# Vanadium complexes containing the 2,4,6-tris(trifluoromethyl)phenyl ('fluoromes') ligand

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**Treatment of [$VCl_3(thf)_3$] (thf = tetrahydrofuran) with Li[$C_6H_2(CF_3)_3$-2,4,6] affords the first early transition-metal complexes containing the σ-bonded fluoromes ligand; the molecular structures of [V{$C_6H_2(CF_3)_3$-2,4,6}$_2$Cl(thf)] 1 and [V{$C_6H_2(CF_3)_3$-2,4,6}$_3$OLi(thf)$_3$] 2 are described.**

In recent years, there has been considerable and growing interest in the bulky, highly electron-withdrawing 2,4,6-tris-(trifluoromethyl)phenyl ('fluoromes') ligand for its ability to stabilise low-valent, low-coordinate main-group compounds, recent examples of which include compounds of Ga,[1] Sn,[2] Pb,[3] and Bi.[4] By contrast, transition-metal compounds containing this ligand remain rare, presently being restricted to $d^{10}$ species such as [M{$C_6H_2(CF_3)_3$-2,4,6}$_2$] (M = Zn,[5] Hg[6]) and [Cu{$C_6H_2(CF_3)_3$-2,4,6}],[6] the homoleptic Ni and Co complexes [M{$C_6H_2(CF_3)_3$-2,4,6}$_2$][7] and recently a series of lead(II) derivatives.[8] To date there have been no examples reported of early transition-metal complexes containing the fluoromes ligand. Here, we describe the synthesis† and molecular structures of two novel vanadium complexes which exhibit multiple intramolecular V···F interactions.

Slow addition of a cold solution of Li[$C_6H_2(CF_3)_3$-2,4,6] (3 equiv.) in diethyl ether to [$VCl_3(thf)_3$] at −78 °C, followed by warming to 25 °C for 4–5 h, afforded a green solution from which paramagnetic green needles of **1** were isolated in 48% yield after recrystallisation from pentane. The EPR spectrum of solid **1** at room temperature consists of an isotopic signal with $g$ = 2.0. The molecular structure† of **1** revealed that two chloride ligands had been replaced by fluoromes groups to give a mononuclear thf adduct (Fig. 1). Two weak V···F interactions [2.306(2), 2.378(2) Å] contribute to an overall pseudo-octahedral geometry at the vanadium centre with mutually *cis* $C_6H_2(CF_3)_3$-2,4,6 [C(1)–V–C(10) 128.70(15)°]. The V–C bond distances [2.145(4), 2.159(4) Å] are longer than those found in the protio-mesityl complexes [V(mes)$_3$·thf] [2.099(6)–2.116(7) Å][9] (mes = $C_6H_2Me_3$-2,4,6) and [V(mes)$_4$] [2.071(6)–2.095(7) Å],[10] most probably due to a combination of the larger size of the fluoromes group and its capacity to enforce an increased coordination number through M···F interactions.

It was of some interest to establish whether or not the remaining chloro group in **1** could be replaced by a fluoromes ligand. Therefore, in a simple extension of the reaction described above, excess Li[$C_6H_2(CH_3)_3$-2,4,6] (*ca.* 3.5 equiv.) was added to [$VCl_3(thf)_3$] in diethyl ether at −78 °C. This resulted in a blue solution from which X-ray quality turquoise hexagons could be isolated. The crystal structure‡ shown in Fig. 2 reveals that three fluoromes ligands are now attached to the vanadium centre plus a linear oxo bridge to a lithium atom attended by three thf groups. The oxo group is believed to arise by abstraction from the ether solvent. Each of the fluoromes groups possesses a close V···F contact [2.668(4) Å]. If these are considered to occupy distinct coordination sites, the structure is best described as a mono-capped octahedron with crystallographic $C_{3v}$ symmetry about the V–O bond. The noncapped face comprises the three V–C bonds [2.179(4) Å] of the fluoromes groups whose aromatic rings are tilted in a propeller-like fashion by 44° to the $C_3$ axis. Complexes of vanadium(IV) normally contain the ($VO^{2+}$) ion,[11] and in such compounds the V=O bonds are much shorter (1.55–1.68 Å) than that observed in **2** [V–O(1) 1.835(3) Å]. Consistent with this, there is no strong V=O stretching band in the IR spectrum between 950 and

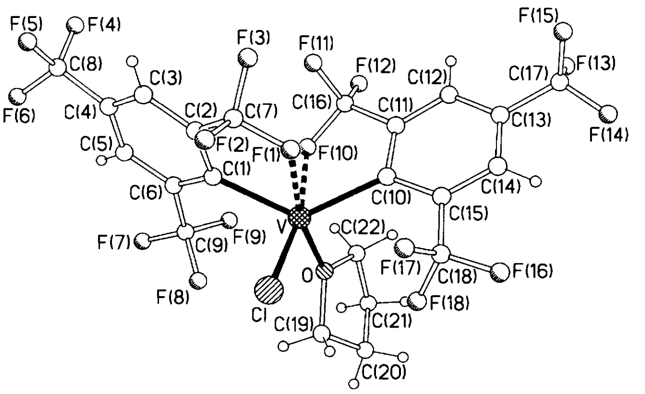

**Fig. 1** Molecular structure of **1** showing V···F interactions. The minor disorder component is omitted. Selected dimensions (Å and °): V–Cl 2.2310(13), V–O 2.013(3), V–C(1) 2.145(4), V–C(10) 2.159(4), V···F(1) 2.306(2), V···F(10) 2.378(2); C(1)–V–C(10) 128.70(15), Cl–V–O 96.72(9), F(1)···V···F(10) 95.63(9).

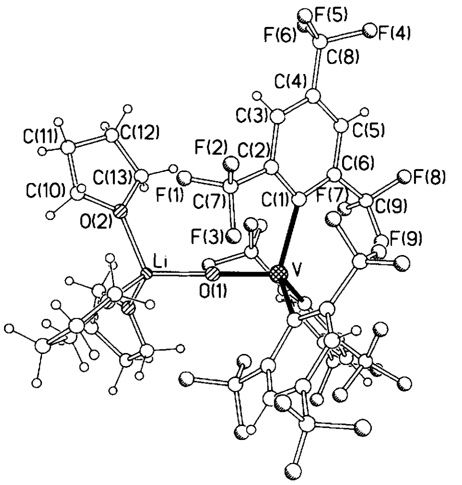

**Fig. 2** Molecular structure of **2** showing the labelling of the unique atoms. The minor disorder component is omitted. Selected dimensions (Å and °): V–O(1) 1.835(3), V–C(1) 2.179(4), Li–O(1) 1.856(11), Li–O(2) 1.939(5), V···F(3) 2.668(4); O(1)–V–C(1) 105.46(9), C(1)–V–C(1′) 113.16(8), O(1)–Li–O(2) 113.7(3), O(2)–Li–O(2′) 104.9(3), V–O(1)–Li 180.0.

1000 cm$^{-1}$. The $^1$H NMR spectrum of **2** is broad and uninformative and samples of **2** are EPR silent, both in the solid state and in toluene solution, at room temperature and frozen at 77 K. EPR silent vanadium(IV) species, though rare, have literature precedent.[12] The magnetic moment (Evans balance) of solid **2** (2.0 $\mu_B$) is higher than the spin-only value, a feature observed in other fluorinated derivatives of V$^{IV}$.[13]

The influence of the bulky, electron-withdrawing fluoromes ligand on the reactivity of these and related complexes will form a focus of interest for future studies.

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## Footnotes

† Satisfactory elemental analyses have been obtained for compounds **1** and **2**.

‡ *Crystal data*: **1**; $C_{22}H_{12}ClF_{18}OV$, $M$ = 720.7, monoclinic, space group $P2_1/c$, $a$ = 16.531(2), $b$ = 8.8360(10), $c$ = 17.711(2) Å, $\beta$ = 102.424(3)°, $U$ = 2526.5(5) Å$^3$, $Z$ = 4, $D_c$ = 1.895 g cm$^{-3}$, $F(000)$ = 1416, $\mu$(Mo-K$\alpha$) = 0.65 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 160 K. 12564 reflections measured on a Siemens SMART CCD area-detector diffractometer yielded 4453 unique data ($2\theta_{max}$ = 50°, $R_{int}$ = 0.062, semi-empirical absorption corrections). The structure was solved by direct methods and refined by full-matrix least-squares methods on $F^2$ with statistical weighting, anisotropic displacement parameters, constrained isotropic H atoms, and two-fold rotational disorder in one $CF_3$ group, to give $R' = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$ = 0.117 on all data, conventional $R$ = 0.055 on $F$ values of 3410 reflections having $F_o{}^2 > 2\sigma(F_o{}^2)$, goodness of fit $S$ = 1.207 for all $F^2$ values and 417 refined parameters. Final difference map features were within ±0.36 e Å$^{-3}$. Programs: Siemens SMART and SAINT control and integration software, Siemens SHELXTL and local programs.

**2**, $C_{39}H_{30}F_{27}LiO_4V$, $M$ = 1133.5, trigonal, space group $P3c1$, $a$ = $b$ = 15.4005(14), $c$ = 22.559(5) Å, $U$ = 4633.6(12) Å$^3$, $Z$ = 4, $D_c$ = 1.625 g cm$^{-3}$, $F(000)$ = 2260, $\mu$(Mo-K$\alpha$) = 0.36 mm$^{-1}$, $\lambda$ = 0.71073 Å, $T$ = 160 K. 2941 reflections measured on a Stoe-Siemens four-circle diffractometer yielded 2736 unique data ($2\theta_{max}$ = 50°, $R_{int}$ = 0.057, no absorption correction). Structure solution and refinement were as for **1** with one disordered $CF_3$ group; $R'$ = 0.171 on all data, conventional $R$ = 0.057 (1901 reflections), goodness of fit $S$ = 1.067 (248 parameters). Final difference map features were within ±0.68 e Å$^{-3}$. Programs: Stoe DIF4 control software, Siemens SHELXTL and local programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/204.

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