A Facile and Efficient Method for Preparing Ring-Alkylated Vanadocenes (RCp)₂V and Mono- and Dichlorides of Ring-Alkylated Vanadocenes (RCp)₂VCl and (RCp)₂VCl₂

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Summary: A convenient procedure for the general preparation of bis(methylcyclopentadienyl)vanadium (1), bis-(isopropylcyclopentadienyl)vanadium (2), and bis(tert-butylcyclopentadienyl)vanadium (3) and their blue monochloride (4−6) and green dichloride (7−9) derivatives is presented. The X-ray structures of compounds 8 and 9 and the electrochemistry and EPR of 7−9 are also presented.

Introduction

Given the number of applications surrounding early transition metal cyclopentadienyl sandwich complexes, the paucity of vanadocene research is truly remarkable. This is even more surprising given their potential application as potent antitumor agents,[1] paramagnetic medical MRI shift reagents,[2ab] Ziegler−Natta catalysts,[3ab] and building blocks for novel magnetic materials.[4] Obviously, one of the major stumbling blocks in this area of research has been the extreme reactivity of the parent vanadocene, in which the V(II) center is violently O_2 sensitive. In addition, the purification of these materials by reported techniques[5ab] is extremely difficult due to the low volatility (as ring substitution increases) and thermal instability of the parent complexes. In this report, we wish to present a simple and efficient method for the preparation of multigram quantities of several ring-alkylated vanadocenes and their mono- and dichloride derivatives with PCl_3. We feel the generality of our new synthetic procedure will allow for the isolation and characterization of several, previously inaccessible vanadium cyclopentadienyl complexes.

The recent synthesis of the first homobimetallic tetrathiafulvalenetetrathiolate has provided a route to numerous new building blocks that can be used in the assembly of new advanced materials. The bimetallic $TTFS_4$ complexes are synthesized by the addition of

$TTFS_4^{4-}$ to 2 equiv of various early transition metal metallocene dichlorides (Cp_2MCl_2).[6−8] We are now focusing on examining the spin ordering and magnetic coupling in high-spin, bivanadium tetrathiafulvalene (TTF) materials. The unpaired electron on the V(IV) center affords an $S \neq 0$ ground state and the possibility of using the vanadium nuclear hyperfine ($I = \,^7/_2$) splitting as a spectroscopic marker were both attractive reasons for exploring this chemistry. Initially, we prepared bimetallic TTFs using the comercially available vanadocene dichloride; however, the isolated final materials were insoluble and impure. As an attempt to rectify this problem, we sought to make ring-alkylated vanadocenes in order to enhance the desired products solubility, as well as prohibit the formation of μ-S bridging dithiolenes,[9] which is a major problem in the unsubstituted systems.

Bis(methylcyclopentadienyl) vanadium dichloride (7), a known substituted vanadium compound, also failed to give reasonably soluble or analytically pure bimetallic tetrathiafulvalene materials.[10] In an effort to synthesized other ring-alkylated vanadocenes, our work was hampered by the tendency of the dichlorides to produce analytically impure products. Also, distillation of the of the purple vanadocene (1) resulted in considerable thermal degradation. We now report the preparation of the branched ring-alkylated vanadocenes (2 and 3) and their dichlorides and new purification routes to further facilitate the scale and solubility of the desired materials.

Results and Discussion

In Scheme 1 is shown the general synthesis of ring-alkylated vanadocenes and their di- and monochlorides. The respective alkali metal cyclopentadienide salt is dissolved, or generated *in situ* using dry THF, and subsequently reacted with VCl_3 to generate the vanadocene. The reaction mixture is filtered in the glovebox, and the filterate is concentrated *in vacuo* and chromatographed on anhydrous silica gel to afford the vandocenes as analytically pure purple oils or crystals.

The chlorination of the vanadocenes (1−3) with PCl_3 in Et_2O affords the dichlorides (7−9). The green solids

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.
(1) Kopf-Maier, P.; Kopf, H. *Z. Naturforsch. B* **1979**, *34*, 805.
(2) (a) Toney, J. H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 947. (b) Toney, J. H.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7263.
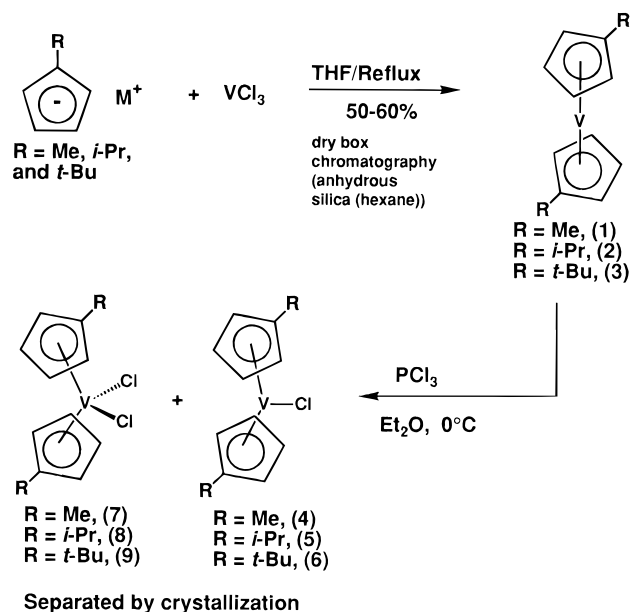(3) (a) Petersen, J. L.; Griffith, L. *Inorg. Chem.* **1980**, *19*, 1852. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science: Mill Valley, CA, 1987.
(4) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201.
(5) (a) Rettig, M. F.; Drago, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 1361. (b) Kohler, H. H.; Prossdorf, W. *Z. Naturforsch. B* **1977**, *32*, 1026.

(6) McCullough, R. D.; Belot J. A. *Chem. Mater.* **1994**, *6*, 1396.
(7) McCullough, R. D.; Belot, J. A.; Rheingold, A. L.; Yap, G. P. A. *J. Am. Chem. Soc.* **1995**, *117*, 9913.
(8) McCullough, R. D.; Belot, S. J.; Rheingold, A. L.; Yap, G. P. A. *J. Mater. Chem.* **1995**, *5*, 1581.
(9) (a) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (b) Fachinetti, C.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1974**, 2433.
(10) Moran, M.; Masaguer, J. R.; Fernandez, V. *J. Organomet. Chem.* **1985**, *291*, 311.

Scheme 1

Figure 1. Single-crystal X-ray structures for **8** (top) and **9** (bottom) with thermal ellipsoids drawn at 30% probabilities. Selected bond distances for **8** (Å): cent(1)−V, 1.998(6); V−Cl(1), 2.414(3). Selected bond angles for **8** (deg): cent−V−cent, 132.5(2); Cl−V−Cl, 85.0(1). Selected bond distances for **9** (Å): cent(1)−V, 1.985(4); V−Cl(1), 2.408(1). Selected bond angles for **9** (deg): cent−V−cent, 133.8(2); Cl−V−Cl, 86.77(7).

can be isolated by filtration to yield dichlorides (**7**−**9**) from the Et_2O mother liquor. If the solution is filtered in air, the Et_2O filtrate solution appears green; however, if care is taken to exclude oxygen, the solution is royal blue. From the blue solution, the monochlorides (**4**−**6**) can be crystallized through slow solvent evaporation in an inert atmosphere.[11,12] Monohalides of vanadocenes can also be prepared the method of Rettig and Wing, in which vanadocene is reacted with alkyl halides to give spontaneous precipitation of the monohalides.[12] The yields of **4**−**6** are proportional to the steric demands of the bulky alkyl substituents, with the amount of **4** > **5** > **6** and the overall mass balance being nearly 100%. Although the monochlorides are extremely reactive species, they serve as starting points for a wide variety of synthetic chemistry[13] and precursors to magnetic materials.[14]

In Figure 1 are the X-ray crystal structures of the vanadocene dichlorides **8** and **9** as recrystallized from anhydrous CH_3CN. Compound **8** has rigorous overall C_{2v} molecular symmetry with the Cp rings being eclipsed, and **8** crystallizes in the highly symmetric space group *Cmcm*. (Table 1). In molecule **8** the *i*-Pr groups are located directly above the Cl atoms, with a short H···Cl contact[15] of 2.84 Å. Compound **9** has rigorous overall C_2 molecular symmetry (Table 1), and the Cp rings are staggered; short Cl−H distances are again present averaging 2.70 Å. The staggered arrangement of the Cp rings in **9** places the bulky *t*-Bu groups far apart. While the angle between the Cp ligand planes for **9** and **8** are similar, 48.3 and 48.5°, respectively, and the coordination geometries are essentially identical, the ligand conformations are markely different. The Cp rings in **8** are eclipsed with a dihedral angle, C(3)−
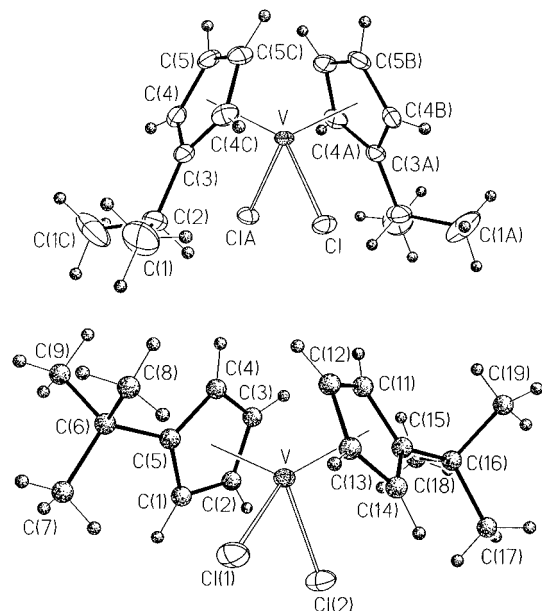
Table 1. Crystallographic Data for 8 and 9

	9	**8**
(a) Crystal Parameters		
formula	$C_{18}H_{26}Cl_2V$	$C_{16}H_{22}Cl_2V$
fw	364.2	336.18
cryst system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	*Cmcm*
a, Å	10.457(4)	11.498(6)
b, Å	1.786(4)	6.822(4)
c, Å	13.208(5)	19.867(5)
V, Å^3	1766(5)	1558(2)
Z	4	4
cryst dimens, mm	0.07 × 0.09 × 0.10	0.12 × 0.14 × 0.17
cryst color	green	green
D(calc), g/cm^3	1.373	1.433
μ(Mo Kα), cm^{-1}	8.58	9.64
temp, K	246	222
(b) Data Collection		
diffractometer	Siemens P4	
monochromator	graphite	
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)	
2θ scan range, deg	4.0−45.0	4.0−45
data collcd (h,k,l)	+11,+13,+12	+12,+7,+21
rflns collcd	1343	1062
indpt rflns	1312	563
indpt obsvd rflns $F_o \geq$ $n\sigma(F_o)$ ($n = 4$)	952	496
std/rfln	3 std/197 rflns	3 std/197 rflns
var in stds, %	<1	<1
(c) Refinement		
$R(F)$, %	5.10^a	2.93^b
$R(wF)$, %	5.92^a	7.67^{b,c}
$\Delta\sigma$(max)	0.00	0.00
$\Delta(\rho)$, e Å^{-3}	0.47	0.20
N_o/N_v	11.6	11.3
GOF	1.20	1.09

centroid′−C(3A), of 0°. This conformer relieves the steric crowding at the nearest edge-to-edge distance between the rings while allowing the chloride ligands to fit in a space enclosed by the *sec*-propyl

(11) (a) Fieselmann, B. F.; Stucky, G. D. *J. Organomet. Chem.* **1977**, *137*, 43. (b) Fischer, E. O.; Vigoureux, S.; Kuzel, P. *Chem. Ber.* **1960**, *93*, 701.

(12) Rettig, M. F.; Wing, R. M. *Inorg. Chem.* **1969**, *8*, 2685.

(13) Curtis, C. J.; Smart, J. C.; Robbins, J. L. *Organometallics* **1985**, *4*, 1283 and references therein.

(14) Kohler, F. H.; Prossdorf, W.; Schubert, U. *Inorg. Chem.* **1981**, *20*, 4096.

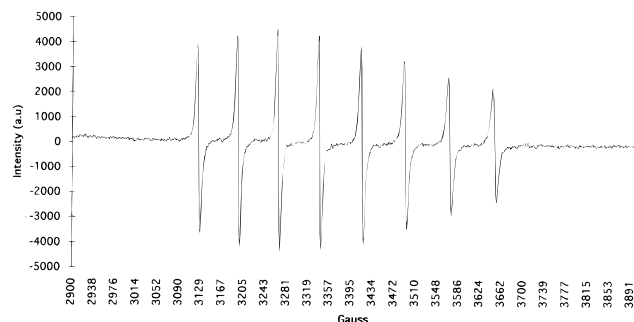(15) Desiraju, G. R. in *Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: New York, 1987.
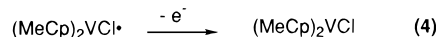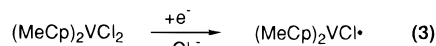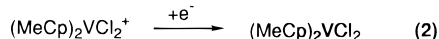
Figure 2. EPR of **7**.

$$(MeCp)_2VCl_2 \xrightarrow{-e^-} (MeCp)_2VCl_2{}^+ \quad (1)$$

$$(MeCp)_2VCl_2{}^+ \xrightarrow{+e^-} (MeCp)_2VCl_2 \quad (2)$$

$$(MeCp)_2VCl_2 \xrightarrow[-Cl^-]{+e^-} (MeCp)_2VCl\bullet \quad (3)$$

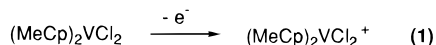$$(MeCp)_2VCl\bullet \xrightarrow{-e^-} (MeCp)_2VCl \quad (4)$$

Figure 3. Proposed electrochemical processes for **7**.

Table 2. Electrochemical Potentials of the Vanadocene Dichlorides

	potential (V)			
complex	$E_{1/2}$(oxdn) rev	$E_{1/2}$(redn) irrev	$E_{1/2}$(redn) irrev	Fc/Fc$^+$ rev
7	0.92	-0.98	0.06	0.40
8	0.93	-0.95	0.01	0.40
9	0.92	-0.96	0.09	0.39

methyls. The wider Cl−V−Cl angle in **8** of 86.77(7)° when compared to the Cl−V−Cl angle in **9** of 85.0(1)° also strongly suggests the relative difference in steric encumbrance at the chloride sites. A similar conformation for **9** would force the methyl groups into the chloride ligands and thus is not favored.

The vanadocene dichlorides are all paramagnetic making characterization by routine NMR quite difficult; however, the V(IV) oxidation state is quite amenable to EPR and electrochemical characterization. In Figure 2 is a representative EPR spectrum concerning **7**. These data, collected at room temperature in anhydrous CH$_3$-CN, show the expected isotropic eight-line nuclear hyperfine attributable to the $I = {}^7/_2$ value of the vanadium nucleus with the signal centered at $g = 2.00$ and an average a value of approximately 75 G. Both the g and a values for **7** are identical for complexes **8** and **9**.

The electrochemical characterization of **7**−**9** shows several interesting features which were observed at scan rates above 1.0 V/s using 0.1 M (C$_4$H$_9$)$_4$NPF$_6$ in CH$_3$CN as the supporting electrolyte.[16] Table 2 summarizes a comparison of the potentials (referenced to the ferrocene/ferrocenium (Fc/Fc$^+$) couple) for **7**−**9** as well as the reversibility of these processes. The reversible V^{4+}/V^{5+} oxidation/reduction couple near 0.9 V (reactions **1** and **2**), as well as the irreversible reduction (V^{4+}/V^{3+}) near −0.98 V (reaction **3**), are completely reproducible in these systems at all scan rates above and below 1 V/s (Figure 3). Reaction **3** is consistent with the work of Geiger.[17] At higher sweep rates ($\geq$1 V/s) a new oxidation couple (perhaps reaction **4**) is evident. Per-

haps we are generating the transient product shown to develop from reaction **3**. It has been known that in the electrochemistry of related compounds a highly reactive reduced compound, which is detectable by EPR, may be characterized as a transient species.[18] These results lead us to believe that the proposed product shown in reaction **3** may the species observed in the electrochemistry.

Presented in this note is a general, convenient, and inexpensive method for the isolation of branched alkyl substituted vanadocenes as well as their mono- and dichloride derivatives. In addition to this synthetic preparation are the crystal structures of two new substituted vanadocene dichlorides as well as their characterization by various methods. The crucial steps in this method are the drybox silica gel chromatography of the parent vanadocenes and the recrystallization conditions for the dichlorides. In addition, preliminary results concerning the formation of the blue monochlorides recovered from the chlorination reaction have also been discussed.

Experimental Section

All reactions and manipulations were performed under prepurified nitrogen or argon. Glassware was dried in a 130 °C oven overnight and then cooled under a stream of argon or nitrogen. *t*-Bu-,[19ab] *i*-Pr-,[20] and Me-substituted cyclopentadienide[21] were prepared from literature procedures, and VCl$_3$ and PCl$_3$ were purchased from Strem and Aldrich Chemical Co., respectively, being used as received. Tetrahydrofuran and diethyl ether were dried over Na benzophenone ketyl radical and hexane was dried from CaH$_2$, all being freshly distilled immediately prior to use. Acetonitrile was doubly distilled first from CaH$_2$ and then P$_2$O$_5$ and stored in the glovebox. IR spectra were recorded on a Mattson Galaxy Series FTIR 5000 using KBr (unless otherwise noted) pellets, UV−vis−near-IR on a Cary 5 spectrophotometer, and the electrochemistry using 0.1 M (C$_4$H$_{10}$)$_4$NPF$_6$ in CH$_3$CN (dried and distilled first from CaH$_2$ and then P$_2$O$_5$) on a Pines Model AFRDE4 potentiostat. Elemental analysis was performed by Midwest Microlabs, Indianapolis, IN.

The procedure for drying silica gel is as follows: A 1000 mL 24/40 one neck round-bottomed flask is filled approximately $^3/_4$ full with flash silica gel (JT Baker brand), while simultaneously an oil bath is heated to 140 °C. The vessel is then fitted with a gas adapter (that has been filled with cotton) and immersed in the hot oil bath. Slowly the flask is evacuated, with the Schlenk traps being emptied periodically (every 30 min) to remove water. After a final vacuum of <0.05 Torr has been reached (this typically may take 3−6 h) the flask is heated under vacuum overnight. Following this time the silica gel is frequently backfilled with argon and then re-evacuated. This step is repeated at least 100 times over the period of 2 d. Fewer deoxygenation cycles will probably work; however they were not tried. After this time the flask is sealed tightly and pumped into the drybox. The silica gel may now be used for the vanadocenes.

Crystal, data collection, and refinement parameters are given in Table 1 of the Supporting Information. Suitable crystals were selected and mounted in thin-walled, nitrogen-flushed, glass capillaries. The unit-cell parameters were

(16) El Murr, N.; Moise, C.; Rivecci, M.; Tirouflet, J. *Inorg. Chim. Acta* **1979**, *32*, 189.

(17) Holloway, J. D. L.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2038.

(18) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112.

(19) (a) Freiesleben, W. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 396. (b) Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213.

(20) Alder, K.; Ache, H. J. *Chem. Ber.* **1962**, *95*, 503.

(21) Rettig, M. F.; Drago, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 1361.

obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\theta \leq 25°$).

The systematic absences in the diffraction data are consistent for orthorhombic space groups $P2_12_12_1$ for **9**, uniquely, and, $Cmc2_1$ or $Cmcm$ for **8**. The E-statistics suggested the centrosymmetric option for **8** which was subsequently verified by chemically reasonable results or refinement. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Absorption corrections were ignored because of the <5% variation in the integrated intensities of the ψ-scan data. Vanadium and chlorine atoms in **9** and all non-hydrogen atoms in **8** were refined with anisotropic displacement coefficients. Carbon atoms in **9** were refined isotropically. Hydrogen atoms were treated as idealized contributions. The compound in **8** is located at an intersection of two perpendicular mirror planes.

All software and sources of the scattering factors are contained either in the SHELXTL PLUS (4.2) or SHELXTL (Version 5) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

General Synthesis of Vanadocenes 1–3. One equivalent of the desired alkylcyclopentadienide alkali metal salt is dissolved, or generated, in 160 mL of dry THF and cooled to 0 °C. To this is added 0.3 equiv of VCl$_3$ (in one portion), and the cold bath is subsequently removed after 15 min. The reaction is then heated to a gentle reflux for 2–3 h, followed by removal of THF by distillation. This leaves a purple-black sludge. Note: *This Material is Extremely Pyrophoric!* This sludge is thinned with 250 mL of dry deoxygenated hexane introduced via a cannula transfer and stirred overnight. After the reaction flask is pumped into the drybox, the white inorganic salts are collected using a coarse or medium 150 mL glass fritted funnel, washed with 2×30 mL of C$_6$H$_{14}$ and discarded. The filtrated is then concentrated *in vacuo*. This yields a viscous black oil which was chromatographed on dry deoxygenated silica gel in the glovebox (hexane). Compounds **1–3** move cleanly with the solvent front and can be quickly isolated as deep purple oils (**1** and **2**) or reddish purple crystals (**3**). Yields are typically on the order of 55–60%.

General Synthesis of Alkyl-Substituted Vanadocene Mono- (4–6) and Dichlorides (7–9). One equivalent of **3**, under argon, is dissolved using 110 mL of dry Et$_2$O and cooled

to 0 °C. A 2.4 equiv amount of fresh PCl$_3$ is added by syringe, and the solution immediately becomes heterogenous, with green solids slowly precipitating from the now deep blue ether solution. After 1.5 h the cold bath is removed and the reaction is allowed to stir overnight. The flask is then pumped into the glovebox and filtered through a 15 mL M porosity glass frit. The blue filtrate contains the monochlorides, while the green solids remaining on the funnel are the crude dichlorides which can be recrystallized using a minimum volume of dry CH$_3$CN to yield **7–9**.

Bis(methylcyclopentadienyl)vanadium Dichloride (7): Pure yield 40%; mp 230 °C (dec); IR (cm^{-1}) 3100, 2920, 1490, 1445, 1375, 1250, 1050, 920, 860, 820, 600; Echem (V vs Fc/Fc$^+$ at 0.40 V in 0.1 M TBAP in CH$_3$CN) -0.98, 0.06, 0.92; EPR (in CH$_3$CN) $g = 2.00$, $a = 75$ G for nuclear hyperfine. Anal. Found (calc): C, 51.26 (51.43); H, 5.11 (5.00).

Bis(isopropylcyclopentadienyl)vanadium Dichloride (8): Pure yield 35%; mp 186 °C (dec); IR (cm^{-1}) 3110, 2950, 2850, 1490, 1460, 1420, 1390, 1370, 1305, 1250, 1165, 1100, 1080, 1060, 925, 890, 860, 690, 590; EPR (in CH$_3$CN) $g = 2.00$, $a = 75$ G for nuclear hyperfine; Echem (V vs Fc/Fc$^+$ at 0.40 V in 0.1 M TBAP in CH$_3$CN) -0.95 (irrev), 0.01 (irrev), 0.93 (rev). Anal. Found (calc): C, 57.07 (57.16); H, 6.69 (6.60). The first recrystallization afforded X-ray-quality crystals.

Bis(*tert*-butylcyclopentadienyl)vanadium Dichloride (9): Pure yield <10%; mp 170 °C (dec); EPR (in CH$_3$CN) $g = 2.00$, $a = 75$ G for nuclear hyperfine; Echem (V vs Fc/Fc$^+$ at 0.39 V in 0.1 M TBAP in CH$_3$CN) -0.96 (irrev), 0.09 (irrev), 0.92 (rev). Anal. Found (calc): C, 59.3 (58.7); H, 7.07 (7.14). A second recrystallization afforded X-ray-quality crystals.

Bis(*tert*-butylcyclopentadienyl)vanadium Monochloride (6): Crude yield ≈ 80%; Echem (V vs Fc/Fc$^+$ at 0.41 V in 0.2 M TBAP in CH$_3$CN) 0.28 (oxdn, irrev), 0.95 (rev), 0.35 (redn, irrev). Anal. Found (calc): C, 65.21 (65.75); H, 7.84 (7.97).

Supporting Information Available: Tables of X-ray parameters, positional and thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.