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Notes

Convenient Synthesis of Dichloro(oxo)(pentamethylcyclopentadienyl)vanadium(V), $(\eta\text{-C}_5\text{Me}_5)\text{V(O)Cl}_2$

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Summary: The details of a high-yield synthesis of $(\eta\text{-C}_5\text{Me}_5)\text{V(O)Cl}_2$ *from an easily handled and readily prepared starting material,* $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]$*, using* O_2 *as the oxygen source are described.*

Organometallic oxo compounds have been the subject of an ever-increasing number of investigations over the past decade,[1] with pentamethylcyclopentadienyl ligands frequently used as ancillary ligands to enhance solubility and to define or limit the reactive sites in these oxo compounds.[2,3] Therefore, it surprised us to find that $(\eta\text{-C}_5\text{Me}_5)\text{V(O)Cl}_2$ has been the subject of only a limited number of investigations.[4−8] Previously reported synthetic routes to this compound[4−6] involve expensive and highly reactive starting materials, which may present a barrier to the development of new chemistry of $(\eta\text{-C}_5\text{Me}_5)\text{V(O)Cl}_2$. In examining possible synthetic routes to cyclopentadienyl-substituted vanadium silylimido and nitrido compounds,[9,10] we discovered a high-yield, straightforward synthesis of $(\eta\text{-C}_5\text{Me}_5)\text{V(O)Cl}_2$[11] that is based on a very easy to handle vanadium reagent, VCl_3, and uses O_2, as a reagent gas or from air, as a readily available oxo source. Because $(\eta\text{-C}_5\text{Me}_5)\text{V(O)Cl}_2$ provides an attractive entry into organovanadium oxo chemistry and is potentially a very useful starting material for other vanadium(V) monopentamethylcyclopentadienyl compounds, we report the details of our synthesis herein.

Experimental Section

General Comments. Experiments were performed using appropriately dried reagent-grade solvents, under standard anhydrous and anaerobic conditions,[12] except where indicated otherwise. $(\text{C}_5\text{Me}_5)\text{SnBu}_3$[13] and $\text{VCl}_3(\text{THF})_3$[14] were prepared according to the literature procedures. NMR spectra were obtained at ambient temperature in benzene-d_6; chemical shifts are reported in ppm relative to SiMe_4 (500.16 MHz, ^{1}H NMR) or neat V(O)Cl_3 (131.56 MHz, ^{51}V NMR).

$[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]$[11,15] (1). (a) $\text{VCl}_3(\text{THF})_3$ (5.09 g, 13.6 mmol) was added to a solution of $(\text{C}_5\text{Me}_5)\text{SnBu}_3$ (5.78 g, 13.6 mmol) in 1:1 toluene:benzene (100 mL). The mixture was stirred and heated at 55 °C until all of the pink solid $\text{VCl}_3(\text{THF})_3$ had dissolved, approximately 1 h, and the resulting brown solution was held at this temperature and stirred for an additional hour. The mixture was cooled to room temperature and filtered. The solvent and volatiles were removed from the filtrate under reduced pressure, and the resulting brown solid was washed with pentane to remove ClSnBu_3 and dried under vacuum, affording 3.20 g of brown $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]_3$ (**1a**, 91% yield).

(b) $(\text{C}_5\text{Me}_5)\text{SnBu}_3$ (2.02 g, 4.75 mmol) was added to a suspension of pink $\text{VCl}_3(\text{THF})_3$ (1.77 g, 4.74 mmol) in toluene (70 mL). The mixture was stirred and heated at 50 °C for 20 h, producing a dark brown solution. The solvent and volatiles were removed under reduced pressure, and the solids were washed with pentane and dried under vacuum. The solids were extracted with toluene (3 × 20 mL), the toluene extracts were combined and reduced to 5 mL, and pentane (25 mL) was added. The resulting brown crystalline solid was collected by filtration, washed with pentane, and dried under vacuum, affording 0.700 g of $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]_3$ (**1a**, 57% yield). The purple insoluble solid (0.408 g) remaining after the toluene extraction analyzes as $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]\cdot 4\text{VCl}_3\cdot 2\text{THF}$ (**1b**, 42% yield).

The ratio of brown $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]_3$ (**1a**) to purple $[(\eta\text{-C}_5\text{Me}_5)\text{VCl}_2]\cdot 4\text{VCl}_3\cdot 2\text{THF}$ (**1b**) varies considerably from reaction to reaction, from essentially no **1b** to ratios of vanadium in **1a**:**1b** as high as 1:2, with the amount of **1b** increasing when longer reaction times, higher temperatures, or older samples of $\text{VCl}_3(\text{THF})_3$ are employed.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1997.

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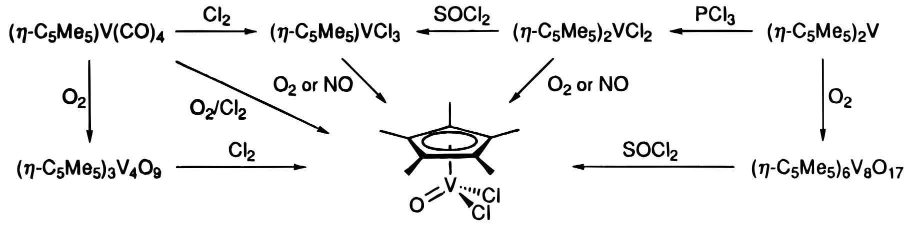


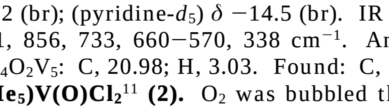
Figure 1. Summary of previously reported routes to **2**.[4−6]

For $[(\eta\text{-}C_5Me_5)VCl_2]_3$ (**1a**): ^1H NMR (C_6D_6) δ −7.9 (br); (THF-d_8) δ −8.0 (br), −13.2 (br); (pyridine-d_5) δ −14.5 (br). IR (Nujol): 1017, 844, 722, 559, 400, 325 cm^{-1}. Anal. Calcd for $C_{30}H_{45}Cl_6V_3$: C, 46.72; H, 5.88. Found: C, 46.63; H, 5.70. For $[(\eta\text{-}C_5Me_5)VCl_2]\cdot 4VCl_3\cdot 2THF$ (**1b**): ^1H NMR (THF-d_8) δ −8.0 (br), −13.2 (br); (pyridine-d_5) δ −14.5 (br). IR (Nujol): 1040, 1008, 921, 856, 733, 660−570, 338 cm^{-1}. Anal. Calcd for $C_{18}H_{31}Cl_{14}O_2V_5$: C, 20.98; H, 3.03. Found: C, 20.90; H, 3.38.

(η-C_5Me_5)V(O)Cl_2[11] (2). O_2 was bubbled through a deep red solution of **1a** (244 mg, 0.95 mmol V) in THF (25 mL) for 30 min at room temperature, producing a bright green solution. (Usual precautions should be taken when bubbling an oxidizing agent through a oxidizable solution.) The solvent and volatiles were removed under reduced pressure, and the resulting green residue containing trapped THF was dried by heating (50 °C) under vacuum to afford 241 mg of NMR-pure green solid **2** (93% yield). If necessary, further purification of **2** can be effected by vacuum sublimation (85 °C, 10^{-4} Torr) or by recrystallization from hot pentane. ^1H NMR, ^{51}V NMR: (C_6D_6) δ 1.80, −49 ($\nu_{1/2}$ = 90 Hz); ($CDCl_3$) δ 2.33, −31 ($\nu_{1/2}$ = 90 Hz); (CD_2Cl_2) δ 2.33, −12 ($\nu_{1/2}$ = 70 Hz); (CD_3CN) δ 2.33, 17 ($\nu_{1/2}$ = 70 Hz). IR (neat): ν_{VO} 967 cm^{-1}. Anal. Calcd for $C_{10}H_{15}Cl_2OV$: C, 43.98; H, 5.54. Found: C, 43.98; H, 5.59.

Results and Discussion

$[(\eta\text{-}C_5Me_5)VCl_2]$ (**1**) reacts readily with dioxygen at room temperature to afford green $(\eta\text{-}C_5Me_5)V(O)Cl_2$ (**2**) quantitatively (eq 1). A THF solution of **1** can be converted to **2** by bubbling O_2 through the solution for 30 min, or by stirring the solution under an O_2 atmosphere or in air[16] for several days. Isolated yields of **2** are excellent under all conditions tested, in the 90−95% range even for small scale preparations. Compound **2** is readily characterized by its ^1H and ^{51}V NMR spectra, both of which show solvent-dependent chemical shifts, and by the strong $\nu_{V=O}$ band in its IR spectrum.[4−6] Compound **2** has been previously shown to adopt a monomeric terminal oxo structure.[4a]



(1)

1 2

The starting material **1** is prepared according to Messerle's procedure,[15] from $(C_5Me_5)SnBu_3$[13] and VCl_3-THF_3.[14] We find that in toluene at elevated temperatures, this reaction produces not only soluble trimeric $[(\eta\text{-}C_5Me_5)VCl_2]_3$[11,15] (**1a**) but also an insoluble purple material (**1b**) formulated as $[(\eta\text{-}C_5Me_5)VCl_2]\cdot 4VCl_3\cdot 2THF$, based on consistent elemental analyses of samples from different preparations. Furthermore, by variation of the conditions for the crystallization of samples, we have obtained solids which analyze with variable formulations in between **1a** and **1b**, such as $[(\eta\text{-}C_5Me_5)VCl_2]_3\cdot {}^1/_3VCl_3$ and $[(\eta\text{-}C_5Me_5)VCl_2]_3\cdot 4VCl_3\cdot {}^1/_2THF$. Our observation of the variable composition of the crystalline materials isolated from Messerle's reaction highlights the importance of knowing the specific composition of the samples used for physical measurements in this system.[11,15] The color of the sample appears to be a useful indicator of the composition: trimeric **1a** is brown, insoluble **1b** is purple, and in-between samples range from maroon to a more purple hue as the amount of VCl_3 increases. Brown **1a** dissolves in C_6D_6 to give a single broad ^1H NMR signal at δ −7.9, whereas purple **1b** is insoluble in aromatic hydrocarbons. In pyridine-d_5, all samples give an identical broad ^1H NMR signal at δ −14.5, and in THF-d_8, they produce two broad ^1H NMR signals at δ −8.0 and −13.2 in relative intensities that are concentration dependent, with increasing concentration favoring δ −8.0.

These observations indicate the following. Trimeric **1a**, characterized by a paramagnetically shifted ^1H NMR signal at approximately δ −8, is soluble in noncoordinating aromatic solvents. Depending on the exact conditions, $[(\eta\text{-}C_5Me_5)VCl_2]$ can crystallize with variable amounts of VCl_3 and THF. It is not clear whether these materials represent stoichiometric compounds or solid mixtures, although in the case of insoluble purple **1b**, the reproducible formulation suggests, at the very least, a stoichiometric solid compound. In coordinating solvents, all samples containing $[(\eta\text{-}C_5Me_5)VCl_2]$ react to form a common monomeric species, likely $(\eta\text{-}C_5Me_5)VCl_2(\text{solvent})$, characterized by a paramagnetically shifted ^1H NMR signal at approximately δ −14. Depending on the ligating ability of the coordinating solvent, this monomer is present as the sole species (e.g., in pyridine) or establishes an equilibrium mixture of monomer and trimer (e.g. in THF), with increasing concentration increasing the amount of trimer present. Interestingly, and consistent with this interpretation, all samples of **1** can be used as starting materials for the synthesis of **2** and other $[(\eta\text{-}C_5Me_5)V]$ compounds[10] in THF, with the yields of products being quantitative based on the amount of $[(\eta\text{-}C_5Me_5)VCl_2]$ present in the sample. We additionally note that the reaction of **1a** with O_2 in benzene or toluene is much slower than that in THF, further supporting the idea of a faster reacting monomeric species present in the coordinating solvent.

Overall, the route to $(\eta\text{-}C_5Me_5)V(O)Cl_2$ (**2**) described herein (eq 1) represents an efficient, high-yield synthesis from the easily handled commercial reagent VCl_3. This is readily converted to the THF adduct in greater than 80% yield, which is, in turn, used to prepare **1**. Use of

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[16] Overall yield of **2** using air is good with little, if any, evidence for formation of hydrolysis products in our hands.

the tin reagent ($(C_5Me_5)SnBu_3$), which is required to obtain **1** in high yield,[17] does increase the expense and hazard of the overall procedure. However, it should be noted that $ClSnBu_3$, which is used to prepare $(C_5Me_5)SnBu_3$,[13] is regenerated in the synthesis of **1** and, thus, can be recovered and reused in subsequent preparations. Dioxygen, the source of the oxo ligand in **2**, can be used as a pure reagent or can come from ambient air. In comparison, previously reported routes to **2** (Figure 1) are nowhere near as facile. These reactions trace back to two pentamethylcyclopentadienyl-substituted vanadium starting materials that are more difficult and costly to prepare and use than **1**, $(\eta\text{-}C_5Me_5)V(CO)_4$[6,18] and $(\eta\text{-}C_5Me_5)_2V$.[19] Several oxidation and/or chlorination reactions produce **2** from these starting materials or their derivatives (Figure 1), with yields ranging from 20−85%, but none rivals the essentially quantitative conversion of **1** to **2** reported here.

In addition to being a facile route to **2**, reaction 1 is a interesting example of the clean use of O_2 to produce a terminal oxo compound.[20] Overall, a net 2-electron oxidation of vanadium(III) in the starting material occurs upon formal addition of one oxygen atom, producing the vanadium(V) oxo product. Several different mechanistic scenarios that might occur in reaction 1 can be envisioned. Interest in understanding the metal-mediated chemistry of dioxygen is widespread,[21] suggesting it will be worth examining this reaction in more detail.

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[17] We have not succeeded in preparing **1** in any useful yield using other C_5Me_5 reagents.

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Additions and Corrections

1996, Volume 15

Jennifer C. Green* and Sergey Yu. Ketkov*: Electronic Structures of η^7-Cycloheptatrienyl η^5-Cyclopentadienyl Derivatives of Vanadium and Tantalum As Studied by Solution-Phase and Vapor-Phase Photoabsorption Spectroscopy in the Ultraviolet and Visible Regions.

Page 4747. The title of this paper should appear as given above.

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