# Monomeric Four-coordinate Vanadium(v) Oxo Complexes Containing a Labile Ligand: Synthesis and X-Ray Structural Characterization of $[(C_{23}H_{30}O_2)V(O)Cl]$

**Paul J. Toscano,*[a] E. James Schermerhorn,[a] Claudia Dettelbacher,[a] Deborah Macherone[a] and Jon Zubieta[a,b]**

[a] *Department of Chemistry, State University of New York at Albany, Albany, NY 12222, USA*
[b] *Current address: Department of Chemistry, Syracuse University, Syracuse, NY 13244, USA*

The reaction of $VOCl_3$ with bulky biphenolic compounds ($H_2L$) provides dark brown complexes of formula, [V(O)(L)Cl]; X-ray diffraction studies revealed that the complex for which L = 2,2′-$CH_2$(4-Me,6-$Bu^tC_6H_2O)_2$ is monomeric in the solid state with approximate tetrahedral geometry about the V atom.

Recently, vanadyl alkoxides and aryloxides have become the objects of increased study. Part of this activity stems from the discovery of vanadate-induced inhibition or stimulation of enzymes involved in phosphorylation.[1,2] In addition, these V complexes are of interest as catalysts for polymerization,[2] oxidation[2] and potential shape-selective transformations.[3]

As part of our investigations aimed at controlling the nuclearity of earlier transition metal complexes by attenuating the steric size of the ancillary ligand set, we have prepared $V^V$ complexes of the type [V(O)(L)Cl], where $H_2L$ is either 2,2′-$CH_2(4\text{-Me},6\text{-}Bu^tC_6H_2OH)_2$ ($H_2$ultra) or 2,2′-MeCH$(4,6\text{-}Bu^t_2C_6H_2OH)_2$ ($H_2$iso). Herein, we also report the molecular structure of the complex [V(O)(ultra)Cl].[†]

When $VOCl_3$ is added to a toluene solution of $H_2L$ under nitrogen at ambient temperature, the reaction mixture immediately turns deep purple. Upon heating under reflux overnight, HCl is evolved and a deep brown solution results, from which dark brown-black microcrystalline [V(O)(L)Cl] (L = ultra, **1a**; L = iso, **1b**) could be obtained in 75–80% isolated yield.[‡] The solution $^1H$ and $^{13}C$ NMR spectra of **1a** and **1b** exhibit a pattern of resonances consistent with the formation of a single [V(O)(L)Cl] isomer having $C_s$ symmetry.[‡] The V=O stretch for **1a** occurs at 1003 $cm^{-1}$.

The eight-membered chelate ring of **1a** (Fig. 1) adopts a flattened boat conformation (Fig. 2), similar to that found in $[Ti(ultra)X_2]$ (X = Cl[4,5] or Me[5]), $[V(ultra)Cl(thf)_2]$ **2**,[6] and $[M(ultra)(BH_4)_2]$ [M = Ti, Zr(thf); thf = tetrahydrofuran].[7] The oxo group of **1a** occupies the coordination site in the partial cavity formed by the aryl rings, while the Cl ligand is synclinal to C(7) of the ring. The V(1)–O(3) and V(1)–Cl(1) bonds of **1a** are significantly shorter (*ca.* 0.10 and 0.09 Å, respectively) than those determined previously in **2**.[6] These results are in accord with the higher formal oxidation state in the present case ($V^V$ for **1a** *vs.* $V^{III}$ for **2**).

[V(O)(L)Cl]
**1a**; L = ultra
**b**; L = iso
$[V(ultra)Cl(thf)_2]$
**2**
$[V(O)(L)(CH_2SiMe_3)]$
**3a**; L = ultra
**b**; L = iso
ultra = 2,2′-$CH_2(4\text{-Me},6\text{-}Bu^tC_6H_2O^-)$
iso = 2,2′-$CH_2(4,6\text{-}Bu^t_2C_6H_2O^-)$

Importantly, the crystal structure of **1a** consists of *discrete* monomers;[8] there are no *inter*molecular contacts within 3 Å. The geometry about the V atom is essentially tetrahedral with the angles of the inner coordination sphere varying from 106.9(2) to 112.9(1)°. The present results contrast sharply with those for previously determined structures of vanadium(v) oxo alkoxo complexes. The compound $[V(O)(OMe)_3]$[9] is dimeric in the solid state, with the geometry about each V atom being approximately tetragonal pyramidal; in addition, a weak interaction occurs for each V atom with an alkoxide oxygen of a neighbouring dimer.[9] The recently reported[10] $[V(O)(Cl)(\mu\text{-pinacolato})]_2$ is also dimeric with distorted trigonal bipyramidal geometry about each V atom. For $[V(O)(OCH_2CH_2Cl)_3]$,[2] the environment at each V atom is approximately trigonal bipyramidal owing to intermolecular bonding interactions [2.261(2) Å] between symmetry-related

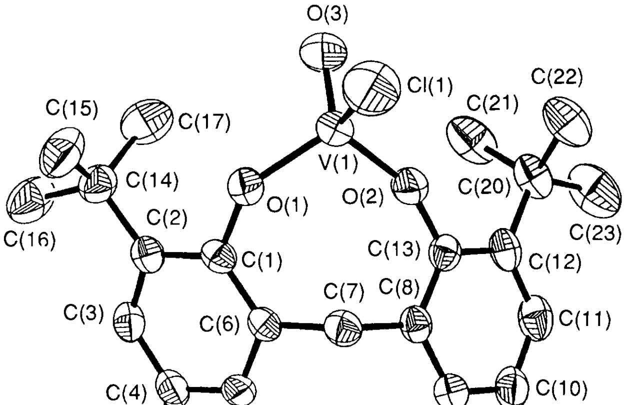

**Fig. 1** ORTEP view of the structure of [V(O)(ultra)Cl] **1a** with the atom-labelling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): V(1)–Cl(1) 2.199(2); V(1)–O(1) 1.752(4); V(1)–O(2) 1.734(3); V(1)–O(3) 1.571(4); Cl(1)–V(1)–O(1) 112.9(1); Cl(1)–V(1)–O(2) 110.6(1); O(1)–V(1)–O(2) 106.9(2); Cl(1)–V(1)–O(3) 108.0(2); O(1)–V(1)–O(3) 109.7(2); O(2)–V(1)–O(3) 108.7(2); V(1)–O(1)–C(1) 141.8(3); V(1)–O(2)–C(13) 153.7(3).

---

[†] *Crystal data*: **1a**, $C_{23}H_{30}ClO_3V$, triclinic, space group $P\bar{1}$, $a$ = 9.286(4), $b$ = 9.745(3), $c$ = 12.911(9) Å, $\alpha$ = 93.89(4), $\beta$ = 90.26(5), $\gamma$ = 95.16(3)°, $U$ = 1160.9(4) Å$^3$, $Z$ = 2, $D_c$ = 1.26 g $cm^{-3}$. Structure solution and refinement based upon 1954 reflections with $F_o \geqslant 6.0\,\sigma(F_o)$ (Mo-K$\alpha$; $\lambda$ = 0.71073 Å) converged at a conventional $R$ factor of 0.0453. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

[‡] *Spectroscopic data*: **1a**, $^1H$ NMR ($C_6D_6$, rel. to $Me_4Si$): $\delta$ 6.84 (br s, 2H, Ph), 6.80 (br s, 2H, Ph), 4.78 (d, 1H, $CH_2$, $^2J_{H\text{-}H}$ 14.5 Hz), 3.22 (d, 1H, $CH_2$, $^2J_{H\text{-}H}$ 14.5 Hz), 2.01 (s, 6H, ArMe) and 1.40 (s, 18H, $CMe_3$); $^{13}C$ NMR ($C_6D_6$, rel. to $Me_4Si$): $\delta$ 171.51, 140.43, 138.25, 136.54, 128.87, 126.07, 35.44, 34.53, 30.43 and 21.25.

**1b**, $^1H$ NMR ($C_6D_6$): $\delta$ 7.51 (d, 2H, Ph), 7.26 (d, 2H, Ph), 5.25 (q, 1H, CH), 1.46 (d, 3H, CH*Me*), 1.43 (s, 18H, $CMe_3$) and 1.21 (s, 18H, $CMe_3$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 170.45, 149.55, 143.87, 137.61, 121.98, 121.51, 35.83, 35.10, 34.24, 31.36, 30.55 and 20.74.

**3a**, $^1H$ NMR ($C_6D_6$): $\delta$ 7.06 (br d, 2H, Ph), 6.95 (br d, 2H, Ph), 4.71 (d, 1H, $Ar_2CH_2$, $^2J_{H\text{-}H}$ 14.1 Hz), 3.63 (d, 1H, $Ar_2CH_2$, $^2J_{H\text{-}H}$ 14.1 Hz), 3.24 (br s, $\nu_{1/2}$ 11.4 Hz, 3H, $VCH_2$), 2.10 (s, 6H, ArMe), 1.48 (s, 18H, $CMe_3$) and 0.35 (s, 9H, SiMe); $^{13}C$ NMR($C_6D_6$): $\delta$ 164.48, 138.10, 134.05, 133.80, 128.84, 126.30, *ca.* 87.0 (v br, V–$CH_2$), 35.31, 34.27, 30.37, 21.19 and 1.00.

**3b**, $^1H$ NMR ($C_6D_6$): $\delta$ 7.69 (d, 2H, Ph), 7.32 (d, 2H, Ph), 5.26 (q, 1H, CH), 3.40 (br s, $\nu_{1/2}$ 8.5 Hz, 3H, $VCH_2$), 1.74 (d, 3H, CH*Me*), 1.52 (s, 18H, $CMe_3$), 1.29 (s, 18H, $CMe_3$) and 0.34 (s, 9H, SiMe); $^{13}C$ NMR ($C_6D_6$): $\delta$ 163.65, 146.88, 137.67, 137.36, 122.01, 121.49, *ca.* 89.0 (v br, V–$CH_2$), 35.73, 34.93, 33.46, 31.60, 30.46, 22.18 and 0.99.

Satisfactory elemental analyses were obtained for **1a** and **3a**.

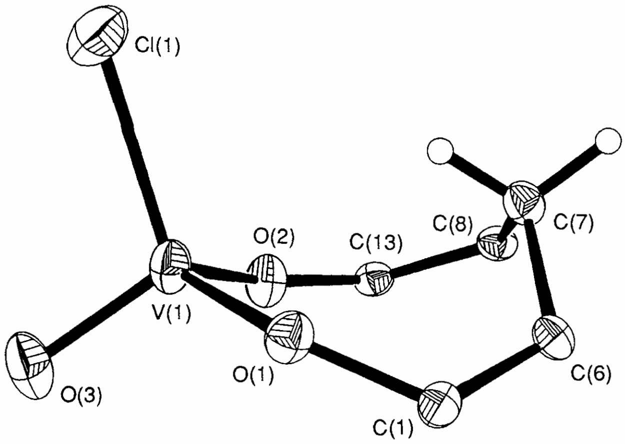

**Fig. 2** View of the conformation of the eight-membered ring of **1a**

molecules of neighbouring unit cells.[2] The monomeric tetrahedral nature of **1a** is probably attained because of the presence of the bulky Bu$^t$ groups at the 6,6′-positions of the diphenolic chelate, which presumably precludes dimerization and intermolecular associations. The dimeric structure of $[V(2,6\text{-}Me_2C_6H_3O)_2(4\text{-}MeC_6H_4N)Cl]$,[11] which contains sterically less demanding Me groups at the 2- and 6-positions of the phenolate ligands, further supports this hypothesis.

The Cl ligand of complexes **1a** and **1b** can be metathesized readily with $Me_3SiCH_2MgCl$ in diethyl ether to provide the orange-brown organometallic complexes, $[V(O)(L)(CH_2SiMe_3)]$ **3a** and **3b**‡ in 65–80% yields. Attempts to substitute the Cl group with MeMgI, MeLi and PhMgBr led to apparent reduction of the V centre. The $^1$H and $^{13}$C NMR spectra of complexes **3a** and **3b** clearly demonstrate the presence of the σ-bonded $CH_2SiMe_3$ ligand[11-15] and are otherwise similar to the spectra of **1a** and **1b**, respectively.‡ This suggests again that only one of two configurational isomers with $C_s$ symmetry is isolated in each instance.

We thank the State University of New York Faculty Research Award Program (to P. J. T.) and the National Science Foundation (Grant CHE-8815299 to J. Z.) for their generous support. We also thank Borg-Warner Chemicals and Schenectady Chemicals, Inc. for their kind supply of $H_2$ultra and $H_2$iso, respectively.

*Received, 11th February 1991; Com. 1/00632K*

## References

1 D. C. Crans and S. M. Schelble, *Biochemistry*, 1990, **29**, 6698 and references therein.
2 W. Priebsch and D. Rehder, *Inorg. Chem.*, 1990, **29**, 3013 and references therein.
3 G. E. Hofmeister, E. Alvarado, J. A. Leary, D. I. Yoon and S. F. Pedersen, *J. Am. Chem. Soc.*, 1990, **112**, 8843.
4 E. Barren, P. J. Toscano, S. Liu and J. Zubieta, unpublished results.
5 C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa and C. Guastini, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 66.
6 M. Mazzanti, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1989, 1793.
7 F. Corazza, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1991, **30**, 145.
8 H. W. Roesky, F. Schrumpf and M. Noltemeyer, *Z. Naturforsch., Teil B*, 1989, **44**, 35.
9 C. N. Caughlin, H. M. Smith and K. Watenpaugh, *Inorg. Chem.*, 1966, **12**, 2131.
10 D. C. Crans, R. A. Felty and M. M. Miller, *J. Am. Chem. Soc.*, 1991, **113**, 265.
11 D. D. Devore, J. D. Lichtenhan, F. Takusagawa and E. A. Maatta, *J. Am. Chem. Soc.*, 1987, **109**, 7408.
12 W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1972, 533.
13 F. Preuss and L. Ogger, *Z. Naturforsch., Teil B*, 1982, **37**, 957.
14 F. Preuss and H. Becker, *Z. Naturforsch., Teil B*, 1986, **41**, 185.
15 J. de With, A. D. Horton and A. G. Orpen, *Organometallics*, 1990, **9**, 2207.