4HPh_4^-$ ligand provides a method for increasing steric bulk comparable to the $C_5Me_5^-$ ligand. Unlike the $C_5Me_5^-$ ligand, which significantly alters redox properties at the metal, the $C_5HPh_4^-$ group exhibits electron donor properties similar to $C_5H_5^-$ [2], and results in similar metal-based redox potentials.

Supplementary material

Tables of positional parameters for all atoms (2 pages), thermal parameters (3 pages), intramolecular distances and angles (5 pages), least-squares planes (3 pages), and observed and calculated structure factors (26 pages) are available from the authors on request.

Acknowledgements

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