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 (10) $R(F_o^2) = \sum |F_o^2 - KF_c^2| / \sum F_o^2$ and $R_w(F^2) = [\sum w(F_o^2 - kF_c^2)^2 / \sum wF_o^4]^{1/2}$. All least-squares refinements were based on the minimization of $\sum w(F_o^2 - F_c^2)^2$ with individual weights $w = 1/\sigma^2(F_o^2)$.
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Vanadium-Olefin and -Acetylene Complexes: Structural Studies on (η^2 -Diethyl fumarato-C,C)- and (η^2 -Dimethyl acetylenedicarboxylato-C,C)bis(η -cyclopentadienyl)vanadium

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Vanadocene, $(\text{cp})_2\text{V}$ ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$), adds as a carbene-like species to the $\text{C}=\text{C}$ bond of diethyl fumarate or diethyl maleate, producing the same monomeric olefinic complex (IV) in which the coordinated olefin assumes the trans configuration. Diethyl maleate isomerizes upon coordination to the metal. Vanadium is η^2 bonded to the two Cp rings, which are in a bent arrangement making a cavity in the equatorial plane for the η^2 -C,C bonded olefinic ligand [$\text{cp}(1)\text{-V-cp}(2) = 135.9^\circ$]. The $\text{C}=\text{C}$ bond distance is significantly lengthened by interaction with the metal to the value [1.468 (11) Å] expected for a single bond. Vanadocene reacts with $\text{CH}_3\text{O}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{CH}_3$ giving complex V with an overall geometry very similar to that found for the olefinic complex. The coordinated C-C bond length [1.287 (4) Å] is nearly close to that of a double bond. Both complexes have rigorous C_2 symmetry. They represent rare examples of vanadocene with an additional V-C bond for which structural data are available [V-C = 2.186 (12) and 2.213 (12) Å for $(\text{cp})_2\text{V}(\text{C}_2\text{H}_5\text{O}_2\text{CCH-CHCO}_2\text{C}_2\text{H}_5)$ and 2.097 (3) and 2.084 (3) Å for $(\text{cp})_2\text{V}(\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3)$]. Crystallographic details for $(\text{cp})_2\text{V}(\text{C}_2\text{H}_5\text{O}_2\text{C-CH-CH-CO}_2\text{C}_2\text{H}_5)$: space group $P2_1/c$ (monoclinic); $a = 7.871$ (1), $b = 18.604$ (3), $c = 13.712$ (3) Å; $\beta = 121.32$ (2)°; $U = 1715.3$ Å³; $Z = 4$; $D_c = 1.368$ g cm⁻³. The final R factor was 6.5% for 2321 observed reflections. Crystallographic details for $(\text{cp})_2\text{V}(\text{CH}_3\text{O}_2\text{C-C}\equiv\text{C-CO}_2\text{CH}_3)$: space group C_2/c (monoclinic); $a = 25.089$ (2), $b = 7.948$ (1), $c = 15.979$ (2) Å; $\beta = 112.14$ (1)°; $U = 2951.4$ Å³; $Z = 8$; $D_c = 1.455$ g cm⁻³. The final R factor was 4.4% for 2408 observed reflections.

Introduction

While the olefin and acetylene metal-promoted reactivity is very well-known in titanium and vanadium bis(cyclopentadienyl) chemistry,¹ structural evidence on acetylene and olefin complexes is practically absent. Only very recently we described the first diphenylacetylene η^2 -C,C bonded to titanium in $(\text{cp})_2\text{Ti}(\text{CO})(\text{Ph}_2\text{C}_2)$ ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$).² The interest in π olefin and π acetylene complexes of titanium and vanadium stems from the special activity of these metals which are able to promote polymerization, oligomerization, and catalytic hydrogenation of these unsaturated substrates.¹⁻³ This notwithstanding, we did not find structural models for vanadium-olefin⁴ and vanadium-acetylene interaction.^{3,5} Moreover, structural data on vanadocenes bearing an additional vanadium-carbon bond are limited to only the few cases reported in Table VIII.^{6,7} As a part of our continuing investigations into the structure and chemical properties of bis(cyclopentadienyl) derivatives of early transition metals, we report here the structural properties of $(\text{cp})_2\text{V}(\text{EtO}_2\text{CCH-CHCO}_2\text{Et})$ ⁴ and $(\text{cp})_2\text{V}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})$.³

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Experimental Section

Sample Preparations. The direct synthesis gave diffraction-quality crystals. Both complexes are reasonably air-stable in the solid state. Complex IV, $(\text{cp})_2\text{V}(\text{EtO}_2\text{CCH-CHCO}_2\text{Et})$, was prepared from diethyl maleate.⁴ The slightly modified version used for the synthesis of complex V,³ $(\text{cp})_2\text{V}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})$, is given below.

Synthesis of $(\text{cp})_2\text{V}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})$. A benzene (20 mL) solution of $(\text{cp})_2\text{V}$ (0.85 g, 4.70 mmol) is reacted with neat $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ (0.72 mL, 5.1 mmol). The solution color turns suddenly to deep green. Green crystals suitable for an X-ray analysis start to separate in 15 min. The yield of $(\text{cp})_2\text{V}(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})$ is increased by adding heptane (50 mL) to the solution. The overall yield is ca. 70%. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{V}$: C, 59.44; H, 4.95. Found: C, 59.11; H, 5.10. The IR spectrum in Nujol shows a strong band at 1820 cm⁻¹ ($\nu_{\text{C}=\text{C}}$) and a strong band of complex envelope centered at 1670 cm⁻¹ ($\nu_{\text{C}=\text{O}}$).

X-ray Data Collection and Structure Refinement.⁸ The crystals examined were wedged into thin-walled glass capillaries which were sealed under nitrogen. They were mounted with the [001] axis along the Φ axis of the diffractometer. A summary of the crystal and intensity data collection is given in Table I. Lattice constants came from least-squares refinements of the 2θ values for 31 reflections [$2\theta > 40^\circ$ for IV, $2\theta > 100^\circ$ for V].

Table I. Summary of Crystal Data and Intensity Collection

| | C ₁₈ H ₂₂ O ₄ V (IV) | C ₁₆ H ₁₆ O ₄ V (V) |
|-----------------------------------|---|--|
| <i>a</i> , Å | 7.871 (1) | 25.089 (2) |
| <i>b</i> , Å | 18.604 (3) | 7.948 (1) |
| <i>c</i> , Å | 13.712 (3) | 15.979 (2) |
| α , deg | 90.0 | 90.0 |
| β , deg | 121.32 (2) | 112.14 (1) |
| γ , deg | 90.0 | 90.0 |
| <i>Z</i> | 4 | 8 |
| <i>M_r</i> | 353.3 | 323.2 |
| calcd density, g cm ⁻³ | 1.368 | 1.455 |
| space group | <i>P</i> 2 ₁ / <i>c</i> | <i>C</i> 2/ <i>c</i> |
| radiation | Nb-filtered Mo K α (λ 0.710 69 Å) | Ni-filtered Cu K α (λ 1.541 78 Å) |
| μ , mm ⁻¹ | 0.63 | 5.79 |
| $\bar{\omega}$ | 0.1 | 0.7 |
| scan type | θ - 2θ | θ - 2θ |
| scan range | | $\pm 0.5^\circ$ from peak center |
| scan speed | | 2.5-10° θ /min |
| bkgd | | stationary cryst at $\pm 0.5^\circ$ |
| 2θ limits, deg | 5-58 | 6-140 |
| criterion for obsn | $I > 2\sigma(I)$ | $I > 2\sigma(I)$ |
| unique obsd data | 2321 | 2408 |
| unique total data | 4333 | 2775 |
| cryst dimens, mm | 0.24 \times 0.39 \times 0.47 | 0.21 \times 0.29 \times 0.55 |

Table II. Final Atomic Fractional Coordinates for Complex IV^a

| | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--------|--------------|------------|-------------|
| V(1) | 0.4333 (2) | 0.2954 (1) | 0.5126 (1) |
| O(1) | 0.0408 (9) | 0.1464 (3) | 0.4160 (5) |
| O(2) | 0.1875 (10) | 0.1477 (3) | 0.6063 (5) |
| O(3) | -0.0182 (9) | 0.3926 (3) | 0.4907 (6) |
| O(4) | -0.0682 (8) | 0.4023 (3) | 0.3144 (5) |
| C(1) | 0.4297 (13) | 0.3780 (5) | 0.6351 (8) |
| C(2) | 0.6077 (14) | 0.3412 (5) | 0.6969 (8) |
| C(3) | 0.7135 (13) | 0.3552 (5) | 0.6426 (7) |
| C(4) | 0.5984 (14) | 0.4007 (4) | 0.5485 (8) |
| C(5) | 0.4223 (14) | 0.4153 (4) | 0.5441 (8) |
| C(6) | 0.4552 (17) | 0.2623 (5) | 0.3571 (9) |
| C(7) | 0.6447 (15) | 0.2637 (5) | 0.4541 (10) |
| C(8) | 0.6595 (14) | 0.2112 (6) | 0.5331 (9) |
| C(9) | 0.4787 (15) | 0.1773 (5) | 0.4846 (10) |
| C(10) | 0.3517 (14) | 0.2083 (5) | 0.3747 (8) |
| C(11) | 0.1048 (11) | 0.3019 (4) | 0.4175 (7) |
| C(12) | 0.1773 (11) | 0.2562 (4) | 0.5188 (7) |
| C(13) | 0.1250 (11) | 0.1784 (4) | 0.5036 (7) |
| C(14) | 0.0046 (11) | 0.3692 (4) | 0.4154 (7) |
| C(15) | 0.1364 (23) | 0.0719 (6) | 0.6001 (11) |
| C(16) | 0.2509 (24) | 0.0415 (7) | 0.7106 (18) |
| C(17) | -0.1691 (18) | 0.4706 (6) | 0.3040 (11) |
| C(18) | -0.2507 (25) | 0.4977 (8) | 0.1890 (12) |
| H(1) | 0.355 (14) | 0.376 (5) | 0.670 (8) |
| H(2) | 0.645 (13) | 0.320 (5) | 0.756 (8) |
| H(3) | 0.854 (14) | 0.333 (5) | 0.677 (8) |
| H(4) | 0.637 (14) | 0.417 (5) | 0.507 (8) |
| H(5) | 0.301 (14) | 0.439 (5) | 0.500 (8) |
| H(6) | 0.406 (13) | 0.285 (5) | 0.284 (8) |
| H(7) | 0.747 (14) | 0.296 (5) | 0.493 (8) |
| H(8) | 0.798 (14) | 0.196 (5) | 0.624 (8) |
| H(9) | 0.418 (14) | 0.134 (5) | 0.526 (8) |
| H(10) | 0.198 (14) | 0.200 (5) | 0.301 (8) |
| H(12) | 0.212 (13) | 0.272 (5) | 0.594 (8) |
| H(13) | 0.044 (14) | 0.286 (5) | 0.340 (8) |
| H(151) | 0.007 (15) | 0.065 (5) | 0.552 (9) |
| H(152) | 0.256 (15) | 0.037 (6) | 0.594 (9) |
| H(161) | 0.167 (14) | 0.074 (5) | 0.752 (8) |
| H(162) | 0.411 (15) | 0.059 (5) | 0.795 (9) |
| H(163) | 0.231 (16) | 0.004 (6) | 0.729 (9) |
| H(171) | -0.050 (4) | 0.498 (5) | 0.381 (8) |
| H(172) | -0.250 (14) | 0.456 (5) | 0.356 (8) |
| H(181) | -0.194 (14) | 0.494 (5) | 0.129 (9) |
| H(182) | -0.346 (15) | 0.449 (6) | 0.161 (9) |
| H(183) | -0.362 (15) | 0.519 (6) | 0.138 (9) |

^a Estimated standard deviations in parentheses.

Data were collected at room temperature with a single-crystal Siemens AED automated diffractometer. The pulse-height dis-

Table III. Final Atomic Fractional Coordinates for Complex V^a

| | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> |
|--------|------------|-------------|------------|
| V(1) | 0.1260 (1) | 0.0526 (1) | 0.1967 (1) |
| O(1) | 0.2414 (1) | -0.0300 (3) | 0.4480 (2) |
| O(2) | 0.2666 (1) | 0.2218 (3) | 0.4120 (2) |
| O(3) | 0.0764 (1) | 0.4067 (3) | 0.3353 (2) |
| O(4) | 0.0600 (1) | 0.1626 (3) | 0.3904 (2) |
| C(1) | 0.1271 (2) | -0.2198 (4) | 0.1575 (3) |
| C(2) | 0.0730 (2) | -0.1610 (5) | 0.1105 (3) |
| C(3) | 0.0486 (2) | -0.1206 (5) | 0.1701 (4) |
| C(4) | 0.0865 (3) | -0.1563 (5) | 0.2541 (4) |
| C(5) | 0.1364 (2) | -0.2178 (5) | 0.2479 (4) |
| C(6) | 0.1267 (2) | 0.3272 (4) | 0.1525 (3) |
| C(7) | 0.1821 (2) | 0.2676 (5) | 0.1797 (3) |
| C(8) | 0.1830 (2) | 0.1364 (6) | 0.1218 (4) |
| C(9) | 0.1270 (3) | 0.1201 (6) | 0.0585 (3) |
| C(10) | 0.0924 (2) | 0.2343 (6) | 0.0782 (3) |
| C(11) | 0.1221 (1) | 0.1696 (3) | 0.3119 (2) |
| C(12) | 0.1737 (1) | 0.1158 (4) | 0.3308 (2) |
| C(13) | 0.2311 (1) | 0.1124 (4) | 0.4005 (2) |
| C(14) | 0.2982 (2) | -0.0478 (5) | 0.5173 (3) |
| C(15) | 0.0842 (1) | 0.2414 (4) | 0.3506 (2) |
| C(16) | 0.0386 (2) | 0.4885 (6) | 0.3718 (3) |
| H(1) | 0.157 (2) | -0.271 (5) | 0.145 (3) |
| H(2) | 0.060 (2) | -0.172 (5) | 0.048 (3) |
| H(3) | 0.011 (2) | -0.052 (5) | 0.159 (3) |
| H(4) | 0.078 (2) | -0.140 (6) | 0.306 (3) |
| H(5) | 0.175 (2) | -0.257 (5) | 0.293 (3) |
| H(6) | 0.108 (2) | 0.395 (6) | 0.184 (3) |
| H(7) | 0.215 (2) | 0.291 (5) | 0.225 (3) |
| H(8) | 0.212 (2) | 0.068 (5) | 0.127 (3) |
| H(9) | 0.118 (2) | 0.038 (5) | 0.009 (3) |
| H(10) | 0.048 (2) | 0.241 (5) | 0.048 (3) |
| H(141) | 0.303 (2) | 0.032 (6) | 0.564 (4) |
| H(142) | 0.325 (2) | -0.022 (6) | 0.491 (3) |
| H(143) | 0.301 (2) | -0.159 (6) | 0.541 (3) |
| H(161) | 0.000 (2) | 0.436 (5) | 0.345 (3) |
| H(162) | 0.049 (2) | 0.480 (6) | 0.429 (3) |
| H(163) | 0.040 (2) | 0.618 (6) | 0.361 (3) |

^a Estimated standard deviations in parentheses.

criminator was set to accept 90% of the incident radiation. The intensity of a standard reflection was monitored every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection for the two compounds. For intensity and background the "five-point technique"⁹ was used. The intensities were reduced to sets of relative $|F_o|^2$ values for use in structure solutions and refinements. No corrections for absorption were made. During data collection the observed systematic absences uniquely determined the space group to be *P*2₁/*c* for IV. The space group *C*2/*c* for V was confirmed by structural analysis.

The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares techniques, first isotropically (two cycles) and then anisotropically (two cycles) down to $R = 0.082$ for IV and 0.066 for V.¹⁰ All the hydrogen atoms were located from difference maps and were subjected to a cycle of isotropic refinement. Final discrepancy R indices were 0.065 and 0.044 for IV and V, respectively, considering the unique observed data (Table I).¹¹ During the final least-squares cycle no parameter shifted by more than 0.3 σ for the two structures. Final difference maps were featureless, the peak heights of the most intense peaks being 0.3 and 0.2 e \AA^{-3} , respectively, for the two structures. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized during least-squares refinements was $w|\Delta F|^2$. The weighting scheme was $w^{-1} = \sigma^2 F + 0.002 F^2$ for V; unit weights were used for IV.

Final atomic coordinates are given in Tables II and III.

Results and Discussion

The wide number of reactions involving olefins and acetylenes promoted by titanium and vanadium is parallel to the very small amount of information so far available on olefin and acetylene complexes of these metals. Even in bis(cyclopentadienyl) chemistry, which provides a considerable amount of model compounds,¹² only a very few complexes

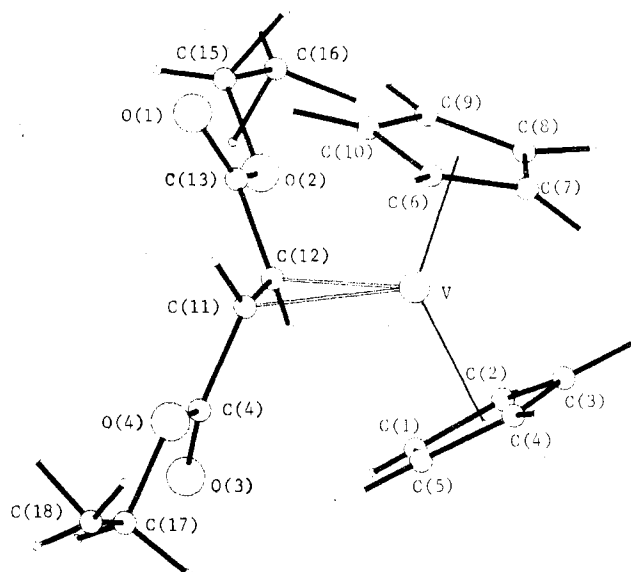


Figure 1. View of the molecular structure of complex IV, $(cp)_2V-(EtO_2CCH-CHCO_2Et)$.

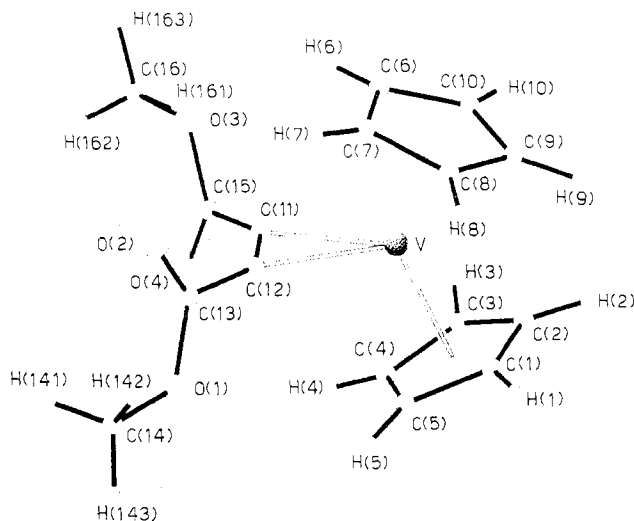
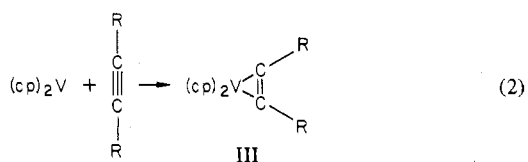
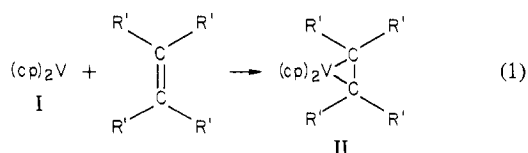


Figure 2. View of the molecular structure of complex V, $(cp)_2V-(MeO_2CC=CCO_2Me)$.

contain the C-C unsaturated group as a ligand.²⁻⁵

As it has been reported, the synthesis of olefin⁴ and acetylene^{3,5} derivatives of vanadocene, $(cp)_2V$ ($cp = \eta^5-C_5H_5$) (I), is simply achieved by reacting vanadocene with the appropriate substrates (eq 1 and 2). Reactions 1 and 2 can be



formally described as the addition of the metal carbene to the C-C multiple bond. This description can be applied to many reactions in which vanadocene is involved, such as the additions to CS_2 ,^{4,7} $PhN=NPh$,¹³ etc. While reaction 2 occurs with acetylene bearing a wide range of substituents,⁵ in reaction

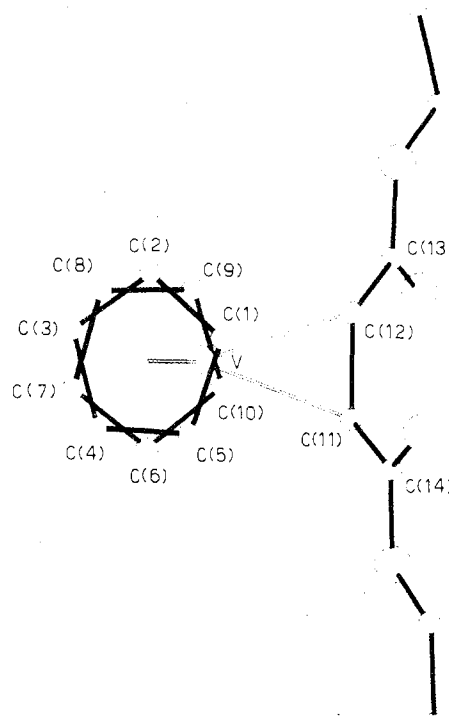
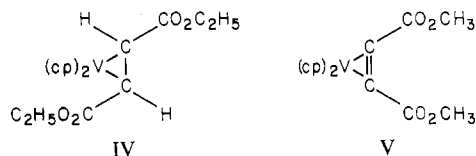


Figure 3. Projection of the environment of the vanadium atom in complex IV onto the plane perpendicular to the $cp(1)-cp(2)$ line.

1 vanadocene requires olefins with electron-withdrawing substituents.⁴ This depends on the fact that bis(cyclopentadienyl)titanium(II) and -vanadium(II) derivatives are highly basic metals activating electrophilic reagents,^{4,14} and the stability of the resulting complexes increases along with the π acidity of the organic substrates. The formal drawing of complexes II and III as metallacyclopropane and metallacyclopropene is justified on the results and considerations outlined below.

Complexes like II and III have been often postulated as reaction intermediates in catalytic reactions promoted by low-valent titanium and vanadium. Very recently we reported structural evidence on an acetylene η^2-C,C bonded to titanium in $(cp)_2Ti(CO)(\eta^2-Ph_2C_2)$,² while we present here the first structural report on vanadocene-olefin and -acetylene complexes. In order to have a homogeneous and consistent comparison between the data of the two compounds, the X-ray analysis was carried out on complexes IV and V containing an olefin and an acetylene bearing the same kind of substituent.



Description of the Structure of IV and V. The structures of complexes IV and V consist of monomeric units (Figures 1 and 2). In both cases, the two cp rings, which are η^5 bonded to vanadium, make a cavity in the equatorial plane (not crystallographic) for the olefin and acetylene ligand, respectively, η^2-C,C bonded to the metal. With the assumption of cylindrical symmetry for each of the cyclopentadienyl rings, the coordination polyhedra ideally conform to C_{2v} symmetry. The distortion from this symmetry is more remarkable in complex V as indicated by the dihedral angles between the planes V, $cp(1)$, $cp(2)$ and V, C(11), C(12), which are 91.2 and 93.6° for complexes IV and V, respectively. The symmetry of the complexes as a whole is approximately C_2 for both

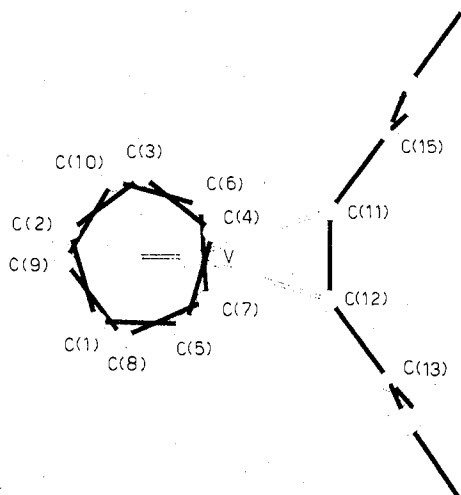


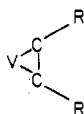
Figure 4. Projection of the vanadium atom environment in complex V onto the plane perpendicular to the cp(1)-cp(2) line.

Table IV. Bond Distances (Å) in Complex IV^a

| | | | |
|-----------|------------|-------------|------------|
| V-C(1) | 2.288 (10) | C(6)-C(7) | 1.390 (18) |
| V-C(2) | 2.322 (10) | C(7)-C(8) | 1.418 (16) |
| V-C(3) | 2.279 (10) | C(8)-C(9) | 1.372 (18) |
| V-C(4) | 2.259 (10) | C(9)-C(10) | 1.427 (15) |
| V-C(5) | 2.282 (8) | C(10)-C(6) | 1.391 (17) |
| av | 2.285 (4) | av | 1.409 (8) |
| V-C(6) | 2.310 (12) | C(11)-C(12) | 1.468 (11) |
| V-C(7) | 2.269 (15) | C(12)-C(13) | 1.490 (11) |
| V-C(8) | 2.277 (13) | C(11)-C(14) | 1.472 (12) |
| V-C(9) | 2.290 (10) | C(13)-O(1) | 1.187 (10) |
| V-C(10) | 2.313 (10) | C(13)-O(2) | 1.353 (10) |
| av | 2.296 (5) | O(2)-C(15) | 1.457 (13) |
| V-C(12) | 2.186 (12) | C(15)-C(16) | 1.417 (24) |
| V-C(11) | 2.213 (12) | C(14)-O(3) | 1.217 (12) |
| V-cp(1) | 1.952 (11) | C(14)-O(4) | 1.342 (10) |
| V-cp(2) | 1.959 (13) | O(4)-C(17) | 1.466 (14) |
| C(1)-C(2) | 1.384 (15) | C(17)-C(18) | 1.499 (19) |
| C(2)-C(3) | 1.400 (16) | | |
| C(3)-C(4) | 1.410 (12) | | |
| C(4)-C(5) | 1.383 (18) | | |
| C(5)-C(1) | 1.402 (14) | | |
| av | 1.401 (7) | | |

^a The distances involving hydrogen atoms range from 0.78 to 1.21 Å. cp(1) and cp(2) are referred to the centroids of the rings C(1)-C(5) and C(6)-C(10), respectively. All the average values were calculated by using the formulas $\mu_{av} = \sum_i(\mu_i/\sigma_i^2)/\sum_i\sigma_i^{-2}$ and $\sigma_{av} = (\sum_i\sigma_i^{-2})^{1/2}$ where μ_i are the individual observations and σ_i are their standard deviations.

complexes. Other crystallographic parameters defining the overall coordination geometry are the cp(1)-V-cp(2) angle (135.9 and 138.4° for IV and V, respectively) and the C(11)-V-C(12) angle (39.0 and 35.8° for IV and V, respectively), the last one being imposed by the nature of the ligand. The reciprocal orientation of the cp rings is staggered in complex IV, while they are rotated about their M-cp vectors from the eclipsed conformation by 23° in complex V (Figures 3 and 4). V-C(cp) and V-cp(centroid) distances (Tables IV and V) fall in the usual range,¹⁵ as well as do the C-C bond distances within the cp rings, which are planar. The structural features of the



unit deserve the major attention in both complexes. Bond

Table V. Bond Distances (Å) in Complex V^a

| | | | |
|-----------|-----------|-------------|-----------|
| V-C(1) | 2.257 (4) | C(6)-C(7) | 1.375 (7) |
| V-C(2) | 2.273 (5) | C(7)-C(8) | 1.400 (7) |
| V-C(3) | 2.286 (6) | C(8)-C(9) | 1.394 (9) |
| V-C(4) | 2.295 (6) | C(9)-C(10) | 1.372 (8) |
| V-C(5) | 2.279 (4) | C(10)-C(6) | 1.388 (7) |
| av | 2.275 (2) | av | 1.386 (4) |
| V-C(6) | 2.296 (4) | C(11)-C(12) | 1.287 (4) |
| V-C(7) | 2.294 (5) | C(11)-C(15) | 1.434 (4) |
| V-C(8) | 2.283 (6) | C(12)-C(13) | 1.451 (4) |
| V-C(9) | 2.282 (5) | C(13)-O(1) | 1.333 (4) |
| V-C(10) | 2.276 (5) | C(15)-O(3) | 1.337 (4) |
| av | 2.287 (2) | C(13)-O(2) | 1.208 (4) |
| V-C(11) | 2.097 (3) | C(15)-O(4) | 1.207 (4) |
| V-C(12) | 2.084 (3) | O(1)-C(14) | 1.445 (6) |
| V-cp(1) | 1.961 (4) | O(3)-C(16) | 1.442 (6) |
| V-cp(2) | 1.959 (5) | | |
| C(1)-C(2) | 1.363 (7) | | |
| C(2)-C(3) | 1.351 (8) | | |
| C(3)-C(4) | 1.351 (8) | | |
| C(4)-C(5) | 1.382 (9) | | |
| C(5)-C(1) | 1.374 (4) | | |
| av | 1.364 (4) | | |

^a The distances involving hydrogen atoms range from 0.85 to 1.05 Å.

Table VI. Bond Angles (deg) in Complex IV^a

| | | | |
|----------------|-------------|-------------------|-------------|
| C(1)-V-C(2) | 34.9 (4) | C(10)-C(6)-C(7) | 106.3 (9) |
| C(2)-V-C(3) | 35.4 (4) | C(6)-C(7)-C(8) | 109.8 (1.1) |
| C(3)-V-C(4) | 36.2 (3) | C(7)-C(8)-C(9) | 107.1 (1.0) |
| C(4)-V-C(5) | 35.5 (4) | C(8)-C(9)-C(10) | 107.9 (1.0) |
| C(5)-V-C(1) | 35.7 (4) | C(9)-C(10)-C(6) | 108.9 (1.0) |
| av | 35.6 (2) | av | 107.9 (4) |
| C(6)-V-C(7) | 35.3 (5) | C(12)-C(13)-O(1) | 126.7 (8) |
| C(7)-V-C(8) | 36.4 (4) | C(12)-C(13)-O(2) | 109.9 (7) |
| C(8)-V-C(9) | 35.0 (5) | O(1)-C(13)-O(2) | 123.5 (7) |
| C(9)-V-C(10) | 36.1 (4) | C(11)-O(2)-C(15) | 114.1 (7) |
| C(10)-V-C(6) | 35.0 (4) | O(2)-C(15)-C(16) | 108.7 (1.1) |
| av | 35.6 (2) | C(11)-C(14)-O(3) | 127.0 (8) |
| C(12)-V-C(11) | 39.0 (3) | C(11)-C(14)-O(4) | 110.3 (7) |
| C(12)-V-cp(1) | 110.8 (4) | O(3)-C(14)-O(4) | 122.6 (8) |
| C(12)-V-cp(2) | 110.9 (4) | C(14)-O(4)-C(17) | 114.7 (8) |
| C(11)-V-cp(1) | 111.4 (4) | O(4)-C(17)-C(18) | 108.6 (1.1) |
| C(11)-V-cp(2) | 109.8 (4) | V-C(12)-C(13) | 120.8 (7) |
| cp(1)-V-cp(2) | 135.9 (5) | V-C(12)-C(11) | 71.5 (5) |
| C(5)-C(1)-C(2) | 110.5 (1.0) | C(11)-C(12)-C(13) | 119.2 (7) |
| C(1)-C(2)-C(3) | 106.0 (9) | V-C(11)-C(14) | 120.5 (7) |
| C(2)-C(3)-C(4) | 108.8 (1.0) | V-C(11)-C(12) | 69.5 (5) |
| C(3)-C(4)-C(5) | 108.1 (9) | C(12)-C(11)-C(14) | 116.9 (8) |
| C(4)-C(5)-C(1) | 106.7 (9) | | |
| av | 107.9 (4) | | |

^a cp(1) and cp(2) are referred to the centroids of the rings C(1)-C(5) and C(6)-C(10), respectively.

lengths and valence angles in the diethyl fumarate and dimethylacetylenedicarboxylate (Tables IV-VII) are in agreement with the values in the literature^{16,17} and fall in the usual range, except for a shortening in the ethyl C-C distances of complex IV due to the high thermal motions by which these groups are affected. Any intramolecular or intermolecular susceptible metal-oxygen contact can be ruled out as we previously suggested on the basis of the IR spectrum.⁴ The coordinated olefin in complex IV exhibits mainly a trans configuration, while the R substituents are cis arranged in V, as confirmed by the torsional angles around the C(11)-C(12) bond direction (129.7° for IV and 13.0° for V). The succession of the torsion angles on the C(11)-C(18) chain is such as to give an almost perfect planar zigzag conformation. The hydrogen atoms bonded to C(11) and C(12) in complex IV were clearly shown by a difference Fourier map. The configuration on the bonded olefin was previously deduced

Table VII. Bond Angles (deg) in Complex V

| | | | |
|------------------|-----------|-------------------|-----------|
| C(1)-V-C(2) | 35.0 (2) | C(5)-C(1)-C(2) | 108.4 (5) |
| C(2)-V-C(3) | 34.5 (2) | C(1)-C(2)-C(3) | 108.4 (5) |
| C(3)-V-C(4) | 34.3 (2) | C(2)-C(3)-C(4) | 108.3 (5) |
| C(4)-V-C(5) | 35.2 (2) | C(3)-C(4)-C(5) | 108.7 (6) |
| C(5)-V-C(1) | 35.3 (2) | C(4)-C(5)-C(1) | 106.3 (5) |
| av | 34.9 (1) | av | 108.0 (2) |
| C(6)-V-C(7) | 34.9 (2) | C(10)-C(6)-C(7) | 108.3 (4) |
| C(7)-V-C(8) | 35.6 (2) | C(6)-C(7)-C(8) | 108.3 (4) |
| C(8)-V-C(9) | 35.6 (2) | C(7)-C(8)-C(9) | 106.6 (5) |
| C(9)-V-C(10) | 35.0 (2) | C(8)-C(9)-C(10) | 108.9 (4) |
| C(10)-V-C(6) | 35.3 (2) | C(9)-C(10)-C(6) | 107.8 (5) |
| av | 35.3 (1) | av | 108.1 (2) |
| C(11)-V-C(12) | 35.8 (1) | V-C(11)-C(12) | 71.5 (2) |
| C(11)-V-cp(1) | 108.6 (2) | V-C(11)-C(15) | 144.4 (2) |
| C(11)-V-cp(2) | 110.9 (2) | C(12)-C(11)-C(15) | 143.5 (3) |
| C(12)-V-cp(1) | 110.8 (2) | V-C(12)-C(11) | 72.6 (2) |
| C(12)-V-cp(2) | 108.7 (2) | V-C(12)-C(13) | 143.5 (2) |
| cp(1)-V-cp(2) | 138.4 (2) | C(11)-C(12)-C(13) | 143.7 (3) |
| C(11)-C(15)-O(3) | 112.8 (3) | C(12)-C(13)-O(1) | 112.1 (3) |
| C(11)-C(15)-O(4) | 124.6 (3) | C(12)-C(13)-O(2) | 124.4 (3) |
| O(3)-C(15)-O(4) | 122.6 (3) | O(1)-C(13)-O(2) | 123.4 (3) |
| C(13)-O(1)-C(14) | 116.3 (3) | | |
| C(15)-O(3)-C(16) | 116.3 (3) | | |


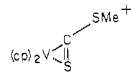
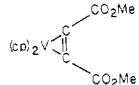
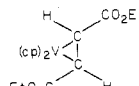
from the reaction of complex IV with dioxygen, which gives diethyl fumarate. It must be pointed out that the complex here investigated was synthesized from diethyl fumarate, and it is the same as that obtained from diethyl fumarate. Therefore, the complexation of the olefin by $(cp)_2V$ occurs with its complete isomerization. Moreover, the reaction with dioxygen makes free the olefin ligand in its coordinated configuration. The C(11)-C(12) distance has a remarkable single bond [1.468 (11) Å] in complex IV and double bond character [1.287 (4) Å] in complex V. The bond angles around C(11) and C(12) indicate a sp^3 hybridization in complex IV, and an sp^2 hybridization in complex V. Both the C(11)-C(12) bond distance and the deformation angles in complex V [V-C(11)-C(15) = 144.4 (2)° and V-C(12)-C(13) = 143.5 (2)°] agree with the corresponding values found in various diphenylacetylene complexes and $(cp)_2Ti(CO)(Ph_2C_2)$. The C-C bond distances lie in a small range around 1.28 Å, and the deformation angles are ca. 143° in many diphenylacetylene complexes.^{2,17} These features indicate that $MeO_2CC=CCO_2Me$ behaves as a bidentate ligand in a metallacyclopropene structure. This description is also justified by the $\nu_{C=C}$ stretching vibration which is significantly lowered at 1820 cm^{-1} .

The C-C coordinated bond length in IV is significantly longer than those found in other diethyl fumarate complexes lying at ca. 1.40 Å. This allows us to describe the vanadium-olefin interaction in terms of two metal-carbon σ bonds or a metallacyclopropane-like structure.

Very few data are so far available on vanadocenes bearing an additional V-C bond. Rare examples of V-C(sp), V-C(sp²), and V-C(sp³) bond lengths are given in Table VIII.

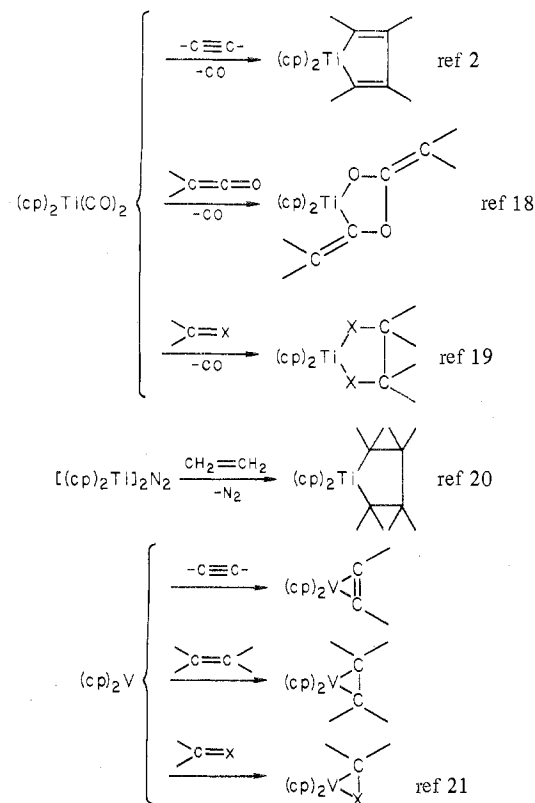
Comparison with Organotitanium Compounds. There are a number of striking differences in chemical behavior of bis(cyclopentadienyl)vanadium(II) and -titanium(II) toward unsaturated substrates. While we observed that the reactions between vanadocene and unsaturated systems give rise, as depicted in reactions 1 and 2, to the addition of the metal carbene to double and triple bonds, the reaction of titanocene sources, such as $(cp)_2Ti(CO)_2$ ^{2,18,19} and $[(cp)_2Ti]_2N_2$ ²⁰ promotes the dimerizations of the same substrates, as summarized in Scheme I where C=X is an activated >C=O group. This reactivity pattern of vanadocene vs. titanocene sources allows one to carry out controlled metal-promoted transformations on unsaturated substrates. Moreover, vanadocene derivatives such as IV and V represent model compounds in which the organic molecule anchored to the metal can undergo further

Table VIII

| compd | V-C bond lengths, Å | ref |
|---|----------------------------------|-----------|
| $(\eta^5-C_5Me_5Et)_2V \equiv CC_6H_5Me_3$ | 2.03 (1) | 6 |
|  | 2.075 (4), 2090 (5) ^a | 7 |
|  | 2.08 (1) | 7 |
|  | 2.084 (3), 2097 (3) | this work |
|  | 2.186 (12), 2.213 (12) | this work |

^a Values relative to the two independent molecules in the asymmetric unit.

Scheme I



reactions by, i.e., electrophilic reagents.

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Registry No. IV, 60674-63-7; V, 12155-24-7; $(cp)_2V$, 1277-47-0.

Supplementary Material Available: Listings of structure factor amplitudes for complexes IV and V, least-squares planes (Table IX), and anisotropic thermal parameters (Tables X and XI) for complexes IV and V (63 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Bis[π -(cyclobutenocyclooctatetraene)]uranium(IV), $U[C_8H_6(CH_2)_2]_2^1$

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Crystals of bis[π -(bicyclo[6.2.0]deca-1,3,5,7-tetraene)]uranium(IV), $U[C_8H_6(CH_2)_2]_2$, are monoclinic: space group $P2_1/n$, $a = 9.906$ (8) Å, $b = 11.039$ (9) Å, $c = 7.221$ (6) Å, $\beta = 98.89$ (5)°, $V = 780.15$ Å³, $Z = 2$, and $D_x = 2.122$ g cm⁻³ at 22 °C. X-ray diffraction data were measured with counter methods and Mo $K\alpha$ radiation. With anisotropic temperature factors for the uranium and carbon atoms and isotropic temperature factors for the hydrogen atoms, $R = 0.020$ for 1315 independent reflections ($I > 3\sigma$). The molecule is a sandwich compound with the C_8 rings in an eclipsed configuration about the uranium atom which is on a center of symmetry. The average U-C distance is 2.64 ± 0.02 Å, and the average C-C distance in the C_8 ring is 1.39 ± 0.01 Å (uncorrected for thermal motion). The cyclobuteno ring is planar and at an angle of 6.8° to the plane of the C_8 ring. The C-C bond length is 1.47 (2) Å in the $-CH_2-CH_2-$ moiety, and it is 1.55 (2) Å where this group is fused to the C_8 ring.

Introduction

Following the initial characterization of bis(cyclooctatetraene)uranium(IV), "uranocene", by Streitwieser and Müller-Westerhoff,² its crystal and molecular structure was determined.³ Subsequently the preparation⁴ and structure⁵ of bis(cyclooctatetraene)thorium(IV), "thoracene", were reported as well as the preparations and structures of octamethyluranocene,^{6,7} $U(C_8H_4(CH_3)_4)_2$, and octaphenyluranocene,^{8,9} $U(C_8H_4(C_6H_5)_4)_2$.

As part of a program to extend knowledge of the chemical and structural properties of compounds of actinide elements, we undertook a study of the structure of butenouranocene synthesized by Berryhill and Streitwieser.¹⁰ The immediate objective was a description of the molecular geometry for use in the interpretation of the NMR spectra.¹⁰

Experimental Section

Crystals grown from a hexane solution were dark green. As the material is extremely air sensitive they were manipulated and kept in an argon-filled drybox until they could be inserted into 0.2-mm quartz capillaries and sealed. Weissenberg photographs were taken of the crystals from which the space group and rough cell dimensions were obtained. Some of the crystals exhibited twinning and were rejected for data collection. A wedge-shaped crystal fragment was placed on a Picker FACS-I automated diffractometer equipped with graphite-monochromated Mo $K\alpha$ radiation (λ 0.709 30 Å) for study. Cell dimensions were obtained from carefully centered settings on the $K\alpha_1$ peaks of 12 reflections where $35^\circ < 2\theta < 38^\circ$. The cell

dimensions, crystal description, and other details of the experiment are given in Table I. The width of ω scans at half-height were typically 0.1°. Intensity data were collected by using the θ - 2θ scan method for the hemisphere $\pm h, +k, \pm l$. Three standards were measured after each 200th scan, and the maximum variation of these measurements from their mean value was about 2%. The data were corrected for absorption.¹¹ Several azimuthal scans in diverse regions of reciprocal space were performed to test the validity of the absorption correction and to make minor adjustments on the crystal dimensions. After the absorption correction the equivalent data were averaged and given estimated standard deviations by using formulas presented in the supplementary material. The factor $p = 0.04$ was used in the calculation of $\sigma(F^2)$.

The position of the uranium atom at the origin was evident from the strong pseudo body centering exhibited by the data. A Patterson function and subsequent Fourier maps after least-squares refinement of part of the structure revealed the positions of all the carbon atoms. The structure was refined by full-matrix least squares where the function $\sum w||F_o| - |F_c||^2 / \sum wF_o^2$ was minimized. The two reflections below $(\sin \theta) / \lambda$ of 0.08 were zero weighted because of excessively large discrepancies. Because the observed values of the larger intensities were consistently below the calculated values, an empirical extinction correction was applied; the largest correction to F due to extinction was 1.2. The uranium and carbon atom parameters were refined by using anisotropic temperature factors. The hydrogen atom positions were estimated from the carbon atom geometry and were refined with isotropic temperature factors. All of the hydrogen atoms with the exception of H(1) refined to acceptable positions; H(1) shifted to a position about 0.5 Å from C(1), and it was then restrained to a distance of 0.95 ± 0.05 Å from the carbon atom in the least-squares refinement in the manner suggested by Waser¹² and described in one of our previous papers.¹³ Scattering factors for U, C, and H were taken from

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