

# Synthesis of protonated carboxylato and trifluoromethanesulfonato derivatives of vanadium(II) by redox reactions on bis(mesitylene)-vanadium(0) †

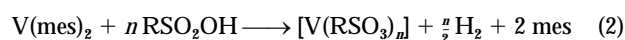
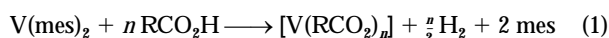
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Bis(mesitylene)vanadium(0),  $V(\text{mes})_2$ , underwent a two-electron redox process in heptane with  $\text{CF}_3\text{SO}_3\text{H}$  affording the vanadium(II) derivative  $[V(\text{CF}_3\text{SO}_3)_2(\text{CF}_3\text{SO}_3\text{H})]$ , an example of a co-ordination compound containing both the acid and its conjugated base in its composition. The vanadium(0) complex and  $\text{CF}_3\text{CO}_2\text{H}$  gave a product resulting from a one-electron transfer process, namely  $[V(\text{mes})_2][\text{CF}_3\text{CO}_2]$ . This compound, which dissolves unchanged in neat  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO})_2\text{O}$ , evolves to the vanadium(II) derivative  $[\text{H}(\text{thf})_n][V(\text{CF}_3\text{CO}_2)_3]$  ( $\text{thf}$  = tetrahydrofuran) by addition of tetrahydrofuran. Deprotonation of the vanadium(II) complexes occurs in the presence of  $\text{thf}$  or heterocyclic nitrogen bases to form the ionic derivatives  $[\text{HB}][\text{VA}_3]$ ,  $\text{B}$  =  $\text{thf}$  or a heterocyclic nitrogen base;  $\text{A}$  =  $\text{CF}_3\text{SO}_3$  or  $\text{CF}_3\text{CO}_2$ . The trifluoroacetato derivative  $[\text{H}(\text{thf})_n][V(\text{CF}_3\text{CO}_2)_3]$  undergoes methylation with  $\text{CH}_2\text{N}_2$  to the vanadium(II) ester adduct  $[V(\text{CF}_3\text{CO}_2)_2(\text{CF}_3\text{CO}_2\text{CH}_3)]$ , and is oxidized to the vanadium(III) trifluoroacetato derivatives  $[V(\text{CF}_3\text{CO}_2)_3]$  and  $[V(\text{CF}_3\text{CO}_2)_2\text{C}_{14}\text{H}_8\text{O}_2]$  by benzoyl peroxide (or dioxygen) and 9,10-phenanthrene-1,10-dione, respectively.

Vanadium(II), of electronic configuration  $3d^3$  and isoelectronic with chromium(III), is currently extensively studied and synthetic routes to vanadium(II) complexes have recently been reviewed.<sup>1</sup>

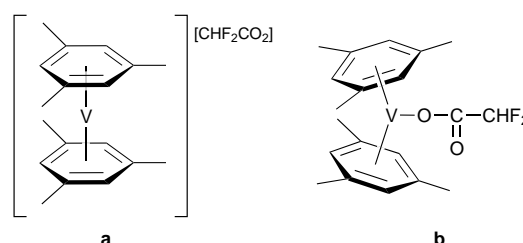
Some of us have recently shown that vanadium(II) halides of general formula  $VX_2(\text{dme})_n$  ( $\text{dme}$  = 1,2-dimethoxyethane;  $X$  =  $\text{Cl}$ ,  $n = 1,1$ ;<sup>2</sup>  $X$  =  $\text{Br}$  or  $\text{I}$ ,  $n = 2,3$ ) can be obtained by oxidation of bis(mesitylene)vanadium(0),  $V(\text{mes})_2$ , with triphenylmethyl halides in  $\text{dme}$ . As an extension of these results, we thus believed that the reaction of  $V(\text{mes})_2$  with carboxylic or sulfonic acids could in principle lead to the corresponding vanadium(II) [or vanadium(III)] derivatives in the absence of difficult to handle by-products, see equations (1) and (2). The paper shows that the



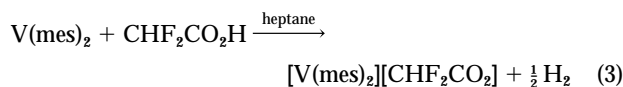
electron transfer reactions represented by equations (1) and (2) do in fact occur leading to vanadium(II) derivatives. However, under strictly anhydrous conditions, 2 equivalents of the acid are used in the reaction and a third one protonates the resulting vanadium(II) compound. Isolation and reactivity of this relatively new class of compounds is reported in this paper.

## Results and Discussion

The reaction of  $V(\text{mes})_2$  with the relatively strong fluorine-substituted carboxylic acids  $[\text{CHF}_2\text{CO}_2\text{H}$ ,  $\text{p}K_a = 1.45$ ,<sup>4</sup>  $1.34$ ;<sup>5</sup>  $\text{CF}_3\text{CO}_2\text{H}$ ,  $\text{p}K_a = 0.49$ ,<sup>5</sup>  $0.23$ ]<sup>6</sup> has been studied in heptane as a medium. The compound  $V(\text{mes})_2$  reacts at room temperature with  $\text{CHF}_2\text{CO}_2\text{H}$  in heptane, even in an excess of acid, with evolution of approximately 0.5 mol of  $\text{H}_2$  per mol of vanadium (as determined by gas-volumetric measurements), forming the dark orange vanadium(I) derivative  $[V(\text{mes})_2][\text{CHF}_2\text{CO}_2]$ , equation (3). The resulting substantially insoluble solid shows a



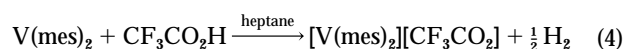
**Fig. 1** Possible structures for  $[V(\text{mes})_2][\text{CHF}_2\text{CO}_2]$ . The ionic possibility **a** is proposed on the basis of the structure of  $[V(\text{mes})_2][\text{AlCl}_4]$ .<sup>10</sup> The possibility **b** takes into consideration a covalent interaction of a carboxylato group with the vanadium(I) centre, see text



magnetic moment,  $\mu_{\text{eff}}$ , of  $2.59 \mu_B$  ( $\mu_B \approx 9.274 \times 10^{-24} \text{ J T}^{-1}$ ) corresponding to two unpaired electrons at the vanadium(I) centre. This is in agreement with the magnetic susceptibility data reported earlier for  $[V(\text{mes})_2][\text{AlCl}_4]$ .<sup>7</sup> Owing to the fact that  $V(\text{mes})_2$  has a magnetic moment of  $1.70 \mu_B$ ,<sup>8</sup> the magnetic data found for the  $[V(\text{mes})_2]^+$  cation may be rationalized with an energy inversion of the highest occupied molecular orbitals (HOMO), in agreement with EPR experiments.<sup>9</sup>

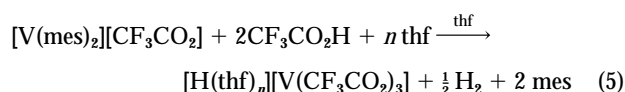
The low solubility of  $[V(\text{mes})_2][\text{CHF}_2\text{CO}_2]$  in non-polar solvents suggests the ionic structure **a** (Fig. 1) for this compound. The alternative possibility of structure **b** is unlikely due to the well established reluctance<sup>11</sup> of vanadium(I) to attain seven-coordination.

A similar product with comparable properties [ $\mu_{\text{eff}}$  (292 K) =  $2.73 \mu_B$ ] was obtained by reacting  $V(\text{mes})_2$  with  $\text{CF}_3\text{CO}_2\text{H}$  in a hydrocarbon medium (heptane or toluene); the use of an excess of acid does not influence the course of the reaction. The compound, identified as  $[V(\text{mes})_2][\text{CF}_3\text{CO}_2]$ , see equation (4), is

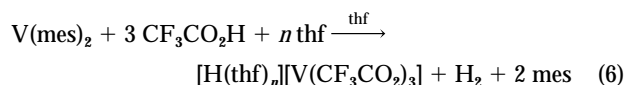


† In memoriam Professor Sir Geoffrey Wilkinson.

stable in tetrahydrofuran (thf) in the absence of free  $\text{CF}_3\text{CO}_2\text{H}$  and reacts with 2 equivalents of  $\text{CF}_3\text{CO}_2\text{H}$  in thf affording the brown vanadium(II) compound  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  [see equation (5)].

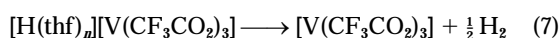


The oxidation of  $\text{V}(\text{mes})_2$  to vanadium(II) with  $\text{CF}_3\text{CO}_2\text{H}$  can be carried out in a single-step reaction of the zerovalent vanadium derivative by using 3 equivalents of  $\text{CF}_3\text{CO}_2\text{H}$  in thf, see equation (6) [as the sum of equations (4) and (5)]. The thf-



soluble brown derivative  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  was isolated by addition of heptane after evaporation of the volatile products (thf and trifluoroacetic anhydride). The product was characterized by analytical, spectroscopic and magnetic data: the magnetic moment at 294 K ( $3.78 \mu_B$ , see Experimental section) is in agreement with the presence of a vanadium(II) centre of  $3d^3$  configuration. The deuterated analogue,  $[\text{D}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  was isolated from the reaction of  $\text{V}(\text{mes})_2$  with  $\text{CF}_3\text{CO}_2\text{D}-(\text{CF}_3\text{CO})_2\text{O}$ .

It is remarkable that  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$  is stable in neat  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO})_2\text{O}$  (orange-red solution) and that only addition of thf promotes the further electron transfer to  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$ . These results suggest that: (a)  $[\text{V}(\text{mes})_2]^+$  as the trifluoroacetato derivative is stable with respect to further electron transfer to  $\text{CF}_3\text{CO}_2\text{H}$ ; (b) if thf is present, the second electron transfer to vanadium(II) occurs, the driving force being presumably the protonation of thf by  $\text{CF}_3\text{CO}_2\text{H}$  in addition to substitution of the two  $\eta^6$  arene rings by  $\text{CF}_3\text{CO}_2^-$ ; (c) further oxidation to vanadium(III), see equation (7), is not a thermodynamically feasible process.

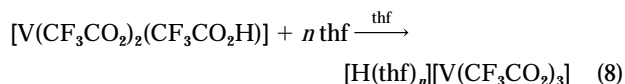


Dihydrogen was found to be a product of reaction (6); however, gas-volumetric measurements showed that the amount of evolved  $\text{H}_2$  ( $\text{H}_2$ -V molar ratio 0.3 : 1) is well below the expected amount ( $\text{H}_2$ -V molar ratio 1 : 1). A gas chromatographic mass spectrum (GC-MS) monitoring of the reaction showed that partial hydrogenation of mesitylene had occurred as evidenced by the peaks at  $m/z = 122$  ( $\text{C}_9\text{H}_{12} + 2\text{H}$ ) and 124 ( $\text{C}_9\text{H}_{12} + 2\text{D}$ ), the latter with  $\text{CF}_3\text{CO}_2\text{D}$ .

Although it has not been possible to grow single crystals of  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  to be used in an X-ray diffractometric study, a possible structure for this compound can be inferred on the basis of the spectroscopic and reactivity data (see below). A Nujol mull of  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  shows a broad absorption at  $3374 \text{ cm}^{-1}$  (which shifts to  $2556 \text{ cm}^{-1}$  on deuteration) assigned to an OH stretching vibration, and two strong absorptions due to the carboxylate ligand at  $1695$  and  $1463 \text{ cm}^{-1}$ ; as the  $\Delta\nu$  between the asymmetric and the symmetric stretching vibrations is  $232 \text{ cm}^{-1}$ , bidentate co-ordination of the carboxylate ligand is suggested.<sup>12</sup> Moreover, the presence of the absorption attributed to an OH stretching vibration indicates that we are probably dealing with protonated thf. Further support for the mononuclear nature of the  $[\text{V}(\text{CF}_3\text{CO}_2)_3]^-$  anion comes from the magnetic moment ( $\mu_{\text{eff}} = 3.78 \mu_B$ ) which is close to that expected ( $3.87 \mu_B$ ) for the spin-only contribution (bridging carboxylato groups in a system of higher complexity should cause a reduction of the magnetic moment due to spin-pairing through the  $\pi$  system of the bridging ligand).<sup>13</sup>

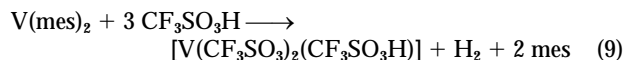
These results strongly suggest that the reaction of bis(mesitylene)vanadium(0) with  $\text{CF}_3\text{CO}_2\text{H}$  under strictly anhydrous

conditions is confined to the one-electron transfer to  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2\text{H}]$ , unless thf is present to carry out the electron- and proton-transfer to give  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$ . A logical precursor to the ionic thf-stabilized product of equation (6) could be the dicarboxylate-carboxylic derivative shown as the reagent of thf-induced deprotonation [equation (8)]. How-



ever, no evidence of such a product was obtained. This is in agreement with the paucity of literature data on complexes containing both co-ordinated carboxylic acid and carboxylate groups; to the best of our knowledge, only a few compounds of this class, namely  $[\text{MM}'(\mu\text{-O}_2\text{CCPh})_4(\text{PhCO}_2\text{H})_2]$  ( $\text{M} = \text{M}' = \text{Cr}^{14}$  or  $^{15} \text{Ru}$ ;  $\text{M} = \text{Cu}$ ,  $\text{M}' = \text{Ni}^{16}$ ),  $[\text{V}_3(\mu\text{-O})(\text{CH}_3\text{CO}_2)_6(\text{CH}_3\text{CO}_2\text{H})_2(\text{thf})]$ ,  $[\text{VCl}_4(\text{CH}_3\text{CO}_2\text{H})_2]$ ,<sup>17</sup>  $[\text{Ru}_2(\text{CH}_3\text{CO}_2)_4(\text{CH}_3\text{CO}_2)_2\text{-H}]\cdot 0.7 \text{ H}_2\text{O}$ ,<sup>18</sup>  $[\{\text{TiCl}_2(\text{O}_2\text{CR})(\text{RCO}_2\text{H})\}_2\text{O}]$  ( $\text{R} = \text{Et}^{19}$  or  $^{20}$ ) and  $[\text{Ti}_2\text{Cl}_7(\text{O}_2\text{CR})(\text{RCO}_2\text{H})]$  ( $\text{R} = p\text{-ClC}_6\text{H}_4$  or  $\text{CH}=\text{CHMe}^{21}$ ) have been fully characterized including crystal structure analyses. Moreover, the solvation of palladium acetate in  $\text{CF}_3\text{CO}_2\text{H}$  has been recently studied by *ab initio* quantum chemical calculations and by IR and  $^1\text{H}$  NMR spectroscopy and evidence has been collected for the formation of dicarboxylate-dicarboxylic species of general formula  $[\text{Pd}(\text{CH}_3\text{CO}_2)_2(\text{CF}_3\text{CO}_2\text{H})_2]_n$ .<sup>22</sup>

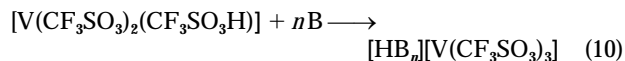
It was therefore worthwhile to further investigate these systems and extend the study to other acids. The reaction of  $\text{V}(\text{mes})_2$  with  $\text{CF}_3\text{SO}_3\text{H}$  (in the presence of the corresponding anhydride) was therefore also attempted. This reaction proceeds quickly even in heptane and, at variance to the reaction with  $\text{CF}_3\text{CO}_2\text{H}$  [see equation (3)], produces a paramagnetic ( $\mu_{\text{eff}} = 3.49 \mu_B$  at 294 K) green solid of composition  $[\text{V}(\text{CF}_3\text{SO}_3)_2(\text{CF}_3\text{SO}_3\text{H})]$ , according to equation (9). The magnetic



moment, the spectral ( $\tilde{\nu}_{\text{OH}} = 3187 \text{ cm}^{-1}$ ) and analytical data indicate that we are dealing with the expected adduct of trifluoromethanesulfonic acid with bis(trifluoromethanesulfonato)vanadium(II). The reaction could not be performed in thf due to the well known polymerization reaction of thf in the presence of  $\text{CF}_3\text{SO}_3\text{H}$ .<sup>23</sup>

The different reactivity of  $\text{V}(\text{mes})_2$  with  $\text{CF}_3\text{CO}_2\text{H}$  [equation (3)] with respect to  $\text{CF}_3\text{SO}_3\text{H}$  [equation (9)] agrees with the presumably lower O-H bond dissociation enthalpy in  $\text{CF}_3\text{SO}_3\text{H}$ .

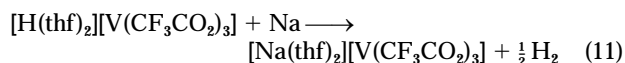
The acidic nature of  $[\text{V}(\text{CF}_3\text{SO}_3)_2(\text{CF}_3\text{SO}_3\text{H})]$  was demonstrated by its deprotonation in the presence of stoichiometric amounts of thf or pyridine [see equation (10) where  $\text{B} = \text{thf}$ ,



$n = 1.6$  or  $\text{B} = \text{pyridine}$ ,  $n = 2$ ]; the resulting ionic products were completely characterized by conventional methods, including magnetic susceptibility data.

### Reactivity of $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$

Our study has concentrated mostly on the trifluoroacetato complex; by reaction with sodium, dihydrogen was evolved with formation of the sodium derivative  $[\text{Na}(\text{thf})_2][\text{V}(\text{CF}_3\text{CO}_2)_3]$  [equation (11)].



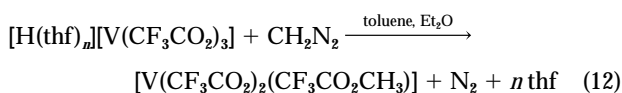
The nature of  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  as a thf-stabilized, trifluoroacetic-trifluoroacetato derivative of vanadium(II) has

**Table 1** The UV/VIS spectra of the heterocyclic nitrogen base derivatives of the  $[\text{V}(\text{CF}_3\text{CO}_2)_3]^-$  anion

HB	Colour <sup>a</sup>	Et <sub>2</sub> O		thf λ <sub>1</sub> <sup>b</sup> /nm
		λ <sub>1</sub> /nm (ε/M <sup>-1</sup> cm <sup>-1</sup> )	λ <sub>2</sub> /nm	
[H(thf) <sub>2</sub> ]	Yellow-brown	442 (1250)	<i>c</i>	455
[Hpy] <sub>2</sub>	Brick-red	435 (2111)	503 (898)	440
[HL <sup>1</sup> ] <sub>2</sub>	Dark-red	442 (1381)	550 (622)	442
[H <sub>2</sub> L <sup>2</sup> ] <sub>2</sub>	Green	437 (1189)	631 (964)	483
[H <sub>2</sub> L <sup>3</sup> ] <sub>2</sub>	Violet	480	527	455
[H <sub>2</sub> L <sup>4</sup> ] <sub>2</sub>	Blue	435	531	<i>i</i>

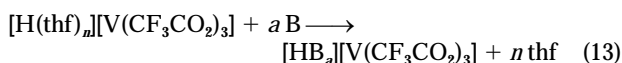
<sup>a</sup> In the solid state. <sup>b</sup> λ<sub>2</sub> not observed. <sup>c</sup> Not observed. <sup>d</sup> py = Pyridine. <sup>e</sup> L<sup>1</sup> = Quinoline. <sup>f</sup> L<sup>2</sup> = 2,2'-Bipyridyl. λ<sub>1</sub> = 462 nm for this compound in acetone. <sup>g</sup> L<sup>3</sup> = 4,4'-Bipyridyl. <sup>h</sup> L<sup>4</sup> = 1,10-Phenanthroline. <sup>i</sup> Not measured.

been confirmed by the reaction of a toluene suspension of  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  with diazomethane [equation (12)], the

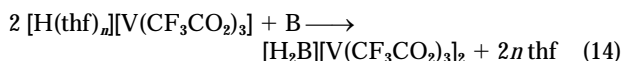


paramagnetic ( $\mu_{\text{eff}} = 3.69 \mu_{\text{B}}$  at 299 K) vanadium(II) compound,  $[\text{V}(\text{CF}_3\text{CO}_2)_2(\text{CF}_3\text{CO}_2\text{CH}_3)]$  was obtained in good yields. The IR spectrum shows two strong absorptions above 1600 cm<sup>-1</sup> assigned to the asymmetric stretching vibration of the trifluoroacetato group (1636 cm<sup>-1</sup>) and to the stretching vibration of the co-ordinated methyl trifluoroacetate (1674 cm<sup>-1</sup>). The CO stretching vibration is at 1792 cm<sup>-1</sup> in the unco-ordinated methyl trifluoroacetate.<sup>24</sup> Even though dinuclear derivatives of vanadium-containing esters as ligands are known,<sup>25</sup>  $[\text{V}(\text{CF}_3\text{CO}_2)_2(\text{CF}_3\text{CO}_2\text{CH}_3)]$  represents the first example of a compound containing a carboxylato group and the ester of the conjugated acid as ligands.

The reactions of  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  with heterocyclic nitrogen bases are fast [equations (13) B = pyridine, *a* = 2 or



B = quinoline, *a* = 1) and (14) (B = 2,2'-bipyridyl, 4,4'-bipyridyl

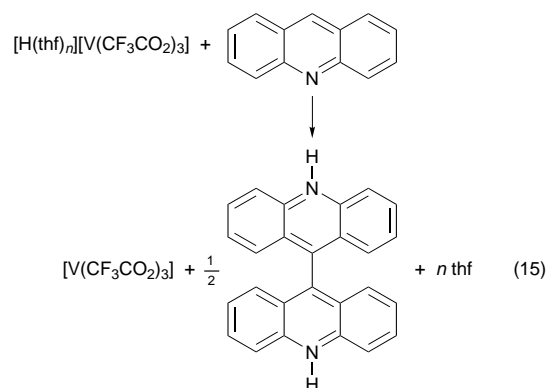


or 9,10-phenanthroline) and give vanadium(II) derivatives ( $\mu_{\text{eff}} = 3.63 \mu_{\text{B}}$  at 293 K for the pyridinium derivative) whose colours depend on the amine, changing from red (pyridine) to dark blue (1,10-phenanthroline).

The UV/VIS data, recorded in solvents of different relative permittivities ( $\epsilon_r$ ), are reported in Table 1. In the media of relatively high relative permittivity [thf ( $\epsilon_r = 7.58$ ) or acetone ( $\epsilon_r = 21.5$ )] only one absorption is observed while two bands are observed in Et<sub>2</sub>O ( $\epsilon_r = 4.35$ ). By taking into consideration that  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  has only one absorption between 300 and 700 nm both in thf and in Et<sub>2</sub>O, the band which disappears with increasing polarity of the solvent may be ascribed to a charge-transfer band within the protonated nitrogen base and the  $[\text{V}(\text{CF}_3\text{CO}_2)_3]^-$  anion. Similar charge-transfer bands with molar extinction coefficients ( $\epsilon$ ) lower than 1000 M<sup>-1</sup> cm<sup>-1</sup> have been observed when ion pairs of general formula D<sup>+</sup>A<sup>-</sup> (D<sup>+</sup> is the electron donor and A<sup>-</sup> is the electron acceptor) are considered.<sup>11a,26</sup> It is interesting to note that when the donor forms a stable complex with the acceptor *via* co-ordination, the complex shows very strong charge-transfer bands in the visible region, in contrast with the medium weak intensity observed for most of the outer-sphere complexes such as those reported in this paper.

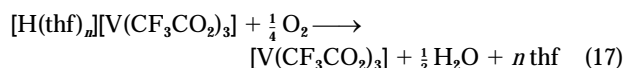
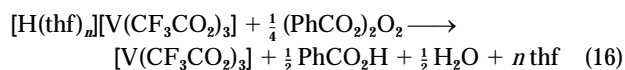
When acridine was used as the nitrogen base, a prompt redox

reaction was observed in heptane or thf, see equation (15)



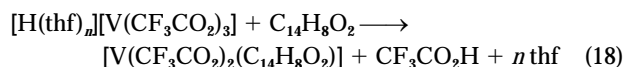
suggesting that the probable intermediate,  $[\text{HL}^5][\text{V}(\text{CF}_3\text{CO}_2)_3]$  (L<sup>5</sup> = acridine), undergoes the observed electron-transfer process, with reductive carbon-carbon coupling of acridine to 9,9',10,10'-tetrahydrobiacridyl and formation of  $[\text{V}(\text{CF}_3\text{CO}_2)_3]$ . A similar reaction was observed in the Na $[\text{V}(\text{CO})_6]$ -acridine-HCl system.<sup>27</sup>

Other oxidizing agents such as benzoyl peroxide, dioxygen and 9,10-phenanthrene-9,10-dione were also used. Benzoyl peroxide and dioxygen promptly react affording high yields of  $[\text{V}(\text{CF}_3\text{CO}_2)_3]$  according to equations (16) and (17).



The compound  $[\text{V}(\text{CF}_3\text{CO}_2)_3]$ , already reported in the literature<sup>28</sup> prepared by a different route, has IR absorptions at 1641 and 1418 cm<sup>-1</sup> due to the asymmetric and symmetric stretching vibrations of the carboxylic group. The separation between the bands suggests the ligands to be bidentate. Moreover, the magnetic moment of 2.55  $\mu_{\text{B}}$  at 295 K is in agreement with the spin-only value for a system of 3d<sup>2</sup> electronic configuration. Thus,  $[\text{V}(\text{CF}_3\text{CO}_2)_3]$  should be mononuclear.

The reaction of  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  with 9,10-phenanthrene-9,10-dione gives a semiquinone derivative of vanadium(III), with elimination of CF<sub>3</sub>CO<sub>2</sub>H [equation (18)]. The IR spectrum



shows a band of medium intensity at 1489 cm<sup>-1</sup> assigned to the C=O stretching vibration of a semiquinone group.<sup>28</sup> The magnetic moment of 1.89  $\mu_{\text{B}}$  (at 293 K) suggests a strong anti-ferromagnetic coupling between the semiquinone ligand and the vanadium(III) centre of 3d<sup>2</sup> configuration.<sup>29</sup>

## Conclusion

The reaction between V(mes)<sub>2</sub> and CF<sub>3</sub>CO<sub>2</sub>H in thf gives the  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  derivative; the formation of this compound suggests the intermediacy of  $[\text{V}(\text{CF}_3\text{CO}_2)_2(\text{CF}_3\text{CO}_2\text{H})]$ . A compound of this type has been isolated in the reaction of V(mes)<sub>2</sub> with CF<sub>3</sub>SO<sub>3</sub>H in heptane, namely  $[\text{V}(\text{CF}_3\text{SO}_3)_2(\text{CF}_3\text{SO}_3\text{H})]$ . On the basis of the results reported in this paper, it may be anticipated that other metal systems of the same type may be prepared once the following conditions are met: (a) the protonated complex does not undergo oxidation by the proton; (b) the acid should be strong enough to protonate the conjugate base; (c) the addition of the acid should cause the typical co-ordination number of the ion to be reached. Work is in progress in this direction.

## Experimental

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. Infrared spectra were measured with an FT-1725X instrument on solutions or Nujol and/or poly(chlorotrifluoroethylene) (PCTFE) mulls prepared under rigorous exclusion of moisture and air;  $^1\text{H}$  NMR spectra were measured with a Varian Gemini 200 instrument. Magnetic susceptibility measurements were performed with a Faraday balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as standard. Pascal contributions were used to calculate the diamagnetic correction.<sup>30</sup>

The compounds  $\text{V}(\text{mes})_2$ ,<sup>10</sup> and ethereal solutions of  $\text{CH}_2\text{N}_2$ ,<sup>31</sup> were prepared as described in the literature. The compounds  $\text{CHF}_2\text{CO}_2\text{H}$  (Aldrich),  $\text{CF}_3\text{CO}_2\text{H}$  (Carbo Erba, Milano),  $(\text{CF}_3\text{CO}_2)_2\text{O}$  (Aldrich),  $\text{CF}_3\text{SO}_3\text{H}$  (Aldrich),  $(\text{CF}_3\text{SO}_3)_2\text{O}$  (Aldrich) were used as received. Each of the acids  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{CF}_3\text{SO}_3\text{H}$  was treated with a given amount of the corresponding anhydride under reflux and the resulting mixture was used for the reaction with  $\text{V}(\text{mes})_2$ ; 9,10-phenanthrene-dione (Fluka) was purified by sublimation.

### Reactions of $\text{V}(\text{mes})_2$

**With difluoroacetic acid in heptane: preparation of  $[\text{V}(\text{mes})_2][\text{CHF}_2\text{CO}_2]$ .** A solution of  $\text{V}(\text{mes})_2$  (0.89 g, 3.05 mmol) in heptane (30  $\text{cm}^3$ ) was treated with  $\text{CHF}_2\text{CO}_2\text{H}$  (0.88 g, 9.16 mmol). Immediate reaction with formation of a sticky solid was observed. After decantation, the residue was washed several times with small portions of heptane and after prolonged drying *in vacuo* at room temperature an orange solid was obtained. It was identified as  $[\text{V}(\text{mes})_2][\text{CHF}_2\text{CO}_2]$  (0.66 g, 56% yield) (Found:  $\ddagger$  V, 12.3.  $\text{C}_{20}\text{H}_{25}\text{F}_2\text{O}_2\text{V}$  requires V, 13.2%).  $\tilde{\nu}_{\text{max}}(\text{cm}^{-1})$  (Nujol and PCTFE): 3016vw, 2960w, 2927mw, 2874vw, 1674vs, 1610vs, 1462s, 1333vs, 1131vs and 1077vs.  $\chi_{\text{m}}^{\text{corr}} = 2930 \times 10^{-6}$  cgsu; diamagnetic correction =  $-233 \times 10^{-6}$  cgsu (cgsu =  $4\pi \times 10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>);  $\mu_{\text{eff}}(294 \text{ K}) = 2.64 \mu_{\text{B}}$ .

A sample of  $[\text{V}(\text{mes})_2][\text{CHF}_2\text{CO}_2]$  was decomposed with dilute  $\text{HNO}_3$  and the aqueous phase was extracted with  $\text{CCl}_4$ . A  $^1\text{H}$  NMR spectrum of the organic phase showed the presence of mesitylene [ $\delta$  6.58 (s, 3 H) and 2.13 (s, 9 H)].

A gas-volumetric control was carried out with  $\text{V}(\text{mes})_2$  (1.15 mmol) and  $\text{CHF}_2\text{CO}_2\text{H}$  (1.15 mmol) in heptane (30  $\text{cm}^3$ ): at 20.5 °C  $\text{H}_2$  (0.56 mmol) corresponding to a  $\text{H}_2$ -V molar ratio of 0.49:1 was evolved.

**With trifluoroacetic acid in heptane: preparation of  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$ .** A solution of  $\text{V}(\text{mes})_2$  (2.504 g, 8.6 mmol) in heptane (75  $\text{cm}^3$ ) was treated with  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO}_2)_2\text{O}$  (2.4  $\text{cm}^3$ , 85:15, v/v) (2.96 g, 26.5 mmol of  $\text{CF}_3\text{CO}_2\text{H}$ ). Immediate reaction with formation of an orange solid was observed. The solid was filtered off, washed with heptane and dried *in vacuo* affording  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$  (2.414 g, 69%) (Found:  $\ddagger$  V, 12.8.  $\text{C}_{20}\text{H}_{24}\text{F}_3\text{O}_2\text{V}$  requires V, 12.6%).  $\tilde{\nu}_{\text{max}}(\text{cm}^{-1})$  (Nujol and PCTFE): 3121vw, 2963w, 2928mw, 1851mw, 1659vs, 1458s, 1207vs and 1158vs.  $\chi_{\text{m}}^{\text{corr}} = 3170 \times 10^{-6}$  cgsu; diamagnetic correction =  $-168 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}(292 \text{ K}) = 2.73 \mu_{\text{B}}$ .

A sample of  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$  was decomposed with dilute  $\text{HNO}_3$  and the aqueous layer was extracted with  $\text{CCl}_4$ . A  $^1\text{H}$  NMR spectrum of the organic phase showed the presence of mesitylene [ $\delta$  6.58 (s, 3 H) and 2.14 (s, 9 H)].

A sample of the substance was treated with thf: the red-orange solution thus obtained was maintained at room temperature for 12 h without apparent alteration.

A gas-volumetric control showed that the reaction of  $\text{V}(\text{mes})_2$  (7.6 mmol) with  $\text{CF}_3\text{CO}_2\text{H}$  (7.6 mmol) in heptane (30

$\text{cm}^3$ ) at 22 °C evolved  $\text{H}_2$  (3.72 mmol) corresponding to a  $\text{H}_2$ -V molar ratio of 0.49:1.

**In neat  $\text{CF}_3\text{CO}_2\text{H}/(\text{CF}_3\text{CO}_2)_2\text{O}$ : preparation of  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$ .** A solution of  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO}_2)_2\text{O}$  (5  $\text{cm}^3$ , 85:15, v/v) (55.3 mmol of  $\text{CF}_3\text{CO}_2\text{H}$ ) cooled at *ca.* -196 °C was treated with  $\text{V}(\text{mes})_2$  (0.983 g, 3.2 mmol). Gas evolution was observed during warming to room temperature. A sample of the orange-red solution (1  $\text{cm}^3$ ) was dried *in vacuo* at room temperature affording a heptane insoluble, orange solid which was identified as  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$  from its IR spectrum in PCTFE.

**In thf: preparation of  $[\text{H}(\text{thf})_{1.5}][\text{V}(\text{CF}_3\text{CO}_2)_3]$ .** A solution of  $\text{V}(\text{mes})_2$  (4.85 g, 16.6 mmol) in thf (100  $\text{cm}^3$ ) was treated with  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO}_2)_2\text{O}$  (4.5  $\text{cm}^3$ , 85:15, v/v) (49.6 mmol of  $\text{CF}_3\text{CO}_2\text{H}$ ). Reaction was observed with formation of a brown-red solution. After stirring for 48 h at room temperature and evaporation of the solvent under reduced pressure, the residue was suspended in heptane, the suspension was filtered and the solid was dried *in vacuo* at room temperature affording  $[\text{H}(\text{thf})_{1.5}][\text{V}(\text{CF}_3\text{CO}_2)_3]$  (7.45 g, 90%) as a brown solid sensitive to oxygen and moisture. The reaction was repeated several times and it was observed that the amount of thf retained by the solid varied depending on the drying procedure (Found: C, 27.8; H, 2.6; V, 9.2.  $\text{C}_{12}\text{H}_{13}\text{F}_9\text{O}_{7.5}\text{V}$  requires C, 28.9; H, 2.6; V, 10.2%).  $\tilde{\nu}_{\text{max}}(\text{cm}^{-1})$  (Nujol and PCTFE): 3374w, 2988ms, 2906ms, 1783w, 1695vs, 1650mw, 1463s, 1207vs, 1162vs, 1039s, 1019w and 858w.  $\chi_{\text{m}}^{\text{corr}} = 6040 \times 10^{-6}$  cgsu; diamagnetic correction =  $-232 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}(294 \text{ K}) = 3.78 \mu_{\text{B}}$ . The pH of a  $2.5 \times 10^{-3}$  M solution of the compound in degassed water was 3.

A gas-volumetric control showed the reaction of  $\text{V}(\text{mes})_2$  (1.93 mmol) with  $\text{CF}_3\text{CO}_2\text{H}$  (5.79 mmol) in thf (30  $\text{cm}^3$ ) at 24.3 °C to evolve  $\text{H}_2$  (0.54 mmol) corresponding to a  $\text{H}_2$ -V molar ratio of 0.28:1. The liquid medium, evaporated under reduced pressure, was examined by GC-MS and the following peaks were found: *m/z* 122 ( $\text{C}_9\text{H}_{12} + 2 \text{H}$ ); 120 ( $\text{C}_9\text{H}_{12}$ ); 107 ( $\text{C}_9\text{H}_{12} + 2 \text{H} - \text{CH}_3$ ) and 105 ( $\text{C}_9\text{H}_{12} - \text{CH}_3$ ).

The compound  $[\text{H}(\text{thf})_n][\text{V}(\text{CF}_3\text{CO}_2)_3]$  is stable in excess  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO}_2)_2\text{O}$  in the presence of thf. After 12 h at room temperature and 4 h at the boiling point of the mixture, the volatiles were removed *in vacuo* at room temperature and the brown solid residue was washed with heptane (3  $\times$  5  $\text{cm}^3$ ) and dried *in vacuo* affording unchanged  $[\text{H}(\text{thf})_2][\text{V}(\text{CF}_3\text{CO}_2)_3]$  (as determined by IR spectroscopy, elemental analysis and magnetic measurements).

In the reaction of  $\text{V}(\text{mes})_2$  (1.62 g, 5.6 mmol) with  $\text{CF}_3\text{CO}_2\text{D}$  (16.8 mmol) in thf (50  $\text{cm}^3$ ) at room temperature, a brown microcrystalline product  $[\text{D}(\text{thf})][\text{V}(\text{CF}_3\text{CO}_2)_3]$  was afforded (2.12 g, 82%) (Found: C, 24.9; H + D, 1.7; V, 11.1.  $\text{C}_{10}\text{H}_8\text{DF}_9\text{O}_7\text{V}$  requires C, 25.9; H + D, 2.2; V, 11.0%).  $\tilde{\nu}_{\text{max}}(\text{cm}^{-1})$  (Nujol and PCTFE): 2980s, 2917ms, 2556w, 1781w, 1699vs, 1650mw, 1460s, 1210vs, 1168vs and 1033ms. The reaction solvent, evaporated under reduced pressure, was examined by GC-MS and the following peaks were found: *m/z* 126 ( $\text{C}_9\text{H}_{12} + 3 \text{D}$ ); 124 ( $\text{C}_9\text{H}_{12} + 2 \text{D}$ ); 120 ( $\text{C}_9\text{H}_{12}$ ); 111 ( $\text{C}_9\text{H}_{12} + 3 \text{D} - \text{CH}_3$ ); 109 ( $\text{C}_9\text{H}_{12} + 2 \text{D} - \text{CH}_3$ ) and 105 ( $\text{C}_9\text{H}_{12} - \text{CH}_3$ ).

**Conversion of  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$  to vanadium(II).** A suspension of  $[\text{V}(\text{mes})_2][\text{CF}_3\text{CO}_2]$  (0.349 g, 0.86 mmol) in thf (30  $\text{cm}^3$ ) was treated with  $\text{CF}_3\text{CO}_2\text{H}-(\text{CF}_3\text{CO}_2)_2\text{O}$  (0.16  $\text{cm}^3$ , 85:15, v/v) (1.77 mmol of  $\text{CF}_3\text{CO}_2\text{H}$ ). Immediate solubilization of the vanadium(II) arene was observed. After 12 h stirring at room temperature, the solvent was evaporated under reduced pres-

$\ddagger$  Due to the extreme sensitivity to air, no reproducible C and H analyses were obtained for this compound.

$\S$  This value refers to the absorption shift upon H/D substitution (2556  $\text{cm}^{-1}$ , see above).

sure and the residue was suspended in heptane (25 cm<sup>3</sup>). The suspension was filtered, the solid was washed with heptane (2 × 20 cm<sup>3</sup>) and dried *in vacuo* at room temperature affording [H(thf)<sub>1.5</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.23 g, 51%) (determined by IR spectroscopy and elemental analysis).

**With trifluoromethanesulfonic acid.** A solution of V(mes)<sub>2</sub> (1.03 g, 3.53 mmol) in heptane (50 cm<sup>3</sup>) was treated with (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>O (0.98 cm<sup>3</sup>, 5% v/v) in CF<sub>3</sub>SO<sub>3</sub>H (10.5 mmol). Evolution of gas (H<sub>2</sub> by gas chromatography) and formation of a green solid was observed. The suspension was filtered and the solid was washed with heptane (5 × 3 cm<sup>3</sup>) and dried *in vacuo* at room temperature affording [V(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>H)]·0.2C<sub>7</sub>H<sub>16</sub> (1.65 g, 90%). The reaction was repeated several times and it was observed that the amount of heptane retained by the solid varied depending on the drying procedure (Found: C, 10.2; H, 0.4; V, 9.6. C<sub>4.4</sub>H<sub>4.2</sub>F<sub>9</sub>O<sub>9</sub>S<sub>3</sub>V requires C, 10.2; H, 0.8; V, 9.8%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3187w, 1651ms, 1235vs, 1049vs and 597vs.  $\chi_{\text{m}}^{\text{corr}} = 5050 \times 10^{-6}$  cgsu; diamagnetic correction =  $-168 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}$  (294 K) = 3.49  $\mu_{\text{B}}$ .

When a suspension of [V(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>H)] (0.53 g, 1.06 mmol) in heptane (30 cm<sup>3</sup>) was treated with thf (0.151 g, 2.1 mmol), [H(thf)<sub>1.6</sub>][V(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>] (0.545 g, 84%) was obtained as an oxygen and moisture-sensitive, green solid. The amount of thf retained by the solid varied depending on the drying procedure (Found: C, 17.5; H, 2.0; V, 7.7. C<sub>9.4</sub>H<sub>13.8</sub>F<sub>9</sub>O<sub>10.6</sub>S<sub>3</sub>V requires C, 18.4; H, 2.3; V, 8.3%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3187w, 1651ms, 1235vs, 1049vs and 597vs.  $\chi_{\text{m}}^{\text{corr}} = 4970 \times 10^{-6}$  cgsu; diamagnetic correction =  $-249.2 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}$  (294 K) = 3.46  $\mu_{\text{B}}$ .

**Reaction of [V(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>H)] with pyridine.** A suspension of [V(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>H)] (0.5 g, 1.00 mmol) in heptane (30 cm<sup>3</sup>) was treated with pyridine (0.16 g, 2 mmol). The colour of the suspension turned brown upon mixing the reagents and become brick-red after 48 h stirring at room temperature. The suspension was filtered, the solid was washed with heptane and dried *in vacuo* at room temperature affording [Hpy][V(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub>]·py (0.5 g, 76%) in the form of an oxygen- and moisture-sensitive brick-red solid (Found: C, 24.8; H, 1.6; N, 3.8; V, 7.0. C<sub>13</sub>H<sub>11</sub>F<sub>9</sub>N<sub>2</sub>O<sub>9</sub>S<sub>3</sub>V requires C, 23.7; H, 1.7; N, 4.3; V, 7.7%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3242mw, 3181mw, 3084mw, 1638w, 1621ms, 1541mw, 1283s, 1236vs, 1167ms, 1031vs and 759s.  $\chi_{\text{m}}^{\text{corr}} = 5550 \times 10^{-6}$  cgsu; diamagnetic correction =  $-266 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}$  (299 K) = 3.66  $\mu_{\text{B}}$ .

#### Reactivity of [H(thf)<sub>n</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>]

**With sodium.** A suspension of [H(thf)<sub>2</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.878 g, 1.64 mmol) in toluene (50 cm<sup>3</sup>) was treated at room temperature with finely divided sodium (0.07 g, 3.04 mmol). Evolution of gas (H<sub>2</sub> by gas chromatography) took place. After 12 h stirring at room temperature, the excess of sodium was filtered off and the deep brown solution was evaporated to *ca.* 10 cm<sup>3</sup>. Addition of heptane caused the formation of a microcrystalline brown solid which was filtered off, washed with heptane and dried *in vacuo* at room temperature affording [Na(thf)<sub>2</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.716 g, 78%) (the thf content of the solid depends on the drying procedure) as a brown solid promptly decomposed by oxygen and moisture (Found: Na, 4.4; V, 8.4. C<sub>14</sub>H<sub>16</sub>F<sub>9</sub>NaO<sub>8</sub>V requires Na, 4.1; V, 9.1%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (PCTFE): 2980mw, 2907mw, 1693vs, 1463ms, 1201vs, 1165vs, 1039s, 1024w and 855w.

**With diazomethane.** A suspension of [H(thf)<sub>2</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.51 g, 0.95 mmol) in toluene (50 cm<sup>3</sup>) was treated at room temperature with diazomethane in diethyl ether (3.1 cm<sup>3</sup> of a freshly prepared 0.31 M solution, 0.96 mmol). After 12 h stirring at room temperature, the deep brown solution was evaporated to *ca.* 10 cm<sup>3</sup>. Addition of heptane caused the formation of a

microcrystalline green solid which was filtered off, washed with heptane and dried *in vacuo* at room temperature affording [V(CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>(CF<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub>)] (0.262 g, 68%) (Found: C, 21.0; H, 0.7; V, 13.2. C<sub>7</sub>H<sub>3</sub>F<sub>9</sub>O<sub>6</sub>V requires C, 20.8; H, 0.7; V, 12.6%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 1674s, 1636vs, 1484ms, 1385mw, 1207vs, 1167s, 1093w, 1034ms and 862mw.  $\chi_{\text{m}}^{\text{corr}} = 5770 \times 10^{-6}$  cgsu; diamagnetic correction =  $-142 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}$  (292 K) = 3.69  $\mu_{\text{B}}$ .

**With heterocyclic nitrogen bases.** A suspension of [H(thf)<sub>1.5</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.752 g, 1.51 mmol) in heptane (25 cm<sup>3</sup>) was treated with pyridine (0.24 g, 3.0 mmol). The suspension, which turned brick-red on addition of the base, was stirred at room temperature for 12 h. The solid was recovered by filtration, washed with heptane and dried *in vacuo* at room temperature affording [H(py)<sub>2</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.69 g, 83%) as a microcrystalline red solid, sensitive to oxygen and moisture. A gas-chromatographic analysis of the reaction medium showed the presence of thf (Found: C, 35.4; H, 2.3; N, 5.6; V, 9.3. C<sub>16</sub>H<sub>11</sub>F<sub>9</sub>N<sub>2</sub>O<sub>6</sub>V requires C, 35.0; H, 2.0; N, 5.1; V, 9.3%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3240w,  $\ddagger$  3180vw, 3118vw, 2962ms, 2925mw, 1689vs, 1610s, 1491w, 1206vs, 1158vs, 1074ms, 1047s, 1017ms, 998mw and 694ms; UV/VIS spectra in Table 1.  $\chi_{\text{m}}^{\text{corr}} = 5590 \times 10^{-6}$  cgsu; diamagnetic correction =  $-101 \times 10^{-6}$  cgsu;  $\mu_{\text{eff}}$  (294 K) = 3.63  $\mu_{\text{B}}$ .

Following the same procedure the deuteriated derivative [D(py)<sub>2</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>]·0.3py was obtained in 85% yield from [D(thf)][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (Found: C, 30.4; H, 1.6; N, 3.6; V, 10.8. C<sub>12.5</sub>H<sub>6.5</sub>DF<sub>9</sub>N<sub>1.3</sub>O<sub>6</sub>V requires C, 30.3; H, 1.7; N, 3.7; V, 10.3%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3107w, 2926mw, 2857m, 2317w, 1688vs, 1610s, 1489w, 1207vs, 1158vs, 1073ms, 1046s, 1017ms, 998mw and 694ms.

By operating under comparable conditions, the following compounds were obtained: [HL<sup>1</sup>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>]: 76% yield, deep red (Found: C, 33.2; H, 1.7; N, 2.6; V, 10.1. C<sub>15</sub>H<sub>8</sub>F<sub>9</sub>NO<sub>6</sub>V requires C, 34.6; H, 1.5; N, 2.7; V, 9.8%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (PCTFE): 3110w, 3070mw, 1695vs, 1603s, 1464w, 1444mw, 1415w, 1397w and 1383w. UV/VIS spectra in Table 1. [H<sub>2</sub>L<sup>2</sup>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>]·2thf: 81% yield, deep green (Found: C, 30.6; H, 1.7; N, 3.4; V, 10.2. C<sub>26</sub>H<sub>18</sub>F<sub>18</sub>N<sub>2</sub>O<sub>13</sub>V<sub>2</sub> requires C, 30.9; H, 1.8; N, 2.8; V, 10.1%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (PCTFE): 3120w, 3093w, 1718vs, 1698vs, 1605s, 1576w, 1498w, 1476s, 1448s, 1403s. UV/VIS spectra in Table 1. [H<sub>2</sub>L<sup>3</sup>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>]·2: 84% yield, deep violet (Found: C, 28.4; H, 1.3; N, 2.9. C<sub>22</sub>H<sub>10</sub>F<sub>18</sub>N<sub>2</sub>O<sub>12</sub>V<sub>2</sub> requires C, 28.2; H, 1.1; N, 3.0%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3082w, 3024w, 1693vs, 1616vs, 1556w, 1536w, 1493ms, 1483ms, 1421ms, 1207vs, 1159vs, 1064w, 1042vw, 1020vw, 858w, 815mw and 641w. UV/VIS spectra in Table 1. [H<sub>2</sub>L<sup>4</sup>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>]·2thf: 78%, deep blue (Found: C, 32.3; H, 1.6; N, 2.5; V, 9.9. C<sub>28</sub>H<sub>18</sub>F<sub>18</sub>N<sub>2</sub>O<sub>13</sub>V<sub>2</sub> requires C, 32.5; H, 1.8; N, 2.7; V, 9.8%).  $\tilde{\nu}_{\max}$ (cm<sup>-1</sup>) (Nujol and PCTFE): 3075w, 1782w, 1698vs, 1610w, 1586vw, 1523w, 1429s, 1403mw, 1078w, 835s, 752m, 730ms and 620m. UV/VIS spectra in Table 1.

**With acridine.** A solution of [H(thf)<sub>2</sub>][V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] (0.783 g, 1.46 mmol) in thf (50 cm<sup>3</sup>) was treated with acridine (0.303 g, 1.69 mmol). The red-brown colour of the solution turned green-brown with formation of a colourless solid. The suspension was stirred for 12 h at room temperature and the solid was filtered off and dried *in vacuo* at room temperature affording 9,9',10,10'-tetrahydroiacridyl (0.25 g, 95%)<sup>32</sup> (determined by the IR spectrum). The solution was evaporated to dryness and the residue was filtered off, washed with toluene and heptane and dried *in vacuo* affording 0.502 g of a nitrogen-containing solid identified as [V(CF<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>] contaminated by small amounts of acridine (determined by analytical and infrared data, see above).

$\ddagger$  This value refers to the absorption undergoing a shift upon H/D substitution (2317 cm<sup>-1</sup>, see above).

In a similar manner, a solution of  $[D(thf)_2][V(CF_3CO_2)_3]$  (1.07 mmol) in thf was treated with acridine (1.1 mmol) affording 9,9'-dideuterio-10,10'-dihydrobiacridyl (0.189 g, 97%)<sup>11a</sup> (determined by the IR spectrum).

**With benzoyl peroxide.** A solution of benzoyl peroxide (0.102 g, 0.42 mmol) in toluene (50 cm<sup>3</sup>) was treated with  $[H(thf)_2][V(CF_3CO_2)_3]$  (0.45 g, 0.84 mmol). A green suspension was quickly obtained which turned emerald green after 15 h stirring at room temperature. Benzoic acid was identified in solution by gas-chromatography. The solid was recovered by filtration, washed with toluene (3 × 5 cm<sup>3</sup>) and dried *in vacuo* at room temperature affording  $[V(CF_3CO_2)_3] \cdot 1.2 C_6H_5Me$  (0.218 g, 52%) as a green solid sensitive to oxygen and moisture (Found: C, 34.4; H, 1.8; V, 10.9.  $C_{14.4}H_{9.6}F_9O_6V$  requires C, 34.5; H, 1.9; V, 10.2%).  $\tilde{\nu}_{max}(cm^{-1})$  (Nujol and PCTFE): 3084mw, 2980m, 1641vs, 1602w, 1511w, 1494w, 1418mw, 1027vs, 1160vs, 1072w, 1027w and 859m.  $\chi_m^{corr} = 2750 \times 10^{-6}$  cgsu; diamagnetic correction =  $-123 \times 10^{-6}$  cgsu;  $\mu_{eff}$  (295 K) = 2.55  $\mu_B$ .

**With dioxygen.** A brown suspension of  $[H(thf)_2][V(CF_3CO_2)_3]$  (1.24 g, 2.32 mmol) in toluene (50 cm<sup>3</sup>) was saturated with dry dioxygen and stirred for 2 h. The colour of the suspension became deep green first and emerald green after 2 h. The green solid was filtered off, washed with toluene and dried *in vacuo* at room temperature affording  $[V(CF_3CO_2)_3] \cdot 0.14 C_6H_5Me$  (0.767 g, 82%) in the form of a microcrystalline solid sensitive to oxygen and moisture (Found: C, 20.3; H, 1.22; V, 12.7.  $C_7H_{1.14}F_9O_6V$  requires C, 20.9; H, 0.3; V, 12.6%).  $\tilde{\nu}_{max}(cm^{-1})$  (Nujol and PCTFE): 3086mw, 2982m, 1646vs, 1601w, 1513w, 1490w, 1419mw, 1029vs, 1157vs, 1070w, 1020w and 862m.  $\chi_m^{corr} = 3250 \times 10^{-6}$  cgsu; diamagnetic correction =  $-137.2 \times 10^{-6}$  cgsu;  $\mu_{eff}$  (295 K) = 2.83  $\mu_B$ .

A gas-volumetric control of the reaction showed that  $[H(thf)_2][V(CF_3CO_2)_3]$  (1.61 mmol) reacted with O<sub>2</sub> (0.43 mmol) at 24.1 °C according to a O<sub>2</sub>-V molar ratio of 3.74:1.

**With 9,10-phenanthrene-dione.** Solid  $[H(thf)_2][V(CF_3CO_2)_3]$  (0.46 g, 0.86 mmol) was added to a solution of 9,10-phenanthrene-dione (0.2 g, 0.96 mmol) in toluene (50 cm<sup>3</sup>). The colour of the solution turned immediately deep green with formation of a dark green solid. After 15 h stirring at room temperature, the suspension was filtered and the solid was washed with toluene (5 × 2 cm<sup>3</sup>) and dried *in vacuo* at room temperature affording  $[V(CF_3CO_2)_2(C_{14}H_8O_2)]$  (0.336 g, 80.5%) as a deep green microcrystalline solid sensitive to oxygen and moisture (Found: C, 43.9; H, 1.5; V, 10.8.  $C_{18}H_8F_6O_6V$  requires C, 44.6; H, 1.7; V, 10.5%).  $\tilde{\nu}_{max}(cm^{-1})$  (Nujol and PCTFE): 3087w, 1788w, 1698s, 1630vs, 1601vw, 1489ms, 1469w, 1299mw, 1207vs, 1159vs, 1039ms, 939vw, 857mw, 756s, 722s, 685vw, 641w and 584ms.  $\chi_m^{corr} = 1290 \times 10^{-6}$  cgsu; diamagnetic correction =  $-199 \times 10^{-6}$  cgsu;  $\mu_{eff}$  (297 K) = 1.89  $\mu_B$ .

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