Substitution on a methyl group of an acetylacetonate ligand: synthesis and structural characterization of oxobis[6-(phenylamino)hexane-2,4-dionato-*O,O′*]vanadium(IV), VO(Phad)$_2$

Deirdre I. Arnold,[a] F. Albert Cotton,*[a] John H. Matonic[a] and Carlos A. Murillo*[a,b]

[a] *Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA*
[b] *Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica*

From a melt reaction of VO(acac)$_2$ and *N,N′*-diphenylformamidine, HDPhF, the title compound is isolated in high yield along with aniline; the new ligand found in 1 arises from the cleavage of a C–N bond in the HDPhF molecule and the substitution of two hydrogen atoms from a methyl group of an acac ligand.

Formamidinates, form$^-$, are known to bind to transition metals in a variety of ways.[1] One of these is the formation of bridges between metal atoms in compounds such as $M_2(form)_4^{n+}$ which can be formed by reaction of the appropriate starting materials and Li(form) salts[2] or by melt reactions of the neutral ligand and species such as $M_2(carboxylate)_4$[3] by driving off the corresponding carboxylic acid. Many of the $M_2(form)_4^{n+}$ species react with oxygen to generate interesting compounds[4] which have been characterized by X-ray crystallography. For M = V, we observed evidence of two compounds, namely VO(form)$_2$ and the corresponding dimer $V_2O_2(form)_4$.[5] To study further the oxidized vanadium derivatives we decided to prepare them using an alternative synthesis by reacting VO(acac)$_2$ and HDPhF as a melt. We found, however, that this reaction does not produce Hacac as a byproduct. Aniline is isolated instead† along with a remarkable new compound, **1**, in which two hydrogen atoms of one of the methyl groups of each acac ligand are substituted by a PhNHCH moiety.‡ The structure of **1** is shown in Fig. 1. The vanadyl V=O distance of 1.582(3) Å in **1**·0.5Et$_2$O§,¶ and the five-coordinate vanadium atom are features common to all VO(diketonate)$_2$ derivatives,[6] as are the magnetic moment of 1.61 μ_B and the V–O stretching vibration at 990 cm^{-1},[7] but the *trans* arrangement of the diketonates found in **1** contrasts with the *cis* arrangement found in bis(1-phenylbutane-1,3-dionato)vanadyl,[6c] presumably because the bulkier ligand in **1** would encounter fewer steric constraints in the *trans* form.

The most striking feature in this reaction is the formation of the new β-diketonate ligand by reaction of the coordinated acac group and HDPhF as shown in Scheme 1.

In such reactions, the cleavage of a formamidine C–N bond is required. We have observed several examples in which different metals assist in the cleavage of the formamidinate anion to generate formimidoyl and imido groups, one or the other of which is found in the metal-containing product. There is at least one case where both groups are found, as in (η-dmpm)Cl$_2$Ta(η-NTol)(μ-η^2-HC=NTol)(μ-dmpm)TaCl(η^2-DTolF),[8] DTolF = *N,N′*-di-*p*-tolylformamidinate.

We believe that the C–N cleavage of HDPhF takes place after it binds to the sixth coordination site of the vanadium atom, *c.f.* VO(acac)$_2$(pyridine). Support for this supposition is given by our attempt to react Rh(acac)$_3$, which is both non-labile and coordinatively saturated, with HDPhF under conditions identical to those used for the preparation of **1**. In this case there was no detectable production of aniline and NMR studies of the reaction mixture showed the absence of any compound other than the reactants. Unfortunately, such an experiment does not provide further clues as to how the reaction proceeds. It is a well known fact that electrophiles substitute the methine hydrogen atom of the coordinated acac groups, (*c.f.* acetylation, halogenation, nitration[9]) and that groups such as OH$^-$ can potentially attack coordinated β-diketonate groups, giving a four-coordinate carbon atom at the site neighbouring an oxygen atom.[10]

The first pathway clearly is not conducive to the formation of **1**. The second pathway cannot be ruled out but would require the migration of a carbon atom of an incoming formimidoyl

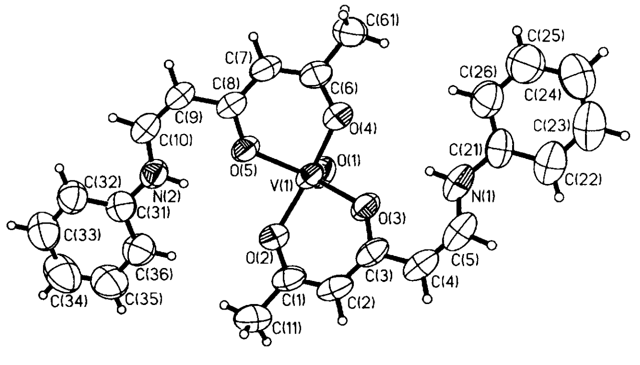
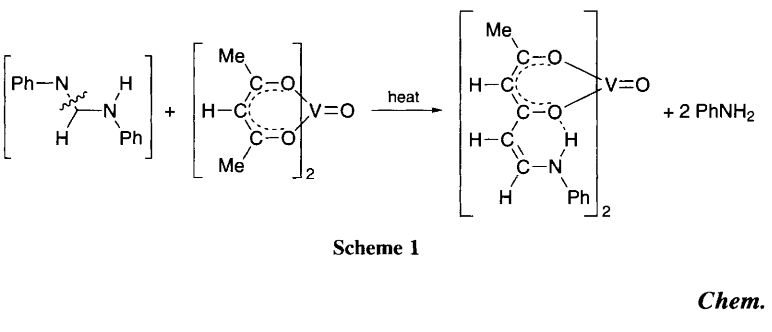


Fig. 1 The molecular structure of VO(Phad)$_2$ in **1**·0.5Et$_2$O. Selected bond lengths (Å) and angles (°): V–O(1) 1.582(3), V–O(2) 1.978(3), V–O(3) 1.952(3), V–O(4) 1.972(3), V–O(5) 1.944(3); O(1)–V(1)–O(5) 108.7(2), O(1)–V(1)–O(3) 109.5(2), O(5)–V(1)–O(3) 141.9(1), O(1)–V(1)–O(4) 103.9(2), O(5)–V(1)–(4) 87.6(1), O(3)–V(1)–O(4) 83.5(1), O(1)–V(1)–O(2) 104.2(2), O(5)–V(1)–O(2) 82.8(1), O(3)–V(1)–(2) 88.0(1), O(4)–V(1)–O(2) 151.9(1).



Scheme 1

fragment to a methyl carbon atom of the acac ligand, eliminating, in the process, two hydrogen atoms of the methyl group. Such a process could possibly be helped by the formation of the very strong hydrogen bonds found between N(2)–H(200)···O(5) and N(1)–H(100)···O(3) for which the N···O distances are 2.651(5) and 2.689(6) Å, respectively. However, as far as we know, there is no other reaction in which there is clearly an activation of C–H bonds on a methyl group such as this one, which leads to the formation of **1** in high yield. Further studies will hopefully shed more light on the way in which this unprecedented reaction takes place.

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Footnotes

† Aniline was identified from both ^{1}H NMR and IR spectra. Addition of neat aniline to the isolated reaction sample did not change any of the NMR spectroscopic features.

‡ A mixture of 0.50 g (1.89 mmol) of $VO(acac)_2$ and 0.75 g (3.82 mmol) HDPhF was heated to *ca.* 150 °C for 7 h during which the formamidine melted and the mixture turned from green to red–brown. A colourless condensate of aniline was also produced. After washing with warm hexanes the red–brown solid was then refluxed for 1 h in toluene. The analytically pure air-stable product was filtered from this mixture. Yield: 74%. A 0.05 g portion of the product was combined with 10 ml CH_2Cl_2 and stirred for 2 h. After filtering the solution was layered with 20 ml Et_2O. After 2 days at room temp. brown needle-like crystals of **1** formed. Crystals of **1**·$0.5Et_2O$ were obtained using similar procedures in which the reaction mixture was initially heated for *ca.* 3.5 h and no special effort was made to remove the aniline. Elemental analysis. Calc. for **1**: C, 61.15; N, 5.94; H, 5.13. Found: C, 60.93; N, 5.64; H, 5.21%; IR (KBr): 3454w, 3275w, 3049w, 2919w, 1638s, 1601s, 1510s, 1455s, 1391s, 1353s, 1293s, 1247s, 1172s, 1077w, 1018m, 990m, 943m, 886w, 807m, 752m, 732m, 688m, 659m, 541m, 507w, 476m, 442m cm^{-1}. Positive FABMS, M$^+$ obs. *m/z* 472. UV–VIS (CH_2Cl_2): 497 nm. Magnetic susceptibility: 1.61 μ_B (uncorrected).

§ *Crystal data* for **1**·$0.5Et_2O$: crystal dimensions 0.30 × 0.15 × 0.15 mm, $C_{26}H_{29}N_2O_{5.5}V$, M = 508.45, triclinic, space group $P\bar{1}$, a = 10.935(2), b = 13.587(2), c = 8.647(1) Å, α = 92.89(1), β = 91.22(1), γ = 78.87(1)°, Z = 2, D_c = 1.341 g mol^{-1}, μ (Cu-Kα) = 3.634 mm^{-1}. Data were obtained at 293(2) K on a Rigaku AFC5R diffractometer. A total of 3160 unique reflections were collected using ω–2θ scans within a 2θ range of 110°. The structure was solved by direct methods and refined by full-matrix least squares using 2798 reflections [$I > 2\sigma(I)$] for 322 parameters. The final refinement converged to $R1$ = 0.057 and $wR2$ = 0.152.

¶ Poorer diffracting crystals of unsolvated **1** had crystal dimensions 0.30 × 0.10 × 0.10 mm, $C_{24}H_{24}N_2O_5V$, M = 471.39, monoclinic, space group $P2_1/n$, a = 8.775(2), b = 10.416(2), c = 25.219(5) Å, β = 95.32(3)°, Z = 4, D_c = 1.364 g mol^{-1}, μ (Mo-Kα) = 0.469 mm^{-1}. Data were obtained at 213(2) K on a FAST diffractometer. A total of 2035 independent reflections were collected. The vanadium atom position was found in a Patterson map. Subsequent least-squares refinement followed by Fourier syntheses revealed the remaining non-hydrogen atoms which were refined by full-matrix least squares using 1930 reflections for 289 parameters. The final refinement converged to $R1$ = 0.136 and $wR2$ = 0.302.

In general, the molecular dimensions of **1** are essentially the same as those of **1**·$0.5Et_2O$. 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 182/195.

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