Organometallic Derivatives of *N,N'*-Ethylenebis(acetylacetoneiminato)vanadium(III) containing a Vanadium–Carbon σ-Bond

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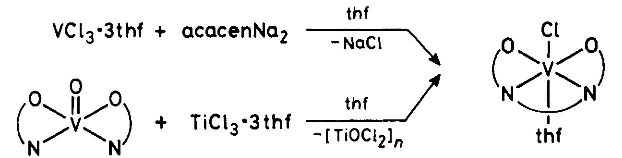
The alkylation of *N,N'*-ethylenebis(acetylacetoneiminato)chlorovanadium(III)tetrahydrofuran, [Cl–V(acacen)(thf)] using Grignard reagents gave the corresponding organometallic derivatives [R–V(acacen)]$_2$ [R = Me, Ph, PhCH$_2$] having a dimeric structure, *via* the sharing of one of the oxygens from the Schiff base, and containing a V–C σ-bond [2.156(7) Å, R = PhCH$_2$].

Polydentate Schiff base ligands seem very effective in stabilizing various oxidation states for metals, and providing stability for metal–carbon σ-bonds. This influence has been mainly observed in cobalt and iron chemistry.[1] We are trying to extend these results to those metals which have a rather poor co-ordination chemistry in low oxidation states and few compounds containing metal–carbon σ-bonds. In this context, we are currently studying the reduction of vanadium(IV) and vanadium(III) Schiff base complexes,[2] and their conversion into compounds containing vanadium–carbon σ-bonds.

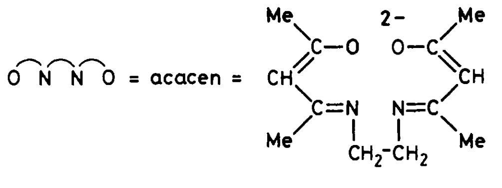
The present report deals with the synthesis and the structural characterization of some organometallic derivatives having the formula [R–V^{III}(acacen)] [acacen = *N,N'*-ethylenebis(acetylacetoneiminato)]. Vanadium–carbon σ-bond containing complexes[3] have been mainly limited to a few vandocene derivatives[4] and to the homoleptic series VMes$_3$[5] and VMes$_4$[6] (Mes = 2,4,6-Me$_3$C$_6$H$_2$).

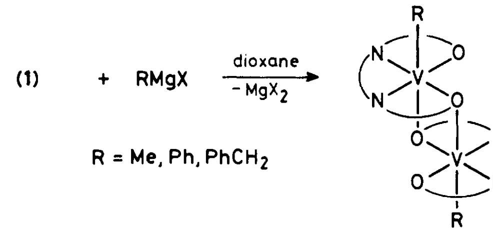
The synthesis of the starting material (**1**) was performed either by reacting VCl$_3$ · 3thf with the sodium salt of the Schiff base, acacenNa$_2$ in thf, or by the reduction of VO(acacen) using TiCl$_3$ · thf$_3$. Both syntheses gave good yields of complex (**1**)† whose structure was determined by an *X*-ray analysis.[7] A thf solution of (**1**) was reacted with an equimolar solution of a Grignard reagent RMgX (R = Me, Ph, PhCH$_2$) at room temperature. The solution turned from maroon to deep red. By addition of dioxane the magnesium salt was precipitated. The resulting filtrate was evaporated to dryness to give a residue (**2**) which was recrystallized from toluene–n-hexane (yields 50—70%).†

Complexes (**2**) are paramagnetic, having two unpaired electrons (μ_B ranging from 2.40 to 2.70 at 293 K), they are soluble in most organic solvents, thermally stable, and very



(**1**)





(**2**)

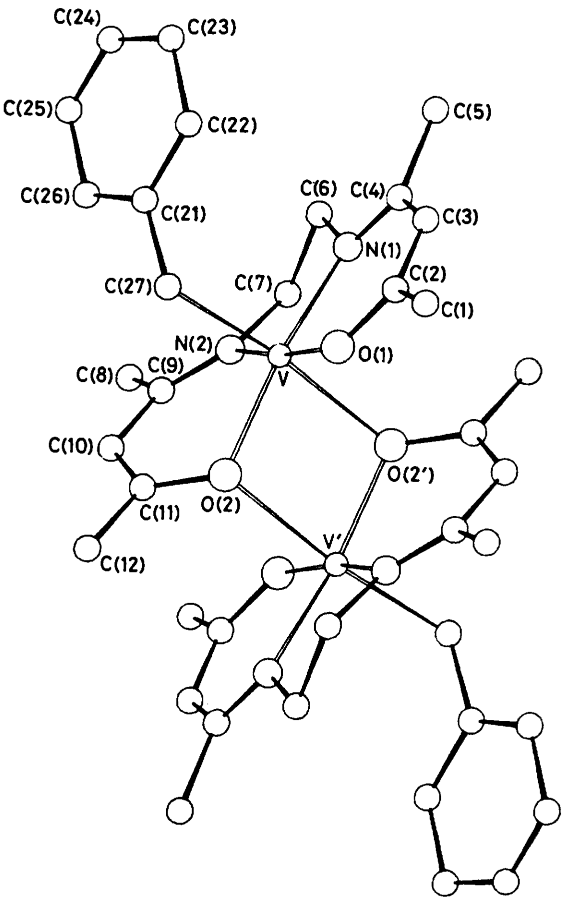


Figure 1. A molecular view of the dimer [V(acacen)CH$_2$Ph]$_2$. Bond distances (Å): V–O(1), 1.960(5); V–O(2), 1.989(4); V–O(2'), 2.296(5), V–N(1), 2.047(5); V–N(2), 2.075(7); V–C(27), 2.156(7) Å. Bond angles (°): O(1)–V–O(2), 102.5(2); N(1)–V–N(2), 81.7(2); N(1)–V–O(1), 90.1(2); N(1)–V–O(2), 162.6(2); N(2)–V–O(1), 171.8(2); N(2)–V–O(2), 85.4(2); C(27)–V–O(2'), 173.4(2)°. Prime indicates a transformation of ($\bar{x}$,$\bar{y}$,$\bar{z}$).

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† Satisfactory analytical data have been obtained.

air-sensitive. The structure was determined using *X*-ray analysis for complex (**2**; R = CH_2Ph). *Crystal Data:* $C_{38}H_{50}N_4O_4V_2$, M = 728.7, monoclinic, space group $P2_1/c$, a = 11.856(3), b = 18.016(5), c = 8.775(3) Å, β = 95.54(2)°, U = 1865.6(9) Å^3, Z = 2, D_c = 1.297 g cm^{-3}, $F(000)$ = 768, μ(Mo-K_α) = 5.26 cm^{-1} (λ = 0.7107 Å). Data were measured ($6° < 2\theta < 46°$) on a Philips PW 1100 diffractometer and 1248 reflections with $I > 3\sigma(I)$ were considered as observed and used in the structure solution and refinement. The structure was solved by the heavy-atom method; final anisotropic refinement converged to R 0.053 (R_w 0.048).‡

Figure 1 shows the centrosymmetric dimer [V(acacen)-CH_2Ph]$_2$ and the most relevant bond distances and angles. Vanadium has a pseudo-octahedral co-ordination with the N_2O_2 set of atoms from the acacen ligand in the equatorial plane and the alkyl group in an axial position, while the sixth co-ordination site is occupied by the oxygen of a second monomeric unit at a rather long distance [2.296(5) Å]. The O_2N_2 set of atoms are significantly distorted from a planar co-ordination geometry. The vanadium atom is out of the mean equatorial plane by 0.123 Å towards the benzylic carbon. Information on V–alkyl σ-bond distances is very scarce. The present value can only be compared with the distances found in $cp_2V(EtO_2CCH{=}CHCO_2Et)$ [2.186(12) and 2.213(12) Å],[4] while it is significantly longer than those found in [$cp_2V(MeO_2C{-}C{\equiv}C{-}CO_2Me)$] [2.084(3) and 2.097(3) Å][4] and in $VMes_3thf$ [2.099(6)—2.116(7) Å][5] and $VMes_4$ [2.071—2.095 Å].[6] A significant difference is observed for V–O(1) and V–O(2) distances [1.960(5) *vs.* 1.989(4) Å] as a consequence of the bridging role of the O(2) oxygen. All the other bond distances and angles are similar to those found for [Cl–V(acacen)thf][7] and VO(acacen).[8]

The reactivity of the V–C σ-bond in these and analogous complexes is under investigation.

Received, 8th March 1985; Com. 307

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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