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A homobimetallic vanadium d²–d² complex $(Cp_2V)_2(3\eta:4\eta\text{-}Me_3SiC{\equiv}C{-}C{=}C{-}C{\equiv}CSiMe_3)$: structure and magnetism

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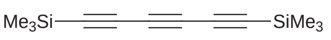
The d²–d² homobimetallic complex $(Cp_2V)_2(3\eta:4\eta\text{-}Me_3SiC{\equiv}C{-}C{=}C{-}C{\equiv}CSiMe_3)$ was synthesized from $Me_3SiC{\equiv}C{-}C{\equiv}C{-}C{\equiv}CSiMe_3$ and Cp_2V and characterized by an X-ray crystal structure; magnetic moment measurements from 300 to 2 K indicated a weak antiferromagnetic *J* exchange coupling of -3.7 cm^{-1}.

The chemistry of transition metal alkynyl and related complexes continues to be an attractive focus, and among its differing chemical and physical properties, their potential non-linear optical properties are of interest.[1] Furthermore, a rich acetylenic chemistry has recently been described with group 4 transition metals in which the synthon 'Cp_2Zr' played an important part.[2] Our research group has extended this concept to group 5 with the reactive isolable vanadocene Cp_2V complex.

The remarkable oxidative addition of vanadocene Cp_2V **1** to ethynyl –C≡C– bonds was demonstrated early and a vanadocyclopropene structure was established.[3] In previous papers, we established that Cp_2V reacts with $Cp'_2Zr(C{\equiv}CPh)_2$ to give $Cp_2V(\mu\text{-}\eta^2:\eta^4\text{-}C{\equiv}C{-}C{\equiv}CPh)ZrCp'_2$, with a vanadacyclopropane moiety containing two planar tetracoordinated carbons on the butadiyne ligand[4] or with the phosphane $ArP(C{\equiv}CPh)_2$ to give the adduct $Cp_2V(PhC{=}C)P(C{\equiv}CPh)Ar$.[5] Alternatively, two Cp_2V units can be added to a diethynyl ligand $RC{\equiv}C{-}C{\equiv}CR$ (R = $SiMe_3$, Ph) to give a homobimetallic V^{IV}–V^{IV} system $(Cp_2V)_2(1\text{–}2\eta:3\text{–}4\eta\text{-}RC{=}C{-}C{=}CR)$ where the Cp_2V units are in *cis* or *trans* positions depending on the nature of R.[6] As such, particular attention is given to the reactivity of Cp_2V with a triyne $Me_3SiC{\equiv}C{-}C{\equiv}C{-}C{\equiv}CSiMe_3$[7] **2**, to establish a synthetic route to an ethynyl vanadium-bridged complex.



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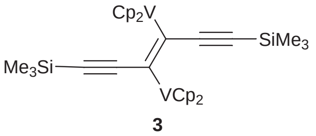
Addition of a pentane solution of **1** (2 or 3 equiv.) to **2** leads to a crystalline black solid $(Cp_2V)_2(3\eta:4\eta\text{-}Me_3SiC{\equiv}C{-}C{=}C{-}C{\equiv}CSiMe_3)$ **3**,† fully characterized by an X-ray structure



3

determination (Fig. 1).‡ Surprisingly, the vanadium atom has an oxidative state of +3, instead of the expected classical V^{IV} which to our knowledge has been observed in all other cases. The main feature of **3** is the bonding mode of the two vanadocene moieties which are attached to both the internal carbon atoms of the triyne *via* a single σ-type V–C(11a) bond of length 2.165 Å which raises the vanadium oxidation state from +2 to +3. The geometrical alteration of ligand **2** is reflected by the *trans* configuration of the triyne: the nearly linear $-C{-}C{\equiv}CSiMe_3$ moiety [C(11a)C(12)C(13) 165.5°, C(12)C(13)Si(1) 173.2°] forms a 113.4° angle with the C(11a)C(11a′) bond. The sum of the angles around C(11a) (nearly 360°) as well as the 1.381 Å bond length of C(11)–C(11a′) (in accord with a double bond) indicate an sp²-ethylene structure. The SiC_6Si skeleton and the vanadium atoms are in the same plane and the dihedral angle between the plane of the Cp_2V unit (obtained from the centroids of the Cp rings and the vanadium atom) and the plane of the SiC_6Si ligand is 98.66°.

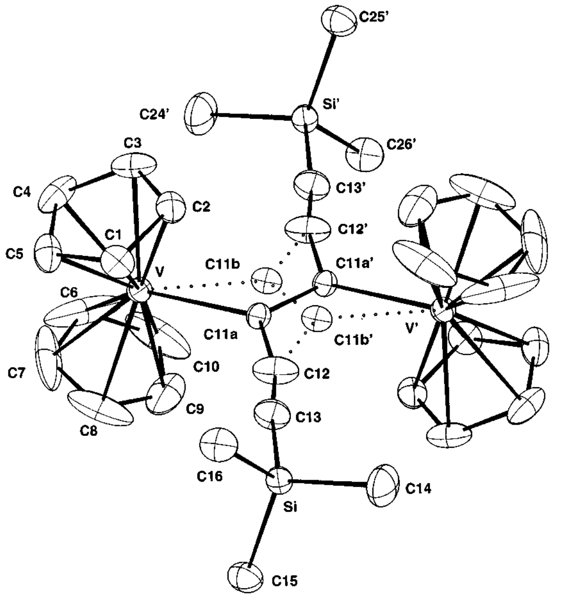


Fig. 1 Molecular structure of **3**. Selected distances (Å) and angles (°), hydrogen atoms omitted: V–C(11a) 2.165(4), C(11a)–C(11a′) 1.381(9), C(11)–C(12) 1.476(5), C(12)–C(13) 1.206(4), V···V′ 5.25, V–Cp 1.947(av.); Cp–V–Cp 147.8(av.) [Cp are the centroids of the C_5H_5 rings C(1)–C(5), C(6)–C(10)].

Variable-temperature magnetic susceptibility measurements have been carried out on the V^{III} homobimetallic d²–d² species **3**.§ The effective moment μ_{eff} is 4.01 μ_B at 300 K, which is consistent with two vanadium(III) units ($\mu_{theor} = 2[\sqrt{\Sigma S(S+1)}] = 4$ for two non-interacting d² vanadium atoms). If the two magnetically equivalent d² centers are totally non-interacting, then μ_{eff} should remain constant over a large temperature range. The effective moment μ_{eff} decreases to 1.51 μ_B at 2 K. Fig. 2 shows a plot of the molar susceptibility per dimer χ_m, *vs. T*. The solid line represents a good fit and was considered to account for the observed dependence with an exchange interaction model, having a weak antiferromagnetism with $J = -3.7$ cm^{-1}.[8]

When 1 equiv. of **1** was treated with only 1 equiv. of **2** in pentane, tiny brown needles were obtained. Unfortunately, efforts to obtain suitable crystals for an X-ray diffraction analysis have to date failed. Elemental analysis and magnetic

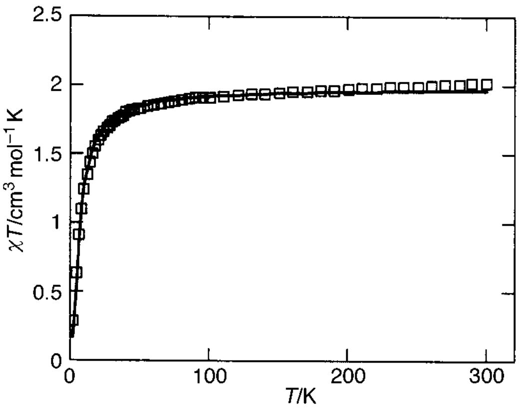
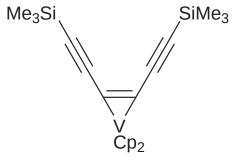


Fig. 2 Temperature dependance of molar magnetic susceptibilities per vanadium (☐) of **3**; the solid line results from a least-squares theoritical fit.

studies (μ_{eff} = 1.9 μ_B) are in agreement with a vanadium(IV) atom bound to **2**,† and a vanadocene cyclopropene structure such as $Cp_2V(3–4\eta^2-Me_3SiC{\equiv}C–C{=}C–C{\equiv}CSiMe_3)$ **4** can be suggested. Treatment of **4** in C_6D_6 with another equiv. of **1** leads to **3**, as revealed by ^1H NMR spectroscopy (the ^1H NMR spectrum of paramagnetic **3** in C_6D_6 consists of an observable low field broad signal of Cp at δ 124 and a well resolved Me_3Si signal at δ 1.0. A comproportionation reaction between V^{IV} (**4**) and V^{II} (**1**) to give $2V^{III}$ (**3**) is probably operative but a mechanistic description must await further experimental evidence.



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In summary, the reaction of **1** with a triyne ligand led to a homobimetallic d^2–d^2 complex. This unexpected reactivity seems to be due to the odd parity of the number of C≡C bonds in **2**.[7] It would be interesting experimentally to test other odd-yne ligands to understand the ligand/metal effects and efforts are currently being made in this direction.

Notes and references

† Satisfactory elemental analysis results were obtained for compounds **3** and **4**.

‡ *Crystallographic data* for **3**: $C_{32}H_{38}Si_2V_2$, M = 580.72, monoclinic, space group $P2_1/c$, a = 11.214(2), b = 113.778(2), c = 10.797(1) Å, β = 112.72(1)°, V = 1538.76 Å^3, Z = 4, D_c = 1.66 g cm^{-3}, μ = 6.82 cm^{-1}, $R(R_w)$ = 0.033(0.036) for 1719 unique data and 173 parameters, GOF = 1.08. Data collection was performed at *ca.* 180 K on a IPDS STOE diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods and subsequent difference Fourier maps. A disordered distribution was observed for C(11) and the best model to fit the electronic density was to consider two positions C(11a) and C(11b) with a ratio of occupancy of 0.6/0.4. CCDC 182/1256. See http://www.rsc.org/suppdata/cc/1999/1099/ for crystallographic files in .cif format.

§ Magnetic susceptibilities were determined using a SQUID susceptometer within the temperature range 2–300 K. Using a Heisenberg Hamiltonian $H = -JS_AS_B$ with the local spin $S_A = S_B = 1$, the magnetic interaction was estimated with a model for dinuclear compounds [eqn. (1)].[9] The J and g parameters were determined by least-squares fitting. The agreement factor R [eqn. (2)] = 2.89 × 10^{-4}. The average value of the g-factor was 1.996.

$$\chi = \frac{2N\beta^2}{kT} g^2 \frac{e^x + 5e^{3x}}{1 + 3e^x + 5e^{3x}} \; (x = J/kT) \tag{1}$$

$$R = \frac{\Sigma(\chi_m^{obs} - \chi_m^{calc})^2}{\Sigma(\chi_m^{obs})^2} \tag{2}$$

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