Imido derivatives of $VOCl_3$ were also found to be useful for oxidative decarboxylation. A series of such complexes, $Cl_3V{=}NC_6H_4X$ ($X = CH_3$,[8] NO_2,[9] or OCH_3[8]), was prepared. Qualitatively, rates for olefin formation from model hydroxy acid **3** were found to increase in the order $X = OCH_3 < CH_3 \leq NO_2$. Interestingly, the stereospecificity of olefination varied with the *opposite* trend. Thus for the *threo* diastereomer **3b**, the complex with $X = OCH_3$ gave an olefin ratio $E/Z = 7{:}1$ at short reaction times, but essentially no selectivity was observed for $X = CH_3$ or NO_2. The tolyl complex is particularly effective for preparing highly substituted olefins[10] (see Table I).

A mechanistic proposal which accounts for observed products and selectivities is shown in Scheme I. This involves formation of a carbon-centered radical via one-electron reduction of V(V) to V(IV) and subsequent decarboxylation.[11] Collapse of this radical would yield the olefin and generate a new V(V) oxo compound. Significantly, 3-hydroxy-3-methyl-2-phenylbutanoic acid (**18**)[12] gave both olefin **2** and benzaldehyde when treated with $VOCl_3$ in refluxing chlorobenzene. For benzaldehyde to be produced in this latter case not only must decarboxylation occur but also a new C–O bond must be formed. In support of a glycolate intermediate it was noted that benzaldehyde and 2-butanone were obtained from 2-ethyl-3-hydroxy-2-methyl-3-phenylpropanoic acid (**3**).[6] When imido complexes were used in place of $VOCl_3$, no cleavage occurred, and only olefins were formed.[13] If initial V–OC(O) homolysis were rate-determining, then an electron-withdrawing group on the aryl imido ligand (for example, NO_2) should accelerate the overall reaction relative to a donor ($X = OCH_3$).[14] The stereospecificity of the overall process would vary in the *opposite* direction: substituent groups which destabilize low-valent versus high-valent vanadyl should accelerate diradical collapse relative to stereochemical reorganization of the intermediate.[15] Cyclization of the 1,4-metallodiradical intermediate to vanadyl oxygen would give a glycolate which could cleave to give the carbonyl products observed.[16] We continue to investigate the mechanism and synthetic possibilities of this novel decarboxylation procedure.

Acknowledgment. We acknowledge support for this work provided by the National Institutes of Health and the National Science Foundation.

Supplementary Material Available: ^1H NMR and IR data for **1**, synthesis, separation, and spectral data (^1H NMR and ^{13}C NMR) for **3**, identification of erythro diastereomer of **3a**, synthesis and spectral data (mp, ^1H NMR, and ^{13}C NMR) for $Cl_3V{=}NC_6H_4NO_2$, **7**, and **15**, spectral data (^1H NMR, ^{13}C NMR, and HRMS) for **16**, and supplement to Table I (3 pages). Ordering information is given on any current masthead page.

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(6) 2-Ethyl-3-hydroxy-2-methyl-3-phenylpropanoic acid (**3**) was prepared (43%) from 2-methylbutanoic acid and benzaldehyde. The diastereomers were separated by column chromatography (50:50:1 hexane/ether/acetic acid). The erythro diastereomer (**3a**)[7] was eluted first (mp 128.0–129.5 °C); the threo diastereomer (**3b**) was eluted next (mp 129.0–131.0 °C).

(7) The erythro diastereomer (**3a**) was identified by its conversion to (*E*)-2-methyl-1-phenyl-1-butene (**4E**) via anti elimination (Mulzer, J.; Pointner, A.; Chucholowski, A.; Bruntrup, G. *J. Chem. Soc., Chem. Commun.* **1979**, 52–4).

(8) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408–16.

(9) $Cl_3V{=}NC_6H_4NO_2$ was prepared[8] from $VOCl_3$ and 4-nitrophenylisocyanate.

(10) Yields for tetrasubstituted olefins are at least comparable to those obtained using any of the three standard methods for making positionally defined olefins from 3-hydroxycarboxylic acids: For routes via β-lactones,[4] see also: (a) Noyce, D. S.; Banitt, E. H. *J. Org. Chem.* **1966**, *31*, 4043–7. (b) Krapcho, A. P.; Jahngen, E. G. E., Jr. *J. Org. Chem.* **1974**, *39*, 1650–3. (c) Schollkopf, U.; Hoppe, I. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 765. (d) Mageswaran, S.; Sultanbawa, M. U. S. *J. Chem. Soc., Perkin Trans. I* **1976**, 884–90. (e) Imai, T.; Nishida, S. *J. Org. Chem.* **1980**, *45*, 2354–9. For procedures via triphenylphosphine–diethylazodicarboxylate adducts[7] see, also: (f) Mulzer, J.; Lammer, O. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 628–9. For a procedure via DMF–acetal, see: (g) Hara, S.; Taguchi, H.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1975**, 1545–8. For ethylpropylidenecyclobutane (**16**), for example, the β-lactone route gave only ~20% (by ^1H NMR) as a component of a complex mixture of products.

(11) Reduction of vanadium(V) to vanadium(IV) followed by rapid C–C bond fission to give the carbon-centered radical, $R_2\dot{C}(OH)$, is proposed as the rate-determining step in the oxidative decarboxylation of lactic, malic, and mandelic acids.[1a]

(12) Petrova, L. A.; Bel'tsova, N. N.; Remizov, A. L.; Vasil'eva, L. M. *J. General Chem. USSR* **1968**, *38*, 1654–7.

(13) Consistent with the notion that decarboxylation is a redox process, olefin synthesis from the imido complex adduct is slower than that from its vanadyl analogue.

(14) The arylimido group is likely a better electron donor than the oxo ligand. For a series of W analogues, see: Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545–3547. Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826–2828.

(15) Similar diradicals have been proposed as intermediates in epoxide deoxygenation in which the stereospecificity of the process is believed to be related to oxidation of the metal in a 1,4-metallodiradical intermediate (Hayashi, Y.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 3473–6).

(16) Apparently only high-valent vanadium glycolates cleave. 2-Methyl-1-phenylpropane-1,2-diol (**17**)[17] reacted with $VOCl_3$, $VOCl_2$, and VCl_3, but benzaldehyde was formed in high yield (47%) only when $VOCl_3$ was used. Reaction with $VOCl_2$ gave rise to a lesser amount of benzaldehyde (3%), and VCl_3 gave no aldehyde; when 0.2 equiv of $VOCl_3$ was added to the VCl_3/diol solution, benzaldehyde was formed (90%) on reflux.

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(19) 2,2-Dimethyl-3-ethyl-3-hydroxypentanoic acid (**7**) was prepared from 2-methylpropanoic acid and 2-pentanone (mp 44.0–45.0 °C).

(20) The relatively low yield of this olefin may be related to conformational problems in the chelate intermediate. We thank a referee for bringing this to our attention.

(21) 2-(1-Hydroxycyclobutyl)-2-ethylbutanoic acid (**15**) was prepared from 2-ethylbutanoic acid and cyclobutanone (mp 68–9 °C).

Insertion of Oxygen into Vanadium–Carbon Bonds: Formation of $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ from $(\eta\text{-}C_5Me_5)_2V$ and O_2

Frank Bottomley,* C. Philippe Magill, and Peter S. White

Department of Chemistry, University of New Brunswick
Fredericton, New Brunswick E3B 5A3, Canada

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It is well-known that oxidation of Cp_2V or $CpV(CO)_4$ ($Cp = \eta\text{-}C_5H_5$) with a large excess of dioxygen, followed by treatment with a source of chloride, gives high yields of $CpVCl_2(O)$.[1,2] The nature of the product of the initial oxidation is unknown. Recently similar reactions have been used to obtain $Cp^*VCl_2(O)$ from Cp_2^*V or $Cp^*V(CO)_4$ ($Cp^* = \eta\text{-}C_5Me_5$).[3-5] We have shown that controlled oxidation of Cp_2V with a deficiency of a reagent containing oxygen gives $[CpV]_m(\mu_3\text{-}O)_n$ clusters and derivatives of these such as $Cp_{14}V_{16}O_{24}$.[6-8] We report here the remarkable controlled oxidation of Cp_2^*V with O_2, giving $[\mu\text{-}\eta^3\text{-}C_5Me_5O_3)\text{-}V(O)]_2$. *Three* oxygen atoms are inserted into adjacent V–C bonds in an all-cis configuration.

When Cp_2^*V was incubated with O_2 (1:2 mol ratio) at −78 °C in hexane, the red solution initially became green, changing very rapidly to red-brown. After 1 h all the O_2 had been consumed. The red-brown solution was poured onto a column (1 × 40 cm glass beads, 120–200 mesh) and eluted with hexane. The first eluate was pale yellow; removal of the hexane under vacuum gave colorless platelets of $(C_5Me_5)_2$ (**1**).[9] A second eluate was ruby

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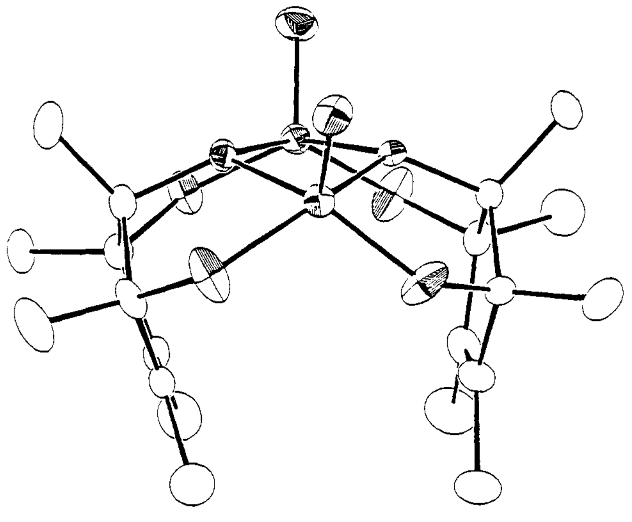
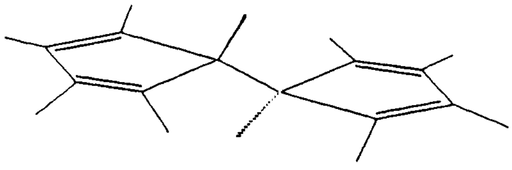


Figure 1. The molecular structure of $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ (**2**) as determined by X-ray diffraction.

red. Crystalline $[(\mu\text{-}\eta^3\text{-}C_5Me_5O_3)V(O)]_2$ (**2**) was obtained from this second eluate by slow removal of hexane in vacuum. The nature of **2** was proven by spectroscopy[12] and X-ray diffraction (Figure 1).[13]



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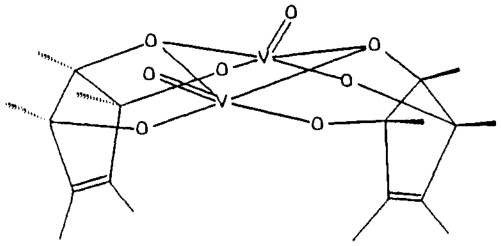

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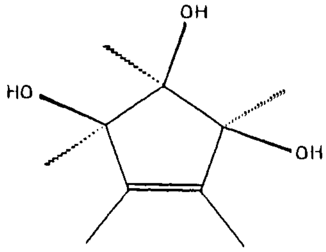

3

2 is a V^V derivative of the triol **3** and is produced by formal insertion of three oxygen atoms into adjacent V–C bonds of $(\eta\text{-}C_5Me_5)_2V$. It is very soluble in hexane and other nonpolar solvents and is stable to O_2. However, it is readily hydrolyzed, particularly in alkaline solution.

Almost as remarkable as **2** itself is that the reaction which produces it is quantitative according to eq 1. Since loss of C_5Me_5

$$2Cp_2{}^*V + 4O_2 \rightarrow \mathbf{2} + (C_5Me_5)_2 \qquad (1)$$

is not a feature of the chemistry of $Cp_2{}^*V$, an intermediate containing one intact Cp* ligand for each vanadium must be formed on oxidation. Preliminary work indicates that this intermediate is $[Cp^*V(O)(OC_5Me_5)]_2$, a vanadium(IV) derivative related to $Cp^*W(O)_2(OC_5Me_5)$ obtained on oxidation of $Cp_2{}^*W(O)$ with O_2.[14] We are presently attempting to confirm the intermediate and to extend the reaction, which has synthetic potential in carbohydrate chemistry, to other cyclopentadienyl derivatives.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and the mass spectral fragmentation pattern for **2** (8 pages); table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(9) Characterization of $(C_5Me_5)_2$ (**1**): mp 53–58 °C dec; ^{1}H NMR 200 MHz ($C_6D_5CD_3$ solution) 1.10 (s, 6 H), 1.65 (s, 12 H), 1.72 (s, 12 H); ^{13}C NMR 50 MHz (C_6H_{14} solution) 10.5, 12.3, 19.4 ($C_5(\mathit{C}H_3)_5$), 60.1, 133.4, 141.8 ($\mathit{C}_5(CH_3)_5$); mass spectrum m/e = 270.2336 (4), calcd for $C_{20}H_{30}{}^+$, 270.2347; other major fragments were 180 ($C_{13}H_{24}{}^+$), 168 ($C_{12}H_{24}{}^+$), 151 ($C_{11}H_{19}{}^+$), 135 ($C_{10}H_{15}{}^+$). The results are in reasonable agreement with those in the literature.[10,11]

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(12) Spectroscopic data for **2**: IR ν(V=O) 935 (m), 957 (sh) cm^{-1}; ^{1}H NMR 200 MHz ($C_6D_5CD_3$ solution) 2.12 (s, 12 H), 2.05 (s, 18 H); ^{13}C NMR 50 MHz (C_6H_{14} solution) 10.5 ($\mathit{C}H_3C$=), 27.2, 29.8 ($\mathit{C}H_3C$—O); 125.3 (C=C), 128.1 (C—O), 128.9 (C—O); ^{51}V NMR 52.5 MHz (C_6H_{14} solution) −672.5; mass spectrum m/e 500 ($\mathbf{2}^+$), 482 ($C_{20}H_{28}O_7V_2{}^+$), 350 ($C_{10}H_{16}O_7V_2{}^+$), 264 ($C_{10}H_{13}O_5V^+$), 249 ($C_{10}H_{14}O_4V^+$), 219 ($C_{10}H_{16}O_2V^+$), 167 ($C_{10}H_{15}O_2{}^+$), 151 ($C_{10}H_{15}O^+$); structural assignments for the fragments are given in the Supplementary Material.

(13) Crystal data for **2** ($C_{20}H_{30}O_8V_2$): monoclinic, $P2_1/n$; a = 11.309 (1) Å, b = 14.163 (1) Å, c = 14.212 (1) Å, β = 95.601 (9)°; Z = 4. Diffraction data: 2931 unique reflections with $2\theta < 45°$ (Mo Kα radiation), 1612 observed ($I > 2.5\sigma(I)$); no absorption correction (μ = 12·2 cm^{-1}). Refinement data: 272 parameters (all non-hydrogen atoms anisotropic, H riding on C with fixed B_{iso}); R = 0.066, R_w = 0.074, goodness of fit 1.553; highest final peak 0.75 e Å^{-3}, deepest hole −0.42 e Å^{-3}. Important molecular parameters (averaged over the two crystallographically inequivalent halves of **2**): V–O 1.581 (7), V–O(A) 1.770 (7), V–O(B) 1.957 (6), C–O 1.45 (1), C–C(ring) 1.52 (1), C–C 1.33 (1), C–CH_3 1.51 (1) Å (O(A) are bonded to a single V, O(B) to both V). Full details have been deposited.

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Synthesis of Difluoropropadienone

John C. Brahms and William P. Dailey*

Department of Chemistry, University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

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While both chemical intuition and ab initio calculations within the Hartree–Fock (HF) level of theory[1] predict that propadienone (H_2C=C=C=O)[2] should maintain a symmetric structure, both experiment[3] and ab initio calculations employing electron correlation[4] reveal that the actual structure is badly bent. A microwave spectrum[5] and matrix-isolated infrared spectrum[6] for

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