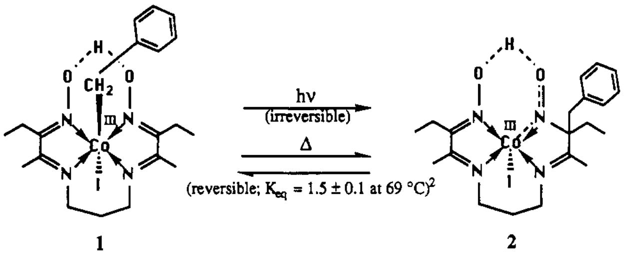
C(7)–C(19), Co–N(2), and Co–I bonds oppose the reaction. These compensating bond changes are consistent with our finding that the overall reaction is enthalpically thermoneutral, $\Delta H° \approx 0$.[2] The results indicate considerable flexibility within the macrocycle ligand system as it accommodates the alkyl migration reaction and bonding changes shown schematically in eq 1.



(1)

One additional crystal structure of interest is that of the migration intermediate, $^{\bullet}Co^{II}[C_2(DO)(DOH)_{pn}]I$, formed upon cobalt–carbon bond homolysis in **1** or carbon–carbon bond homolysis in **2**. The structure of this homolysis product would allow insight into the bonding changes following Co–C or C–C cleavage (in **1** or **2**, respectively). This compound has been synthesized independently, and we are presently attempting to crystallize it and determine its exact structure.

## Experimental

**Preparation of $C_6H_5CH_2Co^{III}[C_2(DO)(DOH)_{pn}]I$ (1) and (*SP*-5-15)-[2-[[3-[[2-(Hydroxyamino)-1-methyl-2-(phenylmethyl)butylidene]amino]propyl]imino]-3-pentanone oximato(2−)-*N,N′,N″,N‴*] iodocobalt(III) (2).** Complex **1** was prepared via our method reported in detail elsewhere.[2] This compound was characterized by $^1$H NMR spectroscopy, visible spectroscopy, elemental analysis, and mass spectroscopy; the results obtained matched identically those obtained from previous reports.[13] A detailed method for the preparation of **2** is also available to the interested reader.[2]

**Equipment.** X-ray crystallographic data were collected on a Rigaku AFC6R diffractometer. All air-sensitive compounds were manipulated either by the Schlenk technique or in an inert atmosphere, double-length, nitrogen-containing glovebox (Vacuum Atmospheres). Oxygen levels averaged 0.3 ppm and did not exceed 2 ppm. Light-sensitive compounds were protected from light by wrapping their containers in foil or electrician's tape or by sealing them in metal canisters.

**X-ray Crystal Structure Determination. 1.** Dark red laths were obtained from an air-free benzene solution of the compound in vapor contact with hexanes. They were vacuum-dried and found to be air-stable when dry. A crystal of dimensions 0.12 × 0.07 × 0.45 mm was glued to a fiber, mounted on the diffractometer with its long axis at *ca.* 20° to the $\phi$ axis and the orientation matrix and cell dimensions determined from the setting angles of 25 centered reflections in the range $11° \leq 2\theta \leq 17°$. Improved values were found by refinement of 25 reflections selected after rapid data collection in the shell $20° \leq 2\theta \leq 25°$. A summary of relevant crystal data is given in Table I and a full table including particulars of data collection and refinement is given in the supplementary materials. The value of $|F_0|$ for each of three standard reflections varied *randomly* over a range of ca. ±2% during data collection, although there was no *systematic* change; this variation was subsequently traced to small fluctuations in the vacuum at the rotating anode. The consequent noise in the data appears to account for the somewhat high *R* factor; note, however, that a similar *R* factor and slightly *larger* standard deviations in bond lengths were obtained for the photoproduct **2** although the above problem was not encountered. The positions of the iodine and cobalt atoms were obtained from the Patterson function. A cycle of DIRDIF[14] then showed all the O, N, and C atoms. The data were corrected for absorption by use of DIFABS[15] and after isotropic refinement of the non-hydrogen atoms. The stronger peaks (maximum 1.0 e Å$^{-3}$) in a difference synthesis after anisotropic refinement lay near the heavy atoms, but a number of hydrogen atoms were also apparent, including that of the –O··H··O– hydrogen bond. The latter was included without refinement in the last cycles of refinement, and all other H atoms were placed at "riding" positions. No solvent of crystallization was present. The TEXSAN program suite,[16] incorporating atomic scattering factors from ref 17, was used in all calculations.

**2.** For a detailed discussion of the X-ray structure determination of **2**, see refs 1 and 2. A full table of crystal data, including particulars of the data collection and refinement, is given in the supplementary materials of refs 1 and 2.

**Acknowledgment.** Support of this work from NIH Grant DK 22614 is gratefully acknowledged.

**Registry No. 1**, 8719-52-6.

**Supplementary Material Available:** Details of the X-ray structural analysis of **1** including an ORTEP diagram and tables of crystallographic data, refined atomic coordinates, bond lengths and angles, calculated hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, intermolecular contacts, torsion angles, and least-squares mean planes (15 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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## Triply Bridged Diruthenium Complexes with $[Ru^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}$ and $[Ru^{IV}Ru^{III}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{3+}$ Cores: Synthesis, Spectra, and Electrochemistry

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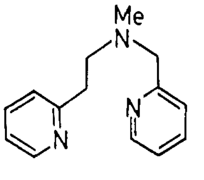
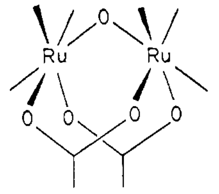
*Received February 21, 1991*

Recently there has been a great deal of interest[1,2] in oxo-bridged dinuclear complexes of Fe(III) because of the discovery of diiron sites in an emerging class of oxo-bridged non-heme iron proteins and enzymes. This has stimulated discovery[3] of a fast growing series of triply bridged iron(III) complexes. The present work originated from our search for $[M_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]^{2+}$ (M = Ru, Fe)[4] cores using MeL as a facially capping ligand. Here we present the rich redox chemistry of the diruthenium complexes of the bridging type as shown in the diagram.



MeL



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0020-1669/92/1331-0139$03.00/0

## Experimental Section

**Materials.** Water was deionized and then distilled from alkaline permanganate. Purification of acetonitrile (MeCN) was achieved by distillation over $CaH_2$. For electrochemical experiments, further purification was achieved by $KMnO_4/Li_2CO_3$ treatment[5] followed by distillation over $P_4O_{10}$. Tetra-*n*-butylammonium perchlorate (TBAP) was prepared and purified as reported previously.[6]

**(2-Pyridylethyl)(2-pyridylmethyl)methylamine.** To a solution of 2-(2-(methylamino)ethyl)pyridine (3.34 g, 24.4 mmol) and $Et_3N$ (2.5 g, 24.7 mmol) in 90 mL of ethyl acetate was added 10 mL of an ethanolic solution of 2-(chloromethyl)pyridine (obtained by neutralization of the monohydrochloride (4.0 g, 24.4 mmol) with a 10% excess of a 2-mL saturated aqueous $K_2CO_3$ solution with vigorous shaking). The mixture was allowed to stir at room temperature for 5 days. After filtration, the solvent was removed under reduced pressure to give a yellowish oil. To this was added 20 mL of ethyl acetate; the mixture was filtered, and the volume of the filtrate was reduced to ~5 mL by rotary evaporation. The remaining solution was extracted with chloroform and dried over anhydrous $Na_2SO_4$. After complete removal of the solvent, the desired product was obtained as a yellowish brown liquid; yield 4.5 g (81%). $^1H$ NMR: $\delta$ 8.57–6.83 (8 H, m, aromatic), 3.85 (2 H, s, $NCH_2$), 2.95 (4 H, s, $NCH_2CH_2$), 2.40 (3 H, s, $NCH_3$).

**(MeL)$RuCl_3 \cdot 3H_2O$.** To a solution of $RuCl_3 \cdot 3H_2O$ (1.0 g, 3.82 mmol) in 50 mL of ethanol was added (2-pyridylethyl)(2-pyridylmethyl)-methylamine (0.87 g, 3.83 mmol). The mixture was stirred for 1 h at room temperature. The greenish brown solid thus formed was collected, washed with small amounts of ethanol and acetone, and air-dried; yield 1.25 g (67%). Anal. Calcd for $C_{14}H_{23}N_3O_3Cl_3Ru$: C, 34.38; H, 4.71; N, 8.60. Found: C, 34.18; H, 4.31; N, 8.40.

**$[Ru_2O(O_2CCH_3)_2(MeL)_2](ClO_4)_2 \cdot 4H_2O$.** To a suspension of (MeL)-$RuCl_3 \cdot 3H_2O$ (0.22 g, 0.47 mmol) in 15 mL of water was added 9.0 g of sodium acetate to adjust the pH of the solution to ~7.1–7.2. The mixture was then refluxed for 30 min, whereupon the color of the resulting solution changed from green to dark purplish blue. The solution was filtered while hot, and to the filtrate was added ~5 mL of a saturated aqueous solution of sodium perchlorate. Immediately blue solid product started separating out. The microcrystalline solid was collected, washed with a small amount of cold water, and dried under vacuum; yield 0.15 g (31%). Anal. Calcd for $C_{32}H_{48}N_6O_{17}Cl_2Ru_2$: C, 36.19; H, 4.52; N, 7.92. Found: C, 35.83; H, 4.42; N, 7.77. IR (KBr, $cm^{-1}$, selected peaks): 3420 (m, $\nu(OH)$), 1545 (m, $\nu_{asym}(CO)$), 1440 (s, $\nu_{sym}(CO)$), 1100 (s, $\nu(ClO_4^-)$), 775 (s, $\nu(RuORu)$). Absorption spectrum [in MeCN; $\lambda_{max}$, nm ($\epsilon_{Ru}$, $M^{-1}$ $cm^{-1}$)]: 247 (12 450), 345 (7350), 564 (4980). Conductivity (MeCN, $10^{-3}$ M solution at 298 K): $\Lambda_M$ = 292 mho $cm^2$ $mol^{-1}$.

**Caution!** Although the preparation of the perchlorate salts described here has been done many times without incident, perchlorate salts of metal complexes with organic ligands have been known to explode spontaneously. Therefore, the preparation and handling of these perchlorate salts deserve special care.

**Physical Measurements.** Spectroscopic data were obtained by using the following instruments: infrared spectra, Perkin-Elmer M-580 spectrophotometer; electronic spectra, Perkin-Elmer Lambda 2 spectrophotometer. $^1H$ NMR spectra were measured in $CDCl_3$ or $CD_3COCD_3$ on a Bruker WP-80 (80 MHz) NMR spectrometer referenced to $Me_4Si$. Solution electrical conductivity measurements were carried out in MeCN with an Elico (Hyderabad, India) Type CM-82 T conductivity bridge. The pH measurements were made with a Systronics (Ahmedabad, India) Type 335 digital pH meter. Solution-state magnetic susceptibility was obtained by the NMR technique of Evans[7] in MeCN with a PMX-60 JEOL (60 MHz) NMR spectrometer. All electrochemical experiments were performed under dinitrogen atmosphere by using a Princeton Applied Research (PAR) Model 370-4 electrochemistry system as previously.[6] All electrochemical data were collected at 298 K referenced to an aqueous saturated calomel electrode (SCE) and are uncorrected for junction potentials. The cyclic voltammetric measurements utilized a planar Beckman Model 39273 platinum inlay as the working electrode. For coulometry a platinum-wire-gauze electrode was used as the working electrode. The solutions were ~1.0 mM in complex and 0.2 M in supporting electrolyte, TBAP.

## Results and Discussion

**Characterization of the Core.** The blue solid, $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2](ClO_4)_2 \cdot 4H_2O$, exhibited the characteristic IR bands assignable to bridging acetates, the RuORu moiety, water of crystallization, and $ClO_4^-$. In MeCN solution, the compound behaves as a 1:2 electrolyte.[8] The ($\mu$-oxo)bis($\mu$-acetato)diruthenium(III) core formulation[9] seems reasonable, given the similarities in the optical spectrum of the present complex (Figure 1) when compared to the spectrum[10] of the related structurally characterized dimer $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(py)_6](ClO_4)_2 \cdot 4H_2O$. As expected,[10–13] the new tribridged compound is diamagnetic (MeCN solution, at 298 K).

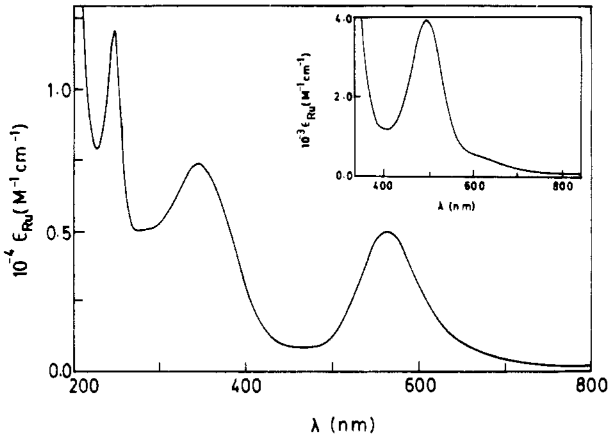

**Figure 1.** Absorption spectrum of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]$-$(ClO_4)_2 \cdot 4H_2O$ in MeCN. The visible spectrum of coulometrically generated $[Ru^{IV}Ru^{III}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$ in MeCN is shown as an inset.

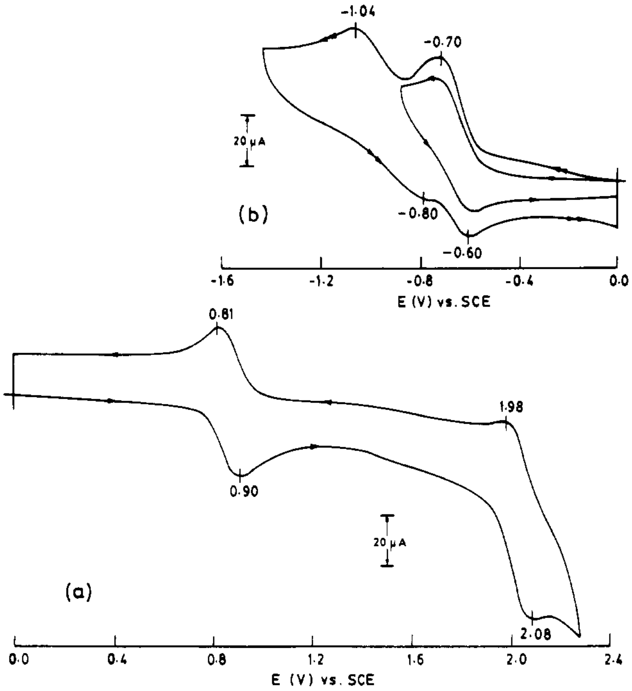

**Figure 2.** Cyclic voltammograms (scan rate 50 mV/s) of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2](ClO_4)_2 \cdot 4H_2O$ in MeCN at a platinum electrode ([Ru] = 1.88 mM; 0.2 M TBAP): (a) anodic scan; (b) cathodic scan.

**Electrochemistry.** Cyclic voltammetry in acetonitrile (0.1 M TBAP) was utilized to identify the core structure and to study the electrochemical properties of this tribridged complex using

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a platinum working electrode. Typical cyclic voltammograms for $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ are shown in Figure 2.

There are two well-defined oxidative responses in the potential region 0.0–2.4 V. The former potentials ($E_f$) were calculated as the average of the cathodic ($E_{pc}$) and anodic ($E_{pa}$) peak potentials, and the values are 0.86 and 2.03 V vs SCE. The peak-to-peak separations ($\Delta E_p = E_{pa} - E_{pc}$) at a scan rate of 50 mV/s are 90 and 100 mV, respectively. Under our experimental conditions, the reversible couple $Fc^+/Fc$ ($E_f = 0.40$ V vs SCE) has a $\Delta E_p$ of 80 mV, which was used as the criterion for electrochemical reversibility. Also, the ratio of anodic to cathodic peak currents ($i_{pa}/i_{pc}$) is ~1 for each of the processes. Coulometric oxidation at 1.06 V gave[14] $n = 1.01$ for the net electrochemical oxidation of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$. The above facts suggest that the $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ ion undergoes a chemically and electrochemically reversible one-electron oxidation process, generating the mixed-valence species $[Ru^{III}Ru^{IV}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$. The cyclic voltammogram of the one-electron-oxidized solution is identical with the voltammogram shown in Figure 2, but as expected, this time the response at 0.86 V becomes reductive. The oxidized solution can be quantitatively reduced (applied potential 0.66 V, $n = 0.88$), giving back $[Ru^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$. Attempted electrolysis at 2.10 V to generate the two-electron-oxidized dimer causes decomposition of the tribridged core. Thus, the species $[Ru^{IV}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{4+}$ is stable only on the time scale of cyclic voltammetry.

The tribridged complex also exhibits two reductive responses (Figure 2). The less negative wave with an $E_f$ of −0.65 V is quasireversible ($\Delta E_p = 100$ mV at a scan rate of 50 mV/s). This is assigned to the reduction of the $Ru^{II}Ru^{III}$ state. At this level of reduction, a μ-hydroxo bridge formation is definitely[2,15] a possibility, given the fact that the diruthenium(III) complex as isolated contained sufficient water of crystallization. An additional irreversible reductive response is seen with $E_f = -0.92$ V and $\Delta E_p = 240$ mV. No attempt was made to examine the chemical and electrochemical properties of the coulometrically reduced solutions, since it is expected that this would lead to decomposition of the tribridged structure, yielding mononuclear ruthenium(II) compounds.[16]

**Stability and Optical Spectrum of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$.** Though stable under dry anaerobic conditions, electrochemically and/or chemically (see below) generated acetonitrile solutions of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$ are very sensitive to air. Under aerobic conditions, such red solutions slowly turn purplish blue, the color of the diruthenium(III) precursor. Figure 1 exhibits the visible spectrum of the coulometrically oxidized 3+ ion in deoxygenated acetonitrile solution. The molar extinction coefficient ($\epsilon_{Ru}$) for the intense peak at 494 nm is estimated to be 3890 $M^{-1}$ $cm^{-1}$. The spectral feature is very similar to[11] that observed with a related species, $[Ru^{IV}Ru^{III}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(Me_3tacn)_2]^{3+}$. The strong band at 564 nm of LMCT origin for $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ is considerably blue shifted ($\lambda_{max} = 494$ nm) for $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$. The oxidation of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ in deoxygenated acetonitrile could also be achieved chemically by 1.06 equiv of ammonium cerium(IV) nitrate.

We have done the following controlled experiments to identify the actual component of air responsible for the quantitative reduction of the 3+ ion to the 2+ ion. Incremental amounts of deoxygenated water (0.05–0.30 mL) were added to the deoxygenated MeCN solutions (0.29 mM in 2+ species) of chemically generated 3+ ion. We observe that the greater the amount of added water, the faster the progress of reduction. These experiments confirm that under aerobic conditions the moisture of air acts as the reducing agent. Clean isosbestic points at 417 and 525 nm are observed when the reaction is followed spectrophotometrically. Thermodynamically, the 3+ ion is capable of oxidizing water. The $E_f$ value of the $Ru^{IV}Ru^{III}/Ru^{III}Ru^{III}$ couple is ~200 mV more positive than that of the $O_2/H_2O$ couple (pH ~7). The high moisture sensitivity of the oxidized species has made its isolation as a pure salt in the solid state thus far unachievable. This novel reactivity property is currently under investigation. Efforts are underway to synthesize this tribridged core with other transition-metal ions using MeL as the capping ligand.

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**Registry No.** $(MeL)RuCl_3$, 137467-27-7; $[Ru_2O(O_2CCH_3)_2(MeL)_2](ClO_4)_2$, 137467-29-9; $[Ru^{III}Ru^{IV}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$, 137467-30-2; MeL, 137495-65-9; 2-(2-(methylamino)ethyl)pyridine, 5638-76-6; 2-(chloromethyl)pyridine, 4377-33-7.

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[14] Coulometric data are averages of at least three independent measurements; *n* is the number of electrons passed per dimer.

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# (2,4-Pentanedionato)vanadium(III) and -vanadium(II) Complexes: Synthesis from the Oxovanadium Reductive Chlorination and Their Structural Characterization

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In spite of the recent active investigations on vanadium(III) and vanadium(II) chemistry,[2] there are still rather few starting materials easily accessible for (i) organometallic functionalization, (ii) reduction at the metal center, or (iii) solubility in organic solvents for carrying out reactions on oxygen-rich substrates,[3] except for the well-known $VCl_3(THF)_3$[4] and $[V_2(\mu\text{-}Cl_3)(THF)_6]^+$,[4] which, however, do not contain any ancillary ligands to be usable for the purposes outlined above. In this context we report the synthesis of some vanadium(III) and vanadium(II) acetylacetonate complexes.

## Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The syntheses of $VCl_3(THF)_3$[5] and $[VO(acac)_2]$[6] have been performed as reported in the literature. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer. The magnetic measurements have been carried out with a Faraday balance.

**Solid-State Structures of 2 and 4.** Crystallographic data, atomic coordinates, and selected bond distances and angles are reported in Tables I–V.

**Preparation of $[V(acac)Cl_2(THF)_2]$ (2). Method A.** To a blue suspension of $TiCl_3(THF)_3$ (13.21 g, 35.6 mmol) in THF (100 mL) was added $[VO(acac)_2]$ (9.40 g, 35.6 mmol) under stirring. The reaction mixture was heated for a few minutes until all the solid dissolved. Very little impurities are filtered out sometimes. A green-red solution was obtained, which was kept on standing at room temperature for 24 h. $[V(acac)Cl_2(THF)_2]$ precipitated as a green crystalline solid (53%). Anal. Calcd for $C_{13}H_{23}Cl_2O_4V$: C, 42.75; H, 6.35; Cl, 19.43. Found: C, 43.02; H, 6.56; Cl, 19.33. The solid was found to be free of titanium by atomic absorption.

**Method B.** To a solution of acacH (2.85 mL, 27.6 mmol) in THF (75 mL) was added NaH (0.66 g, 27.6 mmol). Gas evolution took place, and

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