Homobimetallic vanadium d^1–d^1 complexes: structure and magnetism

Robert Choukroun,*[a] Bruno Donnadieu,[a] Isabelle Malfant,[a] Simone Haubrich,[a] Richard Frantz,[b] Christian Guerin[b] and Bernard Henner[b]

[a] *Equipe Précurseurs Moléculaires et Matériaux, Laboratoire de Chimie de Coordination du CNRS, 205 Route de Narbonne, 31077, Toulouse Cedex, France*

[b] *Laboratoire des Précurseurs Organométalliques des Matériaux, UMR CNRS 44, CC007, Université de Montpellier 2, Place E. Bastaillon, F-34095 Montpellier Cedex 5, France*

From $Me_3SiC{\equiv}C–C{\equiv}CSiMe_3$ and $Ph_2PC{\equiv}C–C{\equiv}CPPh_2$ diynes and vanadocene VCp_2, homobimetallic vanadium d^1–d^1 complexes are synthesized and characterized by X-ray crystal structures of $(Cp_2V)_2(1\text{-}2\eta\!:\!3\text{-}4\eta\text{-}RC{=}C–C{=}CR)$, (R = $SiMe_3$ 1 PPh_2 2); magnetic moments of both complexes from 300 to 2 K indicate an antiferromagnetic *J* exchange coupling of -10.5 and -59.8 cm^{-1} for 1 and 2, respectively.

Many interesting reactions of the highly reactive MCp_2 species have been reported[1] and the zirconocene $ZrCp_2$ is of particular interest.[2] Numerous research has been devoted to the formation of organic synthetic products and more recently as a synthon in the reactivity of the alkynyl C≡C bond. This interest arises from the favourable electronic and structural features of C≡CR ligands *via* σ or σ–π networks. They can be modulated by varying either or both substituents and the metal centers.[3] In particular, vanadocene VCp_2 was studied with different classes of unsaturated molecules and different metallacyclopropene structures were identified.[4] Since the vanadocene unit easily binds alkyne derivatives, the reactivity of diynes $Me_3SiC{\equiv}C–C{\equiv}CSiMe_3$ and $Ph_2PC{\equiv}C–C{\equiv}CPPh_2$ was investigated.[5] One might expect that two identical species possessing one unpaired electron connected by diynes with various R end-groups could produce different structural and magnetic situations.[6]

Treatment of 2 equiv. of VCp_2 with 1 equiv. of $Me_3SiC{\equiv}C–C{\equiv}CSiMe_3$ or $Ph_2PC{\equiv}C–C{\equiv}CPPh_2$ in pentane, resulted in a brown solution from which, *via* the oxidative addition of VCp_2 on the alkyne bonds, $(Cp_2V)_2(1\text{-}2\eta\!:\!3\text{-}4\eta\text{-}Me_3SiC{=}C–C{=}CSiMe_3)$ **1** and $(Cp_2V)_2(1\text{-}2\eta\!:\!3\text{-}4\eta\text{-}Ph_2PC{=}C–C{=}CPPh_2)$ **2** were isolated as crystals in yields of *ca.* 50 and 40%, respectively. Formulation of **1** and **2** as homobimetallic vanadium complexes was confirmed by X-ray crystallography (Figs. 1 and 2).† The bond distances and angles associated with the vanadium acetylene interaction indicate that the acetylene molecule is symmetrically attached to the vanadium atom *via* two σ-type V–C bonds of 2.14 Å (av.) and 2.10 Å (av.) for **1** and **2**, respectively. This produces a metallacyclopropene structure for the central VC_2 moiety, with an acute C–V–C angle of 35° (av.). The acetylene coordination is reflected by the average 0.08 Å increase of the C≡C distance and by the geometrical alterations which accompany the acetylene upon coordination. The C–C–R bond angles (R = $SiMe_3$, PPh_2) are reduced from 180° in a free acetylene to 140° (av.) in the vanadocene adducts.[4] The distance of the C–C bond for **1** [C(2)–C(3) 1.39 Å] and **2** [C(2)–C(2) 1.40 Å] indicates the presence of a partial double bond. The essential aspects of the structures though are the dihedral angle between both VC_2 units in the molecules which are 110.8° for **1** and 165.61° for **2**, which leads to vanadium–vanadium distances of 4.886(5) and 5.384(2) Å in **1** and **2**, respectively. The different orientation of the Cp_2VC_2 unit in **1** and **2** may be due to the steric effects of the substituents $SiMe_3$ and PPh_2 on the diynes. Another difference in the structural aspects of **1** and **2** is the butadiene skeleton. This is deformed for **1** [C(4) is above the plane defined by C(1)–C(2)–

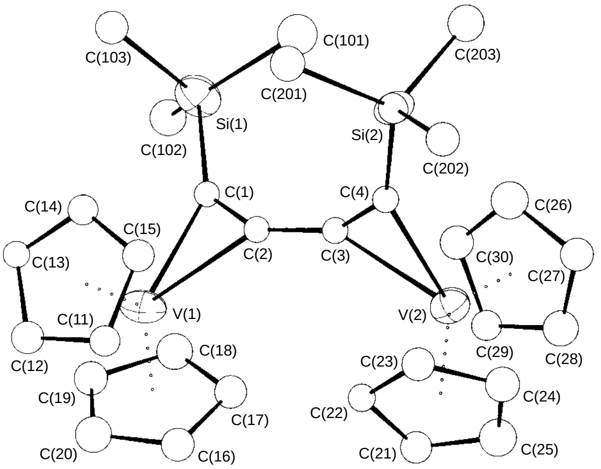


Fig. 1 View of the molecular structure of **1** (bond lengths in Å, angles in °, hydrogen atoms omitted). V(1)–C(1) 2.14(2), V(1)–C(2) 2.15(2), V(2)–C(3) 2.16(2), V(2)–C(4) 2.13(2), C(1)–C(2) 1.25(3), C(2)–C(3) 1.39(2), C(3)–C(4) 1.28(3); C(1)–V(1)–C(2) 34.0(7), C(3)–V(2)–C(4) 34.7(8), Si(1)–C(1)–C(2) 139.8(20), Si(2)–C(4)–C(3) 140.2(20), C(1)–C(2)–C(3) 148.9(23), C(2)–C(3)–C(4) 149.1(23); V(1)···V(2) 4.886(5), V–Cp 1.977 (av.), Cp–V–Cp 138.4 (av.) [Cp are the centroids of the C_5H_5 rings C(11)–C(15), C(16)–C(20), C(21)–C(25), C(26)–C(30)].

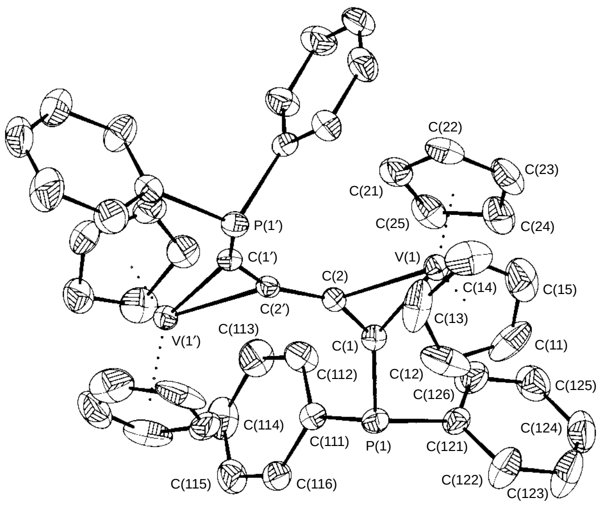


Fig. 2 View of the molecular structure of **2** (bond lengths in Å, angles in °, hydrogen atoms omitted). V(1)–C(1) 2.092(5), V(1)–C(2) 2.116(4), C(1)–C(2) 1.283(6), C(2)–C(2′) 1.404(9); C(1)–V(1)–C(2) 35.5(2), P(1)–C(1)–C(2) 140.1(4), C(1)–C(2)–C(2′) 148.2 (6); V(1)···V(1′) 5.384(2), V(1)–Cp 1.968, V(1)–Cp′ 1.974, Cp–V(1)–Cp′ 137.57 [Cp, Cp′ are the centroids of the C_5H_5 rings C(1)–C(5), C(6)–C(10)].

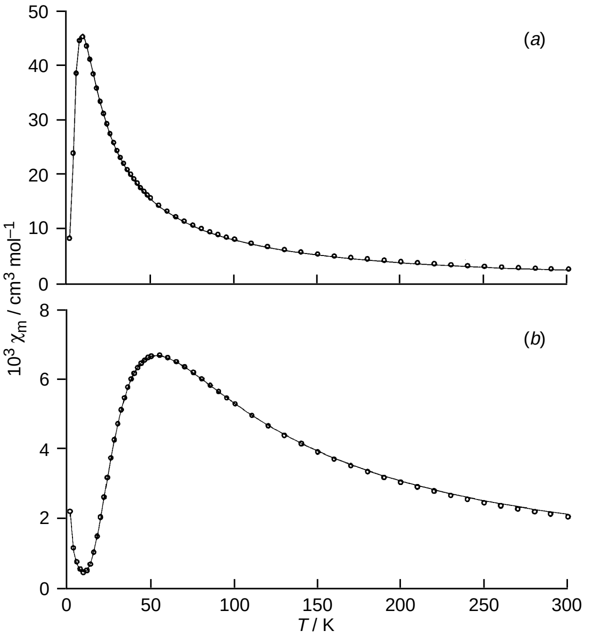
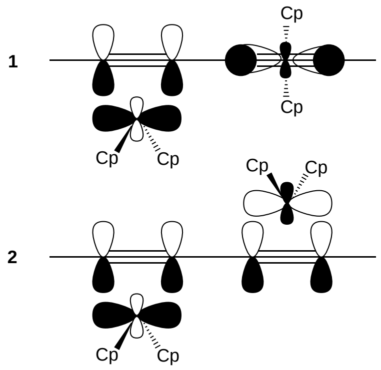


Fig. 3 Temperature dependence of molar magnetic susceptibilities per vanadium (○) of (*a*) **1** and (*b*) **2** (the solid lines result from a least-squares theoretical fit)‡

C(3) by 0.63 Å] whereas all the carbon atoms are contained in a plane for **2**.

As a result of such situations, paramagnetic vanadium centers of d^1 electronic configuration could produce different magnetic behavior.[6,7] Variable-temperature magnetic susceptibility measurements have been carried out.‡ The effective magnetic moment μ_{eff} is 2.65 μ_B for **1** and 2.25 μ_B for **2** at 300 K. They decrease to reach 0.36 μ_B for **1** and 0.19 μ_B for **2** at 2 K. Fig. 3 show the plots of χ_m, molar susceptibility per dimer, *vs.* temperature for **1** and **2**. The solid lines represent the good fit obtained to account for the observed dependence with an exchange interaction model. Fitting the data for **1** and **2** gives $J = -10.5$ and -59.8 cm^{-1}, respectively. The antiferromagnetic interaction for **2** is greater than that for **1** whereas the vanadium–vanadium distances show an opposite relation. In fact, the interaction is propagated by the carbon chain and a consideration of the bonding situation in the complex seems necessary. The orientation of the Cp_2VC_2 unit in the molecule suggests a favorable 'in-plane π type' geometry for complex **2**. This can be described as a linear combination of mainly p orbital character of the carbon of the diyne with the main contribution of the d_{z^2} orbital of the HOMO in a d^1 type system.[4] This is disfavored in the complex **1** where the Cp_2VC_2 unit and their magnetic orbital contributions could be considered as orthogonal (Scheme 1).

In conclusion, our synthetic method is able to produce homobimetallic d^1 systems with organic substrates. Modification of the organic portion leads to different structure situations and varies the coupling propagated by extended bridges. We illustrate a strategy to potentially synthesize homobimetallic d^1 systems designed to produce differing metal–metal separations. The full extent of the interaction of metallocene d^1 VCp_2 with several unsaturated hydrocarbons is under investigation.



Scheme 1

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Footnotes and References

* E-mail: choukrou@lcctoul.lcc-toulouse.fr

† *Crystallographic data*: for **1**: $C_{30}H_{38}Si_2V_2$, M = 557.70, triclinic, space group $P\bar{1}$, a = 8.226(2), b = 12.862(4), c = 13.987(3) Å, α = 78.93(2), β = 84.60(2), γ = 82.05(2) °, U = 1435.0 Å^3, Z = 2, D_c = 1.29 g cm^{-3}, μ = 7.28 cm^{-1}, $R(R_w)$ = 0.080(0.098), GOF = 1.5. For **2**: $C_{46}H_{40}P_2V_2$, M = 780.34, orthorhombic, space group *Pbna*, a = 12.940(2), b = 16.757(2), c = 17.638(2) Å, U = 38.24.5 Å^3, Z = 4, D_c = 1.36 g cm^{-3}, μ = 5.87 cm^{-1}, $R(R_w)$ = 0.048(0.059), GOF = 0.85.

Data collection was performed at *ca.* 294 K on a IPDS STOE diffractometer using graphite monochromatized Mo-Kα radiation. The crystal of **1** is twinned and one of the two domains of the twin have been indexed; the integration was realized by using the program TWIN (STOE IPDS software), the overlapped reflections are automatically discarded by TWIN during the data reduction. The refinement of **1** was performed with the best data set containing once merging 60% of unique reflections. Computations were performed with the aid of CRYSTALS. The structure was solved by direct methods (SIR92[9]). All hydrogen atoms were found on difference Fourier maps but were introduced in the refinement as fixed contributors (C–H 0.96 Å) and recalculated after each cycle. For **2**, all non-hydrogen atoms were anisotropically refined; for **1**, only V and Si atoms were refined anisotropically owing to the low ratio of parameters to observations. CCDC 182/643.

‡ Magnetic susceptibilities were determined using a SQUID susceptometer within between 2 and 300 K. Using a Heisenberg Hamiltonian $H = -JS_AS_B$ with local spins $S_A = S_B = 1/2$, the magnetic interaction was estimated with a Bleaney–Bowers model for dimers[8] (J, g) including a percentage (ρ) of paramagnetic impurities. Parameters J, g and ρ were determined by least squares fitting. The average value of the g-factor was 2.12 for **1** and 1.95 for **2**. ρ assumed as isolated V^{IV} ions with the same molecular mass as the actual compounds **1** or **2**, so that the Curie constant C was taken as $C = [N\beta^2/2k]\,g^2$, was found to be 0.018 for **1** and 0.006 for **2**.

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