**$Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$.** A suitable sample was cleaved from a larger well-formed crystal and transferred to the goniostat by using standard inert-atmosphere handling techniques employed at the IUMSC. The sample was characterized by using a standard reciprocal lattice search technique and found to be monoclinic of space group *A*2/*a*. All measurements were performed at -165 °C.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. All hydrogens were located in a difference Fourier phased on the non-hydrogen isotropic parameters. Final refinement included isotropic hydrogen and anisotropic non-hydrogen thermal parameters.

A final difference Fourier was featureless, the largest peak being 0.45 e/Å$^3$.

The structure lies on a crystallographic twofold axis as shown in one of the ORTEP views. In general the structure is considered well determined, as evidenced by the low residuals, low estimated standard deviations, and well-defined hydrogen positions.

Only one hydrogen atom was located in the difference Fourier synthesis near C(11), and it refined to a position as expected for Mo=CH—Si.

**$Mo_2Br_4(PMe_3)_4$.** A suitable sample was cleaved from a large needle and transferred to the goniostat using standard inert-atmosphere handling techniques employed at the IUMSC. The crystal was characterized at -171 °C by using a reciprocal lattice search technique and found to be monoclinic of space group *A*2/*a* (nonstandard setting of *C*2/*c*).

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques, and all hydrogen atoms were clearly discernible in a difference Fourier phased on the non-hydrogen parameters. Final full-matrix least squares included isotropic hydrogen parameters and anisotropic thermal parameters for non-hydrogen atoms as well as positional parameters and an overall scale factor.

The structure lies on a crystallographic twofold axis and has near *mm* symmetry as well. A final difference Fourier synthesis was essentially featureless, the largest peak being 0.65 e/Å$^3$.

**$MoBr(\equiv CSiMe_3)(Ph_2PCH_2CH_2PPh_2)_2 \cdot$Toluene.** A suitable sample was cleaved from a larger crystal and transferred to the goniostat by using standard inert-atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space at -160 °C revealed no systematic absences or symmetry, indicating a triclinic lattice.

The structure was solved by direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen contributors and were included in the final cycles as fixed atom contributors in idealized positions.

A final difference Fourier was featureless, the largest peak being 0.85 e/Å$^3$.

The asymmetric unit contains a molecule of toluene in addition to the complex. The closest approach between the complex and the solvent molecule is 3.5 Å.

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**Registry No.** I, 83214-27-1; II, 89707-70-0; III, 96413-40-0; III·toluene, 96413-41-1; IV, 96413-43-3; $Mo_2Br_4(PMe_2Ph)_4$, 96413-42-2; $Mo_2Br_4(PEt_3)_4$, 59752-94-2; $MoBr(\equiv SiMe_3)(PEt_3)_4$, 96413-44-4; $MoBr(\equiv cSiMe_3)(PMe_3)_4$, 96413-45-5; $Mo_2Br_2(CH_2SiMe_3)_4$, 75059-90-4; $PMe_3$, 594-09-2; $PMe_2Ph$, 672-66-2; $Ph_2PCH_2CH_2PPh_2$, 1663-45-2; $PEt_3$, 554-70-1; $Me_2PCH_2PMe_2$, 64065-08-3; Mo, 7439-98-7.

**Supplementary Material Available:** Complete listings of bond distances and angles, isotropic thermal parameters for H atoms, anisotropic thermal parameters for non-hydrogen atoms, and structure factor amplitudes (52 pages). Ordering information is given on any current masthead page. The complete structural reports are available from the Indiana University Chemistry Library, in microfiche form only and at a cost of $2.50 per report. Request MSC Report Nos. 82088, 82027, and 83064 for $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$, $Mo_2Br_4(PMe_3)_4$, and $MoBr(\equiv CSiMe_3)(diphos)_2 \cdot$toluene.

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# Two Compounds Containing a Divanadium Tetrabenzoate Frame and Cyclopentadienyl or Pentamethylcyclopentadienyl Ligands

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Two compounds $(\eta^5\text{-}C_5H_5)_2V_2(C_6H_5CO_2)_4$, **1**, and $(\eta^5\text{-}C_5Me_5)_2V_2(C_6H_5CO_2)_4$, **2**, have been prepared from vanadocene and decamethylvanadocene, respectively, and characterized by single-crystal X-ray crystallography. The data are as follows. For **1**: $P\bar{1}$; $a = 10.640$ (2) Å, $b = 10.774$ (3) Å, $c = 8.510$ (2) Å, $\alpha = 112.83$ (2)°, $\beta = 101.41$ (2)°, $\gamma = 69.43$ (2)°, $V = 839.6$ (6) Å$^3$, $Z = 1$, $R_1 = 0.0477$, $R_2 = 0.0547$. For **2**: $C2/c$; $a = 11.576$ (3) Å, $b = 16.721$ (2) Å, $c = 21.452$ (2) Å, $\beta = 90.45$ (3)°, $V = 4152$ (3) Å$^3$, $Z = 4$, $R_1 = 0.0733$, $R_2 = 0.0885$. The V–V′ distances of 3.636 (1) Å for **1** and 3.652 (2) Å for **2** suggest that little if any direct bonding occurs between two vanadium atoms. The presence of pentamethylcyclopentadienyl ligands in the axial positions in **2** causes a twist of the four carboxylate bridges with torsional angles for the two independent O–V–V′–O′ units equal to 5.9° and 10.9°. In the cyclopentadienyl derivative **1** the corresponding torsional angles are each 2.6°.

## Introduction

Vanadocene, $(\eta^5\text{-}C_5H_5)_2V$, represents an interesting starting material for entry into low-valent nonaqueous vanadium organometallic chemistry.[1] Of particular interest to us was the reaction of vanadocene with carboxylic acids in benzene leading to products of empirical formula $CpV(RCO_2)_2$, as reported by Razuvaev, Latyaeva, Lineva, and Zelenev in 1974.[2] Such compounds were prepared for three carboxylic acids, R = H, $CH_3$, and $C_6H_5$, and their composition was postulated to be monomeric on the basis of elemental analyses, IR spectra, and chemical reactions with EtONa and HCl.

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(1) See, for example: Connelly, N. G. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, p 672.

(2) Razuvaev, G. A.; Latyaeva, V. N.; Lineva, A. G.; Zelenev, S. V. *Dokl. Chem.* 1974, *216*, 355.

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**Table I. Crystallographic Data**

| | $[V(O_2CPh)_2Cp]_2$ | $[V(O_2CPh)_2C_5Me_5]_2$ |
|---|---|---|
| formula | $V_2O_8C_{38}H_{30}$ | $V_2O_8C_{48}H_{50}$ |
| fw | 716.54 | 856.81 |
| space group | $P\bar{1}$ | $C2/c$ |
| systematic absences | | $hkl$, $h + k \neq 2n$; $h0l$, $l = 2n$ |
| $a$, Å | 10.640 (2) | 11.576 (3) |
| $b$, Å | 10.774 (3) | 16.721 (2) |
| $c$, Å | 8.510 (2) | 21.452 (5) |
| $\alpha$, deg | 112.83 (2) | 90.0 |
| $\beta$, deg | 101.41 (2) | 90.45 (3) |
| $\gamma$, deg | 69.43 (2) | 90.0 |
| $V$, Å$^3$ | 839.6 (6) | 4152 (3) |
| $Z$ | 1 | 4 |
| $d_{calcd}$, g/cm$^3$ | 1.417 | 1.371 |
| cryst size, mm | 0.3 × 0.3 × 0.2 | 0.35 × 0.15 × 0.1 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 5.881 | 4.872 |
| data collectn instrument | CAD-4 | CAD-4 |
| radiatn (monochromated in incident beam) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) | Mo K$\alpha$ ($\lambda$ = 0.71073 Å) |
| orientatn reflctns, no., range ($2\theta$) | 25, 16.6–37.4 | 25, 9.9–29.9 |
| temp, °C | 22 | 22 |
| scan method | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| data col range, $2\theta$, deg | 4, 50 | 4, 50 |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 2316, 1770 | 2176, 1316 |
| no. of parameters refined | 277 | 177 |
| $R^a$ | 0.0477 | 0.0733 |
| $R_w^b$ | 0.0547 | 0.0885 |
| quality-of-fit indicator$^c$ | 1.371 | 2.068 |
| largest shift/esd, final cycle | 0.09 | 0.05 |
| largest peak, e/Å$^3$ | 0.42 | 0.62 |

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. $^c$ Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Related reactions (but chemically rather different) of $CpV(CO)_4$ with $RCO_2H$ where R = H, $CCl_3$, $CF_3$, $C_6H_5$, $m\text{-}FC_6H_4$, $m\text{-}OCH_3C_6H_4$, 2-furanyl, and 2-thionyl in toluene were reported to give dimeric compounds[3] of the type $CpV(RCO_2)_4VCp$, $CpV(RCO_2)_4VCp$, as evidenced by X-ray studies for R = $CF_3$[4] and 2-furanyl.[5] Also, X-ray analysis showed the product of the reaction of $CpNb(CO)_3PPh_3$ with formic acid in xylene to be trimeric, e.g., $(CpNbHCO_2)_3(OH)_2(O)_2$.[6]

In the light of these results we decided to investigate the crystal structure of the product of the reaction of vanadocene with benzoic acid in benzene in order to see whether that product is monomeric or oligomeric. We also hoped that the product of such a reaction might be divanadium tetrabenzoate because, as reported by our laboratory some time ago, reactions of chromocene with carboxylic acids lead to dichromium tetracarboxylates.[7] Our X-ray analysis of the product of the reaction of $Cp_2V$ with PhCOOH shows that this reaction affords a dimeric compound with a $V(\mu\text{-}PhCO_2)_4V$ core and two cyclopentadienyl rings in axial positions. To assess the role of steric factors in retention of one cyclopentadienyl ring on each vanadium atom in this type of reaction with carboxylic acids, we also examined and report here a new reaction of decamethylvanadocene with benzoic acid and full X-ray analysis of its main product.

## Experimental Section

All manipulations were performed under an atmosphere of argon using standard Schlenk techniques, a double-manifold vacuum line, and a drybox. Vandocene[8] and decamethylvanadocene[9] were prepared according to literature methods. Benzoic acid was deaerated under vacuum for at least an hour before use at room temperature. Benzene, toluene, and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulae and/or syringes.

**$(\eta^5\text{-}C_5H_5)_2V_2(PhCO_2)_4$.** In a drybox, benzoic acid (3.6 g, 29.8 mmol) and freshly sublimed vandocene (2.7 g, 14.9 mmol) were placed in a 250-mL Schlenk tube equipped with a magnetic stirrer. The Schlenk tube was connected to the vacuum/argon line, and 60 mL of benzene was added. The purple reaction mixture was stirred for 12 h at room temperature to give a shiny purple crystalline solid. It was filtered off, washed with benzene (1 × 5 mL) and then hexane (2 × 10 mL), and dried under vacuum for several hours (3.5 g, yield 66.0%).

**$(\eta^5\text{-}C_5Me_5)_2V_2(PhCO_2)_4$.** In a drybox, benzoic acid (0.57 g, 4.68 mmol) and freshly sublimed decamethylvanadocene (0.5 g, 1.56 mmol) were placed in a 100-mL Schlenk tube equipped with a magnetic stirrer. The Schlenk tube was connected to the vacuum/argon line, and 10 mL of benzene was added. The red reaction mixture was stirred for 12 h at room temperature, and no apparent color change occurred. Toluene (10 mL) was added to the mixture, and the reaction was continued at reflux for an additional 12 h during which time the color of the solution became dark red. After cooling of the reaction mixture to room temperature and partial removal of the solvents under vacuum, freshly distilled hexane was added to the solution (ca. 40 mL) to precipitate a dark red shiny crystalline solid. It was filtered off, washed three times with hexane, and dried under vacuum for several hours (0.3 g, yield 57%).

Crystallographic quality crystals of $(\eta^5\text{-}C_5H_5)_2V_2(PhCO_2)_4$ were prepared by careful layering, with hexane, of the tetrahydrofuran solution of $(\eta^5\text{-}C_5H_5)_2V_2(PhCO_2)_4$. Similarly, X-ray quality crystals of $(\eta^5\text{-}C_5Me_5)_2V_2(PhCO_2)_4$ were prepared by covering a benzene–toluene (v/v, 1:1) solution of $(\eta^5\text{-}C_5Me_5)_2V_2(PhCO_2)_4$ with a layer of hexane.

**X-ray Crystallography.** General procedures have been described previously.[10] Basic information about data collection and

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(10) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

**Table II. Positional and Isotropic Equivalent Thermal Parameters for $V_2(O_2CPh)_4Cp_2$[a,b]**

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| V | 0.36532 (7) | 0.04995 (7) | 0.13562 (8) | 2.89 (2) |
| O(1) | 0.3283 (3) | 0.1988 (3) | 0.0298 (4) | 4.80 (8) |
| O(2) | 0.5010 (3) | −0.1386 (3) | 0.1258 (4) | 4.92 (8) |
| O(3) | 0.5172 (3) | 0.1273 (3) | 0.2657 (4) | 4.80 (9) |
| O(4) | 0.3134 (3) | −0.0608 (4) | −0.1066 (4) | 5.4 (1) |
| C(1) | 0.3884 (4) | 0.2184 (4) | −0.0658 (5) | 3.1 (1) |
| C(2) | 0.3237 (4) | 0.3454 (4) | −0.1164 (5) | 3.1 (1) |
| C(3) | 0.3980 (5) | 0.4027 (5) | −0.1646 (6) | 4.8 (1) |
| C(4) | 0.3388 (5) | 0.5220 (5) | −0.2081 (7) | 6.2 (1) |
| C(5) | 0.2023 (6) | 0.5798 (5) | −0.2100 (7) | 7.0 (2) |
| C(6) | 0.1262 (5) | 0.5212 (5) | −0.1645 (7) | 6.9 (2) |
| C(7) | 0.1872 (5) | 0.4052 (5) | −0.1189 (6) | 5.1 (1) |
| C(8) | 0.6313 (4) | 0.1228 (4) | 0.2448 (5) | 3.2 (1) |
| C(9) | 0.7105 (4) | 0.1956 (4) | 0.3949 (5) | 3.3 (1) |
| C(10) | 0.8491 (4) | 0.1495 (5) | 0.4033 (6) | 4.3 (1) |
| C(11) | 0.9214 (5) | 0.2159 (6) | 0.5424 (7) | 6.2 (2) |
| C(12) | 0.8553 (5) | 0.3317 (7) | 0.6728 (7) | 7.5 (2) |
| C(13) | 0.7165 (6) | 0.3781 (7) | 0.6641 (7) | 7.4 (2) |
| C(14) | 0.6443 (5) | 0.3102 (5) | 0.5256 (6) | 4.8 (1) |
| C(15) | 0.1428 (4) | 0.1287 (6) | 0.1853 (6) | 6.0 (2) |
| C(16) | 0.2006 (5) | 0.2184 (5) | 0.3120 (7) | 6.0 (1) |
| C(17) | 0.2859 (5) | 0.1447 (7) | 0.4070 (6) | 7.5 (2) |
| C(18) | 0.2844 (6) | 0.0097 (6) | 0.3402 (6) | 8.9 (2) |
| C(19) | 0.1940 (5) | −0.0002 (6) | 0.2016 (7) | 7.1 (2) |
| H(3) | 0.484 (4) | 0.367 (4) | −0.153 (5) | 5 (1)* |
| H(4) | 0.409 (5) | 0.567 (5) | −0.238 (6) | 8 (1)* |
| H(5) | 0.159 (5) | 0.660 (5) | −0.244 (6) | 8 (1)* |
| H(6) | 0.045 (5) | 0.555 (5) | −0.169 (7) | 9 (2)* |
| H(7) | 0.138 (3) | 0.371 (3) | −0.091 (4) | 2.9 (8)* |
| H(10) | 0.893 (4) | 0.065 (4) | 0.311 (5) | 6 (1)* |
| H(11) | 1.006 (4) | 0.196 (4) | 0.555 (5) | 6 (1)* |
| H(12) | 0.905 (5) | 0.388 (5) | 0.763 (6) | 7 (1)* |
| H(13) | 0.675 (4) | 0.454 (4) | 0.737 (5) | 5 (1)* |
| H(14) | 0.554 (4) | 0.334 (4) | 0.515 (4) | 3.6 (9)* |
| H(15) | 0.087 (5) | 0.157 (5) | 0.103 (6) | 7 (1)* |
| H(16) | 0.190 (5) | 0.300 (5) | 0.320 (7) | 9 (2)* |
| H(17) | 0.333 (4) | 0.174 (4) | 0.486 (5) | 6 (1)* |
| H(18) | 0.316 (6) | −0.063 (5) | 0.366 (7) | 9 (2)* |
| H(19) | 0.160 (5) | −0.073 (5) | 0.118 (7) | 9 (2)* |

[a] Atoms with an asterisk were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}$.

structure refinement for both compounds is summarized in Table I. Polarization and Lorentz corrections were applied to the intensity data. No absorption corrections were deemed necessary.

**$(\eta^5\text{-}C_5H_5)_2V_2(PhCO_2)_4$, 1.** The position of the V atom was determined from a three-dimensional Patterson function. All non-hydrogen atoms were located and refined, first isotropically and then anisotropically, by an alternating series of difference Fourier syntheses and full-matrix least-squares refinements. The hydrogen atoms were also found in the difference Fourier map and included in the refinement.

**$(\eta^5\text{-}C_5Me_5)_2V_2(PhCO_2)_4$, 2.** The structure was partially solved by direct methods. The complete set of atoms was located and refined as described above. The closeness of the $\beta$ angle to 90° and the similarity of some atomic positional parameters raised the possibility of an orthorhombic space group. However, the lack of equivalency of reflections of the type $hkl$ and $hk\bar{l}$ ruled this out. The refinement was completed with anisotropic thermal parameters assigned to selected atoms (see Table III).

Tables of observed and calculated structure factors and anisotropic thermal parameters are provided as supplementary material.

## Results and Discussion

**Syntheses.** The reaction between vanadocene, $(\eta^5\text{-}C_5H_5)_2V$, and benzoic acid in benzene at room temperature furnishes purple crystals, proved by X-ray crystallography to contain $(\eta^5\text{-}C_5H_5)V(PhCOO)_4V(\eta^5\text{-}C_5H_5)$ molecules, in 66% yield. The structural details will be discussed fully below, but one important conclusion that we drew from that structure can be stated now. It seemed to us that a more sterically demanding cyclopentadienyl ligand might possibly create enough spacial crowding in the vicinity of the bridging carboxylate ligands that such a ligand could not be retained in the axial position at all, thus allowing the preparation of $V_2(O_2CPh)_4$ with a multiple metal–metal bond between the two vanadium atoms. To evaluate the possibility, we reacted decamethylvanadocene with benzoic acid in benzene/toluene. We have found, however, that this reaction affords a dark red compound, shown by X-ray crystallography to be $(\eta^5\text{-}C_5Me_5)V(PhCOO)_4V(\eta^5\text{-}C_5Me_5)$. Two pentamethylcyclopentadienyl rings are retained in the vanadium axial positions, even though they impose a great deal of strain on the four carboxylate bridges. This structural feature will be discussed below.

**Table III. Positional and Isotropic Equivalent Thermal Parameters for $V_2(O_2CPh)_4(C_5Me_5)_2$[a,b]**

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| V | −0.1567 (1) | 0.1278 (1) | 0.23971 (8) | 2.27 (3) |
| O(1) | −0.0797 (6) | 0.0414 (4) | 0.1876 (3) | 3.4 (2) |
| O(2) | −0.1120 (6) | 0.0566 (5) | 0.3120 (3) | 3.7 (2) |
| O(3) | −0.1141 (6) | 0.2144 (4) | 0.3034 (3) | 3.7 (2) |
| O(4) | −0.0764 (6) | 0.2045 (4) | 0.1788 (4) | 3.6 (2) |
| C(1) | 0.0201 (9) | 0.0253 (6) | 0.1671 (5) | 2.9 (2) |
| C(2) | 0.0289 (8) | −0.0320 (6) | 0.1143 (5) | 2.6 (2)* |
| C(3) | −0.047 (1) | −0.0952 (7) | 0.1096 (5) | 3.6 (3)* |
| C(4) | −0.037 (1) | −0.1490 (7) | 0.0589 (6) | 4.6 (3)* |
| C(5) | 0.048 (1) | −0.1361 (8) | 0.0135 (6) | 5.5 (3)* |
| C(6) | 0.124 (1) | −0.0697 (8) | 0.0195 (7) | 5.6 (3)* |
| C(7) | 0.116 (1) | −0.0188 (7) | 0.0709 (6) | 4.2 (3)* |
| C(8) | 0.0226 (9) | 0.2306 (6) | 0.1682 (5) | 2.9 (2) |
| C(9) | 0.0320 (9) | 0.2895 (6) | 0.1150 (5) | 2.7 (2)* |
| C(10) | −0.0637 (9) | 0.3356 (7) | 0.0966 (5) | 3.1 (2)* |
| C(11) | −0.0557 (9) | 0.3866 (7) | 0.0472 (5) | 4.0 (3)* |
| C(12) | 0.0469 (9) | 0.3922 (7) | 0.0123 (6) | 4.1 (3)* |
| C(13) | 0.138 (1) | 0.3471 (7) | 0.0297 (6) | 4.0 (3)* |
| C(14) | 0.1331 (9) | 0.2957 (6) | 0.0818 (5) | 3.1 (2)* |
| C(15) | −0.3333 (9) | 0.0632 (6) | 0.2500 (5) | 3.5 (3) |
| C(16) | −0.3398 (8) | 0.1390 (7) | 0.2793 (5) | 3.5 (3) |
| C(17) | −0.3278 (9) | 0.1970 (6) | 0.2311 (6) | 3.2 (3) |
| C(18) | −0.3158 (8) | 0.1564 (7) | 0.1740 (5) | 3.6 (3) |
| C(19) | −0.3223 (8) | 0.0733 (7) | 0.1872 (5) | 3.7 (3) |
| C(20) | −0.348 (1) | −0.0170 (9) | 0.2853 (6) | 5.7 (3)* |
| C(21) | −0.363 (1) | 0.1545 (8) | 0.3480 (7) | 5.6 (3)* |
| C(22) | −0.330 (1) | 0.2876 (8) | 0.2389 (7) | 5.3 (3)* |
| C(23) | −0.306 (1) | 0.1937 (8) | 0.1094 (6) | 4.9 (3)* |
| C(24) | −0.320 (1) | 0.0081 (8) | 0.1370 (6) | 5.9 (3)* |

[a] Atoms with an asterisk were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}$.

The reactions of vanadocene or decamethylvanadocene with benzoic acid seem not to be dependent upon the number of moles of acid used. The same product was obtained when vanadocene and benzoic acid were reacted regardless of whether the molar ratio of reactants was 1:3 or an excess of benzoic acid was used at reflux. These experiments were carried out to see if we could remove the axial Cp ligand by a simple protonation reaction but apparently this is a difficult task. Reduction reactions using NaK alloy or Na in THF also failed to remove the cyclopentadienyl ligands from the carboxylate dimer.

**Molecular Structures.** The atomic positional parameters for 1 and 2 are presented in Tables II and III. Selected interatomic dimensions are compared in Table IV. A full listing of bond distances and angles, including contacts of less than 3.5 Å between oxygen atoms and atoms in the axial ligands, are included in the supplementary material. ORTEP drawings of both molecules are shown in Figure 1.

The molecule of $V_2(O_2CC_6H_5)_4Cp_2$ resides on a crystallographic inversion center while that of its $CpMe_5$

**Table IV. Important Interatomic Dimensions for $V_2(O_2CPh)_4X_2$ Complexes**

| | X = Cp | X = $C_5Me_5$ |
|---|---|---|
| | A. Distances (Å) | |
| V-V′ | 3.636 (1) | 3.652 (2) |
| V-O(1) | 2.019 (4) | 2.037 (5) |
| V-O(2) | 2.018 (3) | 2.020 (6) |
| V-O(3) | 2.014 (3) | 2.047 (6) |
| V-O(4) | 2.020 (3) | 2.058 (6) |
| V-C(15) | 2.282 (5) | 2.324 (8) |
| V-C(16) | 2.304 (5) | 2.298 (8) |
| V-C(17) | 2.329 (5) | 2.300 (8) |
| V-C(18) | 2.324 (7) | 2.358 (8) |
| V-C(19) | 2.294 (7) | 2.396 (8) |
| V-$O_4$ plane | 0.712 | 0.718 |
| V-$C_5$ plane | 1.999 | 2.002 |
| | B. Angles (deg) | |
| O(1)-V-O(2) | 138.8 (1) | 83.8 (3) |
| O(1)-V-O(3) | 83.3 (1) | 139.8 (2) |
| O(1)-V-O(4) | 81.3 (1) | 83.7 (2) |
| O(2)-V-O(3) | 84.0 (1) | 81.2 (2) |
| O(2)-V-O(4) | 82.9 (1) | 137.8 (2) |
| O(3)-V-O(4) | 138.5 (2) | 82.8 (3) |
| V′-V-O(1) | 71.10 (9) | 68.1 (2) |
| V′-V-O(2) | 67.8 (1) | 70.0 (2) |
| V′-V-O(3) | 68.13 (9) | 71.6 (2) |
| V′-V-O(4) | 70.5 (1) | 67.9 (2) |
| V′-V-C(15) | 151.7 (1) | 149.6 (2) |
| V′-V-C(16) | 151.3 (2) | 150.9 (2) |
| V′-V-C(17) | 149.8 (1) | 149.8 (2) |
| V′-V-C(18) | 148.1 (1) | 147.4 (2) |
| V′-V-C(19) | 149.6 (1) | 147.9 (2) |

**Table V. Torsion Angles (deg) in the $V_2O_8$ Skeleton for the $V_2(O_2CPh)_4X_2$ Complexes**[a]

| | X = Cp | X = $C_5Me_5$ |
|---|---|---|
| O(1)-V-V′-O(1)′ | 180.0 | -80.3 |
| O(1)-V-V′-O(2)′ | 2.6 | 10.9 |
| O(1)-V-V′-O(3)′ | -89.8 | 98.0 |
| O(1)-V-V′-O(4)′ | 92.8 | -172.4 |
| O(2)-V-V′-O(2)′ | 180.0 | 102.2 |
| O(2)-V-V′-O(3)′ | 87.6 | -170.8 |
| O(2)-V-V′-O(4)′ | -89.8 | -81.1 |
| O(3)-V-V′-O(3)′ | 180.0 | -83.7 |
| O(3)-V-V′-O(4)′ | 2.6 | 5.9 |
| O(4)-V-V′-O(4)′ | 180.0 | 95.5 |

[a] See Figure 2 for atom numbering scheme.

analogue is located on a two fold axis. The substitution of Cp by a sterically more demanding pentamethyl ligand has practically no effect on the bond lengths and angles. The V-C distances in **2** cover a wider range (2.298–2.396 Å) than they do in **1** (2.282–2.329 Å), but the position of the V atoms with respect to the $O_4$ and Cp planes is almost identical in the two compounds. Slight asymmetry in the relationship of the rings to the V atoms is probably due to steric rather than electronic factors. The $O_4$ and Cp planes are almost parallel with dihedral angles equal 1.8 and 2.4° for the Cp and $C_5Me_5$ complexes, respectively.

The discussion so far has stressed the similarities between the two compounds but the presence of the more sterically demanding $C_5Me_5$ ring does introduce a significant distortion. The V-V′ line in **2**, unlike that in **1**, is far from coplanar with the $CO_2$ planes, as can be seen in Figure 2. The observed twist (see Table V for torsional angles) probably has some effect on the V-O bond lengths, which are slightly longer in the case of compound **2**.

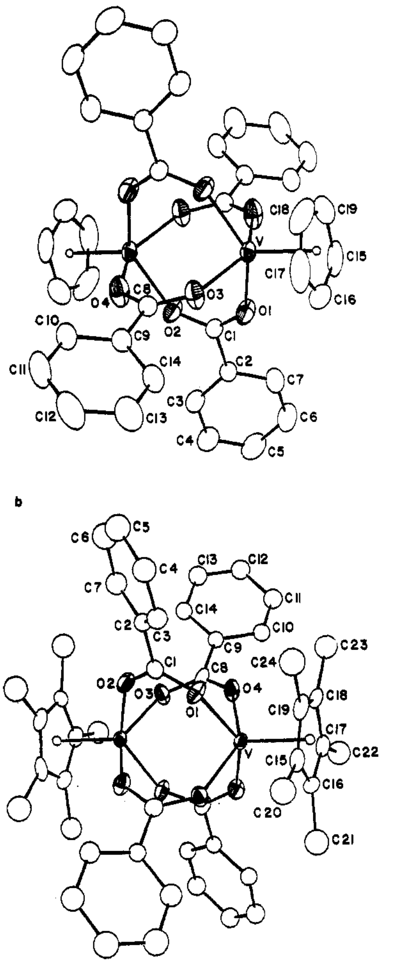

**Figure 1.** ORTEP drawings of the $V_2(O_2CPh)_4X_2$ molecules, with thermal ellipsoids drawn at 30% probability level: (a) X = $C_5H_5^-$ (with the molecule having an inversion center); (b) X = $C_5(CH_3)_5^-$ (where there is a twofold axis roughly perpendicular to the plane of the drawing).

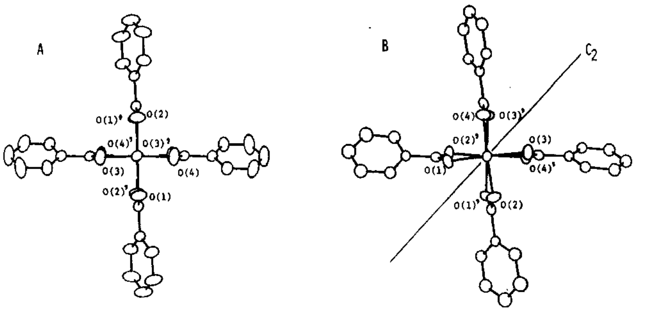

**Figure 2.** Views of the central regions of the $V_2(O_2CPh)_4X_2$ molecules along the V-V′ vector: (a) X = $C_5H_5^-$; (b) X = $C_5(CH_3)_5^-$.

The complexes described here appear to be basically similar to those of the previously reported $[V(O_2CR)_2Cp]_2$ species with R = $CF_3$[4] and 2-furanyl[5] although it may be noted that these earlier structures have ca. 14% *R* factors. All have very long metal to metal distance of the order 3.6 Å, which can be attributed to the presence of the axial Cp or $C_5Me_5$ ligands, since closer approach of the metal atoms would shorten the O-Cp contacts.

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**Registry No.** **1**, 39366-69-3; **2**, 96109-93-2; vanadocene, 1277-47-0; decamethylvanadocene, 74507-60-1.

**Supplementary Material Available:** Tables of observed and calculated structure factors, full lists of bond distances and angles, tables of anisotropic thermal parameters, *B*'s, and tables of selected least-squares planes (27 pages). Ordering information is given on any current masthead page.