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Adventures in Vanadocene Chemistry

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This review surveys some aspects of the chemistry of [VCp$_2$]. The high potential of vanadocene [VCp$_2$] (and [V(CO)Cp$_2$]) in organometallic chemistry is illustrated by new organometallic architectures. The rich redox chemistry of [VCp$_2$] is shown by incorporation of this fragment into various C≡C and C≡N bonds. This molecular approach allows the connection of two (or more) paramagnetic centers through an organic linker in order to build magnetic nanoscopic organometallic wires. [VCp$_2$] has also been studied in the field of materials such as vanadium carbide (VC) ceramics and in its role as a reducing agent toward elements of groups 8–10 to prepare Fe, Rh, and Pd colloids.

Introduction

Vanadocene, which is the only stable and easily accessible metallocene of the early transition metals, is an electronically and coordinatively unsaturated molecule. Other metallocenes of the early transition metals, such as titanocene and zirconocene, do not exist in their original sandwich structure and need another ligand (alkyne, butadiene) to stabilize the metallocene fragment.[1] The reactivity of vanadocene [VCp$_2$], in spite of its accessibility,[2] has scarcely been studied, probably due to the formation of various paramagnetic V^{III} and V^{IV} compounds that prevent further spectroscopic analysis. This paramagnetism excludes classical NMR techniques, and the literature on the reactivity of vanadocene is often dominated by EPR and IR spectroscopic characterization, chemical derivatization, or by analogy with its diamagnetic titanium analogue.[3,4]

Robert Choukroun was born in Alger (in the former French department of Algeria) on June 24, 1944, and arrived in France in 1962. He received all of his degrees from the Université Paul Sabatier, in Toulouse, where he joined the CNRS in 1968 (Doctorat d'Etat, in 1975, under the Supervision of Professor Danièle Gervais). After a postdoctoral stay in 1975–1976 at the Unit of Nitrogen Fixation, University of Sussex (Brighton, U.K.) under the direction of Professor Chatt, he joined the Laboratoire de Chimie de Coordination de Toulouse, where he has remained to this day, becoming Directeur de Recherche in 1996. His current research interests are concerned with organometallic chemistry of the early transition metals of groups 4 and 5 and their development and use as catalysts for homogeneous catalysis and molecular precursors to ceramic materials and colloids.

Christian Lorber did his undergraduate studies at Louis Pasteur University in Strasbourg (France; 1985–1989). In 1989 he joined the group of Professor John A. Osborn at the Chemistry Department of Louis Pasteur University, where he studied homogeneous catalysis with oxo complexes of transition metals (oxidation and isomerization reactions). He obtained his PhD in 1995 and spent three years as a Postdoctoral Fellow, first at the Inorganic Chemistry Department of Lund University (Sweden) with Dr. Ebbe Nordlander (1996), and then in the group of Professor Richard H. Holm at the Chemistry and Chemical Biology Department of Harvard University (Cambridge, USA; 1997–1998) where he participated in the synthesis and studies of new models of Mo- and W-oxotransferase enzymes. In fall 1998 he obtained a research position at the Centre National de la Recherche Scientifique (CNRS) and moved to the Laboratoire de Chimie de Coordination in Toulouse (France). His interests include the inorganic and organometallic chemistry of high-oxidation-state early transition metal complexes, especially those that contain an amido, imido, diamido, alkyl, or alkoxy group, and related cationic species, catalytic reactions and mechanisms of reactions involving these complexes, especially in olefin-polymerization reactions, the controlled synthesis of polymers prepared using well-defined organometallic initiators, and hydroamination of alkynes. He is also involved in the synthesis of nanoparticles and their use in various catalytic transformations.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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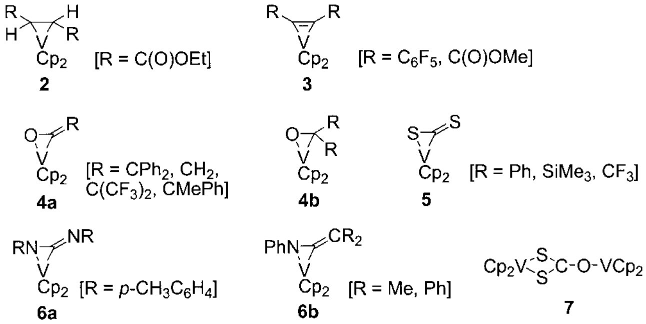
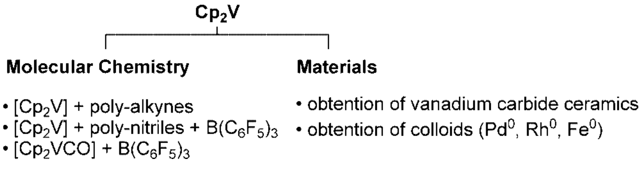
Ideally, X-ray structure analysis is a highly recommended tool to determine the real chemical environment around the metal center.

The starting point of our research was, in part, the recent development of the so-called "carbon-rich chemistry", which allows access to different kinds of polyalkynes,[5] and also the pioneering work of Floriani and others[6] on the addition of an activated alkyne to [VCp$_2$] (**1**). The synthesis of olefin and acetylene derivatives of vanadocene is readily achieved by treating **1** with the appropriate substrates. The reaction can be formally described as the addition of the metal carbene to the C–C multiple bond to afford a metallacyclopropane [Cp$_2$V(η^2-EtO$_2$CCHCHCO$_2$Et)] (**2**) and metallacyclopropene [Cp$_2$V(η^2-C$_2$R$_2$)] (**3**; Scheme 1). It behaves as a carbene-like unit and adds to many organic functional groups (ketene, thioketene, ketene imine, ...; Scheme 1).[7–9] The interest in this η^2-C,X (X = C, O, S, N) bonding was originally as model compounds for studying molecular activation promoted by transition metals and associated to the problem of CO$_2$ activation. All these complexes can be related both structurally and chemically to some intermediates believed to be formed in the reaction between a metal center and carbon dioxide. As an example, carbonylsulfide (COS), when it reacts with vanadocene, undergoes a disproportionation reaction to form COS$_2^-$ and CO, resulting in the formation of divalent [Cp$_2$V(CO)] and [(Cp$_2$V)$_2$(COS$_2$)] (**7**) in which the COS$_2^-$ ligand is chelated to one metal center through both sulfur atoms and to the second metal center through the O atom.[10]



Scheme 1.

This review covers mostly our work aimed at the reactivity of vanadocene (or the carbonyl vanadium complex [Cp$_2$VCO], another form of the d^2 vanadocene) with polyalkynes, polynitriles, and tris(perfluorophenyl)borane. Materials are also emerging from the chemistry of [VCp$_2$] that illustrate the diversity of its potential applications (Scheme 2). Only the literature dealing with [VCp$_2$] is reviewed.

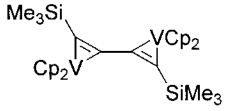


Scheme 2.

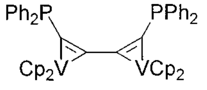
Reactivity of [VCp$_2$] with Polyalkynes

From the reactivity of vanadocene toward C=C and C≡C described above, it appeared to us that we could use the same strategy to prepare new vanadocene systems using polyalkynes R–(C≡C)$_n$–R′ (n = 2–4; R, R′ = Me, tBu, PPh$_2$, SiMe$_3$). One might expect that two identical species possessing one unpaired electron connected by an acetylenic carbon chain could produce different structural and magnetic situations. Synthetic work is facilitated by the solubility of [VCp$_2$] (**1**) and many yne ligands in pentane, a solvent in which crystalline compounds are usually formed.

Treatment of **1** with the diyne R–C≡C–C≡C–R (R = SiMe$_3$, PPh$_2$) resulted in the oxidative addition of **1** to both alkyne bonds and the formation of homobimetallic vanadium complexes [(Cp$_2$V)$_2$(1,2-η:3,4-η-R–C=C–C=C–R)] (**8a**: R = SiMe$_3$; **8b**: R = PPh$_2$) whatever the stoichiometry of the reaction.[11]

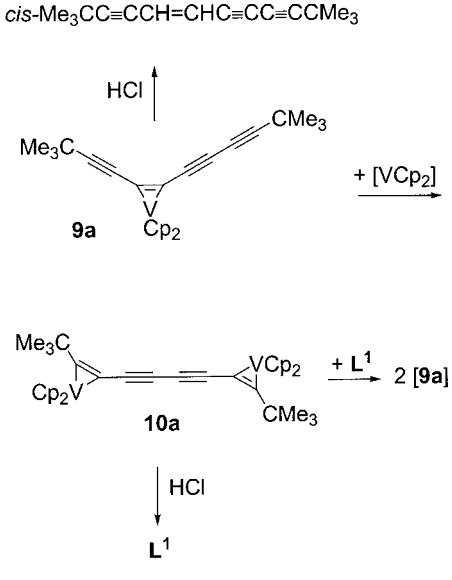


8a



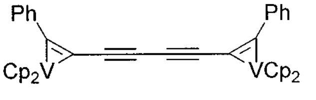
8b

This result encouraged us to pursue the reactivity of **1** with tri- and tetraynes. The reaction of the octatetrayne ligand RC≡C–C≡C–C≡C–C≡CR (**L^1**: R = tBu; **L^2**: R = Ph) is dependent on the substituent R attached to the tetrayne and on the stoichiometry of the reaction (Scheme 3).[12] First, the reaction performed with one equivalent of **1** and **L^1** in pentane gives the organometallic complex [Cp$_2$V(3,4-η-tBuC≡C–C$_2$–C≡C–C≡CtBu)] (**9a**) in which the [VCp$_2$] unit is located at the internal position of the C8 carbon chain, whereas the reaction of two equivalents of **1** with one equivalent of **L^1** in pentane leads to the homodimetallic complex [(Cp$_2$V)$_2$(1,2-η:7,8-η-tBuC$_2$–C≡C–C≡C–C$_2$$t$Bu)] (**10a**). The Cp$_2$V units are nearly *trans* and are located at both extremities of the C8 carbon chain.



Scheme 3.

On the other hand, the reaction of one or two equivalents of **1** with $\mathbf{L^2}$ in toluene gives exclusively the homodimetallic complex $[(Cp_2V)_2(1,2\text{-}\eta{:}7,8\text{-}\eta\text{-}PhC_2\text{–}C{\equiv}C\text{–}C{\equiv}C\text{–}C_2Ph)]$ (**10b**).



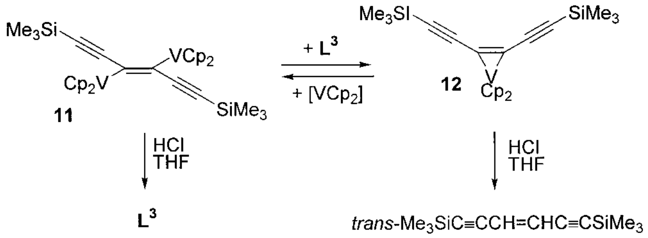
10b

These results offer synthetically attractive but puzzling features as the $[VCp_2]$ unit could migrate reversibly by sliding from an internal 3,4-η position to an external 1,2-η position on the carbon chain of the tetrayne ligand. The shift of the vanadocene unit could be dependent on a dissociation process between $[VCp_2]$ and the ligand in solution or on the existence of an η^4 complex $[Cp_2V(\eta^4\text{-}t\text{Bu}C_4\text{–}C{\equiv}C\text{–}C{\equiv}Ct\text{Bu})]$.[13]

The bond lengths and angles associated with the vanadium–acetylene interaction in **8**–**10** indicate that the acetylene molecule is symmetrically attached to the vanadium atom by two σ-type V–C bonds. This produces a metallacyclopropene structure for the central VC_2 moiety. The different orientation of the Cp_2VC_2 unit could be due to the steric effects of the substituent R ($SiMe_3$, PPh_2, *t*Bu, Ph) on the polyynes. Another difference in the structural aspects is the carbon skeleton of the ligand, which is distorted for **8a** and **10b** whereas all the carbon atoms are nearly coplanar in **8b** and **10a**.

As a result of such a situation, paramagnetic vanadium centers of d^1 electronic configuration could produce different magnetic behavior.[14] The antiferromagnetic interaction was calculated and found to be J = –10.5 and –59.8 cm^{-1} for **8a** and **8b** respectively, and J = –12.5 and –4.1 cm^{-1} for **10a** and **10b**, respectively. The antiferromagnetic interaction for **8b** and **10a** is greater than that for **8a** and **10b**, 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" interaction for the complexes **8b** and **10a**. 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.[6b,6c] This is disfavored in **8a** and **10b**, where the Cp_2VC_2 unit and its magnetic orbital contributions can be considered to be orthogonal.

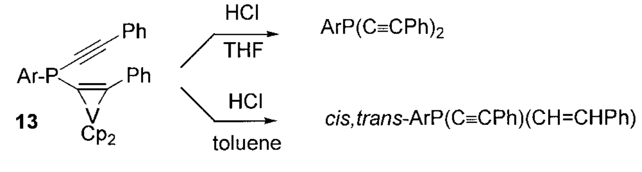
Particular attention was given to the reactivity of **1** with the triyne $Me_3SiC{\equiv}C\text{–}C{\equiv}C\text{–}C{\equiv}CSiMe_3$ ($\mathbf{L^3}$), which gives a crystalline black solid of a homodimetallic d^2-d^2 complex $[(Cp_2V)_2(3,4\text{-}\eta\text{-}Me_3SiC{\equiv}C\text{–}C{=}C\text{–}C{\equiv}CSiMe_3)]$ (**11**; Scheme 4). The main feature of **11** is the bonding mode of the two vanadocene moieties, which are attached to both the internal carbon atoms of the triyne by a single σ-type V–C bond of 2.165 Å. This brings the vanadium oxidation state from +2 to +3 instead of the expected classical V^{IV} that has been observed in all other cases. This unexpected reactivity seems to be due to the odd number of C≡C bonds in $\mathbf{L^3}$. The central C≡C bond of $\mathbf{L^3}$, which is more electron-rich than the other C≡C bonds, may favor the reaction at the central core of the ligand.[15] Variable-temperature magnetic susceptibility measurements have been carried out to confirm the V^{III} homobimetallic d^2-d^2 nature of **11**. The effective moment (μ_{eff} = 4.01 μ_B at 300 K) is consistent with two noninteracting vanadium(III) units, and a weak antiferromagnetism (J = –3.7 cm^{-1}) is observed.



Scheme 4.

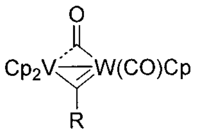
When one equivalent of **1** was treated with only one equivalent of $\mathbf{L^3}$, in pentane, small, brown needles of the vanadium(IV) complex $[Cp_2V(3,4\text{-}\eta^2\text{-}Me_3SiC{\equiv}C\text{–}C{=}C\text{–}C{\equiv}CSiMe_3)]$ (**12**) were obtained (μ_{eff} = 1.9 μ_B). A vanadocene cyclopropene structure could be suggested on the basis of its hydrolysis with HCl (*trans*-$Me_3SiC{\equiv}C\text{–}CH{=}CH\text{–}C{\equiv}CSiMe_3$ was obtained; $\mathbf{L^3}$ is liberated upon hydrolysis of **11** with HCl). Treatment of **12** in C_6D_6 with another equivalent of **1** leads to **11**. A comproportionation reaction between V^{IV} (**12**) and V^{II} (**1**) to give two V^{III} centers (**11**) is probably operative, but a full mechanistic description must await further experimental evidence.

The reaction of the phosphane $ArP(C{\equiv}CPh)_2$ (Ar = 2,4,6-$t\text{Bu}_3C_6H_2$) with one equivalent of **1** in pentane, at room temperature, leads to the formation of the V^{IV} complex $[Cp_2V(\eta^2\text{-}PhC{=}C)P(C{\equiv}CPh)Ar]$ (**13**) as a crystalline product.[16] The reactivity of **13** towards HCl was examined (Scheme 5). Reaction of **13** in THF with HCl gives, selectively, the starting phosphane as the main product, along with a green precipitate of $[Cp_2VCl_2]$. The same reaction performed in toluene leads to the alkenyl-alkynylphosphane (1:1 ratio of *cis* and *trans* isomers), isolated as its sulfur derivative, and $[Cp_2VCl_2]$. The solvents (THF, toluene) could account for the reactivity of **13**. However, the IR and EPR spectra of **13** in these solvents do not show any detectable difference; similar data are observed for both solvents. This observation supports the view that the facile protonation of **13** could occur equally in toluene or in THF, in contrast to the release of the phosphane observed in THF.



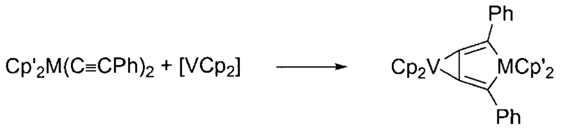
Scheme 5.

Another interesting reactivity is the reaction of $[VCp_2]$ with carbyne complexes. A typical example for the formation of a dimetallic compound containing **1** has been realized with [W(≡CR)(CO)$_2$Cp] (R = 4 Me-C_6H_4), since this complex and alkynes have similar reactivity patterns.[17] The reaction of **1** with the tungsten complex afforded black crystals of [$Cp_2V(\mu$-CR)W(CO)$_2$Cp] (**14**). A weak attachment between **1** and the tungsten complex is observed from the structure, as exemplified by the dissociation of the heterodimetallic complex in solution.



14

Oxidative addition of a diyne of a ligand-stabilized metallocene of a group 4 element, or reaction of an alkyne compound of a group 4 element with a Lewis metal complex, have been reported to give dimetallic complexes.[18] These results showed the way towards heterodimetallic [Ti,V] or [Zr,V] complexes involving the reaction of acetylenic titanium or zirconium compounds with **1**. Reaction of [$(C_5H_4R)_2$M(C≡CPh)$_2$] (M = Ti, R = H; M = Zr, R = H, Me, *t*Bu, $SiMe_3$) with **1** yields the heterobimetallic complex [$Cp_2V(\mu$-η^2:η^4-butadiyne)M$(C_5H_4R)_2$] (Scheme 6).[19,20] The measured magnetic moments show that the formal oxidation state of vanadium has increased from II to IV.

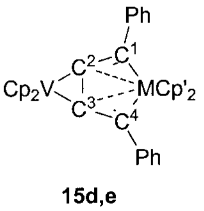


15

15a: M = Ti, Cp' = C_5H_5
15b: M = Zr, Cp' = C_5H_5
15c: M = Zr, Cp' = C_5H_4Me
15d: M = Zr, Cp' = $C_5H_4CMe_3$
15e: M = Zr, Cp' = $C_5H_4SiMe_3$

Scheme 6.

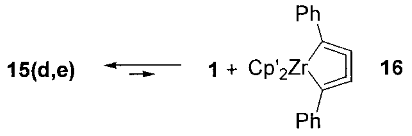
The ease of solving the crystal structure of the series of compounds **15** seems to be very much dependent on the nature and size of the different substituents on the cyclopentadienyl groups of the metal–alkyne compound. Nevertheless, an overall arrangement similar to that observed in the fully resolved structures of **15d** and **15e**, in which the two metal centers are strongly differentiated by the substituents on their respective cyclopentadienyl groups, was found. The vanadium atom adopts a metallacyclopropane environment. The interatomic distances between C^2 and C^3 and their four neighboring atoms (Zr, V, C^1, and C^3 and Zr, V, C^2, and C^4, respectively), and the 360° value for the sum of the angles around C^2 and C^3, indicate that these carbon atoms are planar tetracoordinate carbons (ptC). Most of the ptC-containing transition metal complexes reported to date, mainly by Erker et al., are group 4 homo- and groups 4 and 10 or 13 heterodimetallic complexes.[21]



15d,e

ELF analysis[22] reveals the existence of three multicenter bonds involving the Zr atom and the four carbon atoms of the butadiyne fragment. The existence of electron-sharing interactions between each of the two central carbon atoms of the butadiyne fragment and four neighbors (for example, C^2 interacts with Zr, V, C^1, and C^3) has been established.[20] Both these central carbon atoms are involved in three bonds, two of which are three-center bonds. Therefore, these central carbon atoms may be considered as planar tetracoordinate.

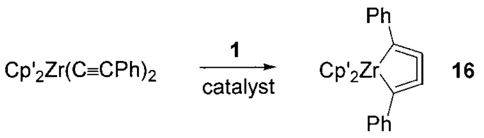
The mechanism of formation of these complexes has been elucidated. Analogous complexes obtained by reaction of [Ni(PPh$_3$)(η^2-PhC≡C–C≡CPh)] and "Cp_2Ti" or "Cp_2Zr" to give heterodimetallic [$Cp_2M(\mu$-η^2:η^4-PhC≡C–C≡CPh)Ni(PPh$_3$)$_2$][23] show the same skeletal (μ-η^2:η^4-PhC≡C–C≡CPh) arrangement as that observed in compounds **15**, and the formation of an intermediate zirconacyclocumulene species [$Cp_2Zr(\eta^4$:1,2,3,4-PhC=C=C=CPh)] was therefore suggested.[23] Some partial dissociation of **15** in solution (estimated by EPR spectroscopy to be ca. 10–20%; Scheme 7) shows the presence of the zirconacyclocumulene species **16**.



Scheme 7.

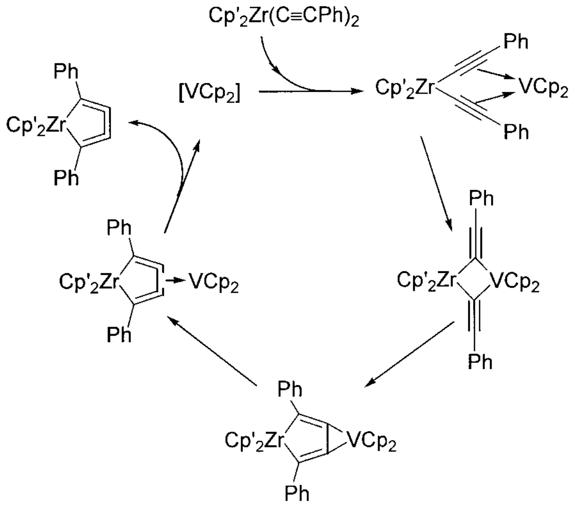
Interestingly, the formation and the reactivity of **16** is governed by the nature of the substituents attached to the alkyne.[18e,24,25] In contrast, attempts to prepare a similar heterodimetallic complex from **1** and [Cp_2Zr(C≡CSiMe$_3$)$_2$] failed.[26] On the other hand, the use of different electron-donating R groups on the Cp ring of the dialkyne zirconocene (H in **15b**, Me in **15c**, *t*Bu in **15d**, and $SiMe_3$ in **15e**) does not change the nature of the resulting heterodimetallic [Zr,V] complex.

The transformation of the dialkynylzirconocene precursors [$(C_5H_4R)_2$Zr(C≡CPh)$_2$] (R = H, Me, *t*Bu, $SiMe_3$) into the corresponding zirconacyclocumulene species **16** in daylight is complete in around four days. Zirconacyclocumulene complexes **16** can also be generated by treating the corresponding dialkynylzirconocene with a catalytic amount of **1** (ratio 10:1) for about two days (this is a shorter time than the same reaction in daylight), which implies the involvement of **1** in forming the zirconacyclocumulene (Scheme 8). Finally, complexes **15d** and **15e** can be generated from the corresponding zirconacumulene by treatment with a stoichiometric amount of **1**.



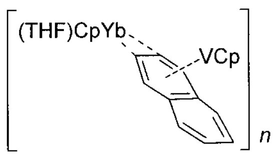
Scheme 8.

The observed reaction between the bis(phenylethynyl-metallocene and -vanadocene and the formation of the heterodimetallic [M,V] compounds can be understood as resulting from the partial transfer of the phenylethynyl group from M to vanadium. Thus, both pathways, i.e. irradiation and/or Cp_2V catalysis, lead to the same zirconacyclocumulene species, and their relative importance in our reactions is difficult to assess. Nevertheless, our results clearly show that, the two C≡CPh alkynyl moieties of [$Cp'_2Zr(C≡CPh)_2$] undergo a C–C coupling, vanadocene being actually involved in the mechanism of formation of compounds **8** through a transfer of the C≡CPh moiety from Zr to V, and that a zirconacyclocumulene species is a key intermediate in this mechanism. The formation of the zirconacyclocumulene species may proceed through the catalytic cycle proposed in Scheme 9.



Scheme 9.

Other dimetallic complexes containing a vanadium atom have been prepared from **1**. Reduction of **1** with naphthalenylpotassium leads to a suitable source of the CpV fragment from isolated [$CpV(C_{10}H_8)$].[27] Reduction of **1** to vanadium(0) by naphthalenylytterbium [$(C_{10}H_8)Yb(THF)_2$] in THF generates the polymeric, two-dimensional, multidecker complex [$CpV(\mu\text{-}\eta^6{:}\eta^2\text{-}C_{10}H_8)Yb(THF)Cp]_n$ (**17**),[28] the molecular structure of which consists of infinite zig-zag chains formed by CpYb moieties with one CpV(η^6-$C_{10}H_8$) unit η^2-coordinated through the naphthalene to each Yb atom.



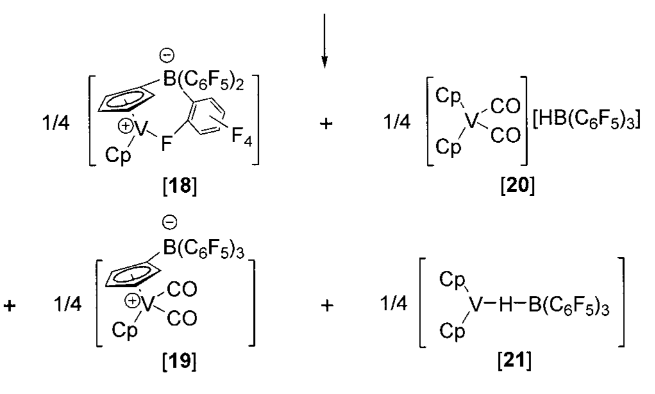
17

The reactivity of **1** towards the cobalt complex [$Co_2(CO)_8$] was also re-examined and the salt [$Cp_2V(CO)_2$][$Co(CO)_4$] was isolated.[29]

Reactivity of [Cp_2VCO] – Another Source of Vanadocene

Turning now to another source of vanadocene, carbonylbis(cyclopentadienyl)vanadium(II) [Cp_2VCO] is easily obtained by treatment of **1** with CO.[30] A few reactivity studies have been conducted with olefins[31] and dinitrogen oxides[32] in which, in the absence of X-ray analysis, IR spectroscopy plays an important role in the characterization of the resulting compounds.

In light of the tremendous amount of work on the reactivity of tris(perfluorophenyl)borane [$B(C_6F_5)_3$] with organometallic complexes and as an activator in olefin polymerization,[1a,33] we explored the reactivity of $B(C_6F_5)_3$ towards our vanadium compounds.[34] In this context, the reactivity of [Cp_2VCO] and $B(C_6F_5)_3$ was studied as an extension of our previous report showing that a related dicarbonyltitanocene gives the acylborane complex [$Cp_2Ti(CO)\{\eta^2\text{-}OCB(C_6F_5)_3\}$] by attack of the Lewis acid at the carbonyl carbon atom.[35] Although the reaction with [Cp_2VCO] resulted in the formation of four complexes, all of them were fully characterized by X-ray structure elucidation after careful separation by hand.[36] Particularly interesting and intriguing is the formation of the zwitterionic, ring-borylated vanadium(III) complex [$(Cp)\{C_5H_4B(C_6F_5)_3\}V$] (**18**) and [$(Cp)\{C_5H_4B(C_6F_5)_3\}V(CO)_2$] (**19**), and of the salt [$Cp_2V(CO)_2$][$HB(C_6F_5)_3$] (**20**) and the hydride [$Cp_2V(\mu\text{-}H)B(C_6F_5)_3$] (**21**).[37] In **18**, the borane is linked to one of the cyclopentadienyl rings, and an *ortho*-fluorine atom of one perfluorophenyl group of the borane is coordinated to the vanadium center. Complex **21** can be described as a vanadocene hydride stabilized by the borane. Formation of the vanadium(IV) hydride [$(Cp)\{C_5H_4B(C_6F_5)\}_3VH(CO)$] by the electrophilic addition of the borane at the Cp ring, followed by redox and disproportiona-

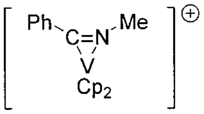


Scheme 10.

tion reactions, is thought to account for these results (Scheme 10).

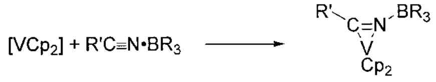
Reactivity of [VCp$_2$] with Nitrile Ligands

The literature reveals that the reaction between vanadocene and the nitrilium salt [RC≡NMe][BF$_4$] (R = Me, Ph) produces iminoacyl vanadocene; the ionic complex [Cp$_2$V{η^2-(Ph)C=NCH$_3$}][BF$_4$] (**22**) was characterized by an X-ray structure determination.[38] On the other hand, adducts of nitriles RC≡N with a Lewis acid have been known for a long time and have been widely studied.[39] From the large increase in the ν(C≡N) stretching frequency induced by complexation with a strong Lewis acid, it was found that the polarity of the nitrile group is increased in the complex.[40] Considering that the Lewis acid could modify the reactivity of the C≡N bond, the RCN·Lewis acid adduct can be considered as a ligand containing an "activated" C≡N bond.



22

Addition of various BR$_3$ Lewis acids to acetonitrile and trifluoro-*p*-tolunitrile (R′C≡N) in toluene to form the expected RC≡N·BR$_3$ adduct in situ, followed by the addition of **1** in toluene, gives, after two to three days, the crystalline borane adduct of the vanadaazirine complexes [Cp$_2$V{η^2-(R′C=N·BR$_3$)}] (**23** and **24**; Scheme 11).



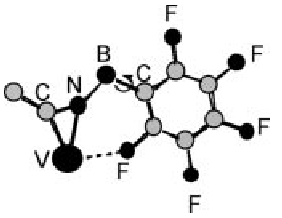
23, 24

	23	**24a**	**24b**	**24c**	**24d**	**24e**
R'	CH$_3$	F$_3$C(C$_6$H$_4$)	F$_3$C(C$_6$H$_4$)	F$_3$C(C$_6$H$_4$)	F$_3$C(C$_6$H$_4$)	F$_3$C(C$_6$H$_4$)
R	C$_6$F$_5$	C$_6$F$_5$	2,6-F$_2$C$_6$H$_3$	3,4,5-F$_3$C$_6$H$_2$	Ph	Cl

Scheme 11.

These complexes are paramagnetic due to the presence of one unpaired electron, in agreement with the spin value for a formally vanadium(IV) (d^1) system. The main feature of the X-ray structures is that the nitrile group attached to the vanadium atom by two σ-type V–C and V–N bonds of 2.04 Å (av.) and 2.08 Å (av.). This produces a metallacycloimine structure. Changing B(C$_6$F$_5$)$_3$ to B(C$_6$H$_5$)$_3$ or BCl$_3$ in the vanadaazirine(IV) complex adduct produces slight differences in the VNC cycle, in which a C=N double bond is now formed. In contrast, the B–N distances are modified according to the expected Lewis acidity of the boranes [BCl$_3$ > B(C$_6$F$_5$)$_3$ > BPh$_3$] and in agreement with the $\nu_{C=N}$ frequencies observed for these complexes.

X- and Q-band EPR studies were carried out in THF solution. An expected eight-line pattern was observed for **24c**–**e** [average: g = 1.998; $A(^{51}V)$ = 41 G]. For **23** and **24a**,**b**, the formation of a doublet of octets was observed. An additional hyperfine coupling of the unpaired electron of the vanadium atom with a fluorine atom of the borane B(C$_6$F$_5$)$_3$ is responsible for the second coupling constant [average: g = 1.997, $A(^{51}V)$ = 42 G; $a(^{19}F)$ = 15 G]. This fact can be explained by the absence of any fluorine atom in the *ortho* position of the boranes in **24c**,**d**. The presence of two fluorine atoms in the *ortho* position of the phenyl rings in **23** and **24a**,**b** contributes to the C–F···V interaction and a subsequent $a(^{19}F)$ hyperfine coupling is observed. A careful investigation of the X-ray structures of **23** and **24a**,**b** does not indicate such an interaction in the solid state. However, a dynamic process involving the rotation of B–C and N–B allows the fluorine atom to approach the vanadium center in solution. A model can be drawn to take into account this flexibility, and the best situation for a C–F···V interaction is a plane containing the V–C(1)–N–B–C$_{ipso}$(C$_6$F$_5$) atoms where one *ortho* fluorine atom of the fluorophenyl ligand could approach the vanadium center by the formation of a six-membered ring (Scheme 12). Moreover, the presence of a doublet signal indicates the retention of only one V···F coordinative bond in solution. These results support the view that the *ortho* fluorine atom of the phenylborane interacts with the vanadium.

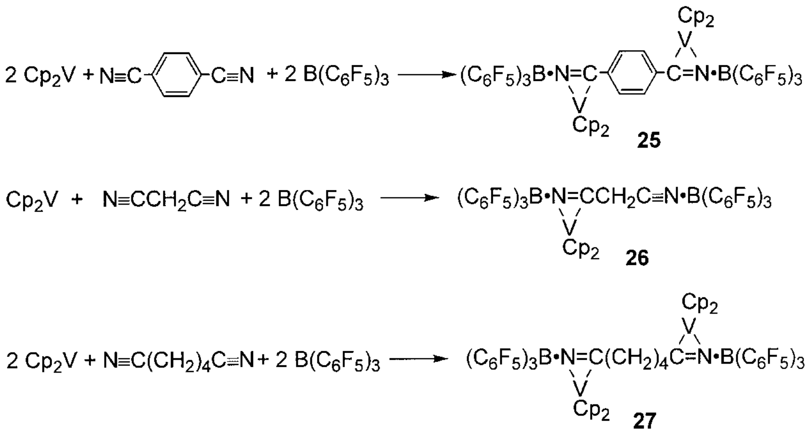


Scheme 12.

It is remarkable that the nitrile RC≡N can react with the borane BPh$_3$ in the presence of **1**. In the absence of **1**, the IR spectra of a mixture of the nitrile F$_3$CC$_6$H$_4$C≡N and BPh$_3$ (1:1 or 1:5 ratio) in toluene do not show any change in the position of the ν_{CN} absorption due to an eventual formation of the borane–Lewis acid adduct. Nevertheless, it is clear that an undetectably small amount of the adduct is formed, which allows the formation of **24d**.

In attempts to synthesize a bimetallic vanadium d^1-d^1 complex with a potential magnetic interaction between the two metal centers,[41] the first ligands of choice were 1,4-benzene dicarbonitrile N≡C–(C$_6$H$_4$)–C≡N, malononitrile N≡CCH$_2$C≡N, and adiponitrile N≡C(CH$_2$)$_4$C≡N. Microcrystalline, blue-violet solids of [(VCp$_2$)$_2${η^2:*C*,*N*-(C$_6$F$_5$)$_3$B·N=C(C$_6$H$_4$)C=N·B(C$_6$F$_5$)$_3$}] (**25**), [VCp$_2${η^2:*C*,*N*-(C$_6$F$_5$)$_3$B·N=C–CH$_2$C≡N·B(C$_6$F$_5$)$_3$}] (**26**), and [(VCp$_2$)$_2${η^2:*C*,*N*-(C$_6$F$_5$)$_3$B·N=C(CH$_2$)$_4$C=N·B(C$_6$F$_5$)$_3$}] (**27**), respectively, were isolated (Scheme 13).

The X-band EPR spectra of **25**–**27** in THF were recorded and the formation of a doublet of octets was observed. Coupling of the unpaired electron of the vanadium atom with the ^{51}V (I = 7/2) nucleus and the *ortho*-fluorine atoms of the borane B(C$_6$F$_5$)$_3$, via a C–F···V interaction, give rise to these spectra [average: g = 1.996, $a(^{51}V)$ = 43 G, $a(^{19}F)$



Scheme 13.

= 17 G]. Complexes **25** and **27** were also studied by variable-temperature magnetic susceptibility measurements resulting from homobimetallic d^1-d^1 situations. Unfortunately, these paramagnetic d^1-d^1 systems do not present any antiferromagnetic interaction due to the presence of a long sp^3 alkyl chain when adiponitrile is used (in **27**) and to a suggested disfavored orientation of the VCp_2CN units within the $NC(C_6H_4)CN$ ligand (in **25**). This latter situation has already been observed in the case of **8b** and **10b**, where the dihedral angle between both Cp_2VC_2 units is nearly 110–120° and thus prevents a favorable "in-plane π-type" geometry in the molecule.[11]

[VCp$_2$] as a Source for VC-Containing Ceramics

Transition metal nitrides or carbides, like other ceramic materials, show outstanding physical and chemical properties. They are usually prepared by reaction of the corresponding metal halides with nitrogen and ammonia, and sometimes in the presence of hydrogen. These reactions have to be carried out at high temperature, usually above 1000 °C. Such drastic conditions restrict applications such as the protective coating of materials whose mechanical properties are sensitive to high temperature, i.e. steel or materials for electronics. The use of coordination compounds as organometallic precursors allows the preparation of thin-film ceramic materials by the so-called organometallic chemical vapor deposition (OMCVD), which is a process that involves much lower temperatures.[42] Compound **1** is a suitable precursor for CVD of vanadium carbide (VC). The precursor sublimes at 60 °C/20 Pa and has a sufficient vapor pressure under these conditions. Films containing crystalline vanadium carbide (VC) have also been deposited from **1** by plasma-assisted CVD (PACVD).[43]

Compound **1** was also selected for the preparation of the quaternary ceramic system vanadium-titanium carbonitride,[44] which is a solid solution though to exhibit better mechanical properties than those of the binary ones TiN, TiC, VN, and VC, by OMCVD.[45] To reach this goal, appropriate molecular organometallic precursors are needed. The most elegant approach, but maybe not the most efficient, could be the use of a single precursor containing all the desired elements. However, to date, such molecules are not known.

An introduction to this type of molecule was provided by the dimetallic [Ti,V], complex described above by reaction of [$Cp_2Ti(C{\equiv}CPh)_2$] with **1**. However, this molecule is not suitable for OMCVD due to its poor volatility.[46] Therefore, the use of pairs of independent precursors was investigated, each precursor being the source of the desired elements, for example TiN and VC or TiC and VN. Moreover, as the pairs of precursors are introduced simultaneously into the CVD reactor, they should exhibit compatible thermal behaviors. Given the applied aspects of this work, the selection of the precursors should rest on criteria based on industrial and economic grounds. Among the several VC precursors studied for this purpose, **1** (under H_2, at 700 °C in a cold wall reactor) yields 13-µm-thick, crystallized, vanadium carbide films which were characterized by XRD (X-ray diffraction) and EPMA/WDS (electron probe microanalysis with wavelength-dispersive spectroscopy).[47] The influence of deposition rate and grain size on the composition of the deposits was investigated by varying three factors: the substrate temperature, the hydrogen carrier flow rate, and the distance between the substrate and the precursor handling crucible. The residence time of the gaseous species in the reactor was found to be an important factor, leading to a maximum of the deposition rate. Even when drastic conditions are applied (high purity hydrogen carrier gas) the use of a low temperature is not thermodynamically in favor of the formation of carbides over that of oxides, and the high C-to-metal ratio in the precursor molecule often leads to contamination of the films by graphitic carbon. Therefore, it is worth noting that *tert*-butyl-substituted vanadocene [$V(C_5H_4\text{-}t\mathrm{Bu})_2$] was shown to be an excellent precursor for the preparation of crystalline VC thin films not contaminated by graphitic carbon or oxygen.[48] These films were fully characterized by XRD, scanning electron microscopy, X-ray photoelectron spectroscopy, and EPMA/WDS. Within the "pairs of precursors" approach it should be noted that another vanadium derivative, namely [Cp_2VMe_2], and [$CpTiCl_2(NSiMe_3)_2$] afford (Ti, V, C, N)-containing films.[49]

[VCp_2]: A Reducing Agent for Chloride Organometallic Precursors to Colloids

The use of **1** as a reducing agent in the fabulous area of nanoparticles must be cited. The past decade has demonstrated the importance of the role of colloids in various catalytic reactions, primarily for hydrogenation of arenes. Different synthetic pathways are presently studied to obtain various types of colloids displaying a controlled size and chemical environment.[50] The most popular method for the preparation of noble metal particles involves reduction of chloride precursors by various reducing agents, for example refluxing alcoholic solutions in the presence of a polymer. The role of vanadocene [VCp_2] as an organometallic reducing agent to prepare metal colloids embedded in a PVP polymer matrix [PVP: poly(vinylpyrrolidone)] has been successfully demonstrated in the case of $FeCl_2$, [$Rh(C_2H_4)_2Cl]_2$, and [$Pd(\eta^3\text{-allyl})_2Cl]_2$ to give Fe, Rh, and Pd nanoparticles, respectively.[51–53] This unusual synthetic organometallic route allows the preparation of colloids from organometallic complexes containing chloride group(s) (Scheme 14).

$$2\,[VCp_2] + FeCl_2 \xrightarrow{PVP} [Fe^0(PVP)] + 2\,(Cp_2VCl)$$

$$[VCp_2] + MCl(L)_x \xrightarrow{PVP} [M^0(PVP)] + (Cp_2VCl) + L_x$$

$$MCl(L)_x = [Rh(\mu\text{-}Cl)(C_2H_4)_2]_2,\ [Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)_2]_2$$

Scheme 14.

The reaction of a THF solution of [$Rh(C_2H_4)_2Cl]_2$, [$Pd(\eta^3\text{-allyl})_2Cl]_2$, or a solid suspension of $FeCl_2$ with a stoichiometric amount of [VCp_2] per chloride atom in the presence of poly(vinylpyrrolidone) (K30-PVP; average molecular weight: 40000) as protecting polymer, at room temperature, leads to metal colloids dispersed in PVP and isolated as the black solid [M-PVP]. A low-magnification TEM micrograph registered for each solid shows that the particles are well dispersed. The HREM micrograph evidences fringes in the particles. The regular periodicity of the fringes allows the determination of the fcc structure of the particles. From $FeCl_2$, big agglomerates of Fe particles with diameters ranging from 50 to 200 nm are present in which individual nearly 8-nm-diameter nanoparticles are observed. All these individual grains have a common orientation inside one large Fe grain, as observed by HRTEM experiments.[51] A relatively narrow size distribution is observed for Rh particles, with a mean diameter of about 1.3 nm. Structural characterization of the metal colloids by wide-angle X-ray scattering (WAXS) was performed in the solid state on the same batch that was used for the TEM experiments, using procedures previously validated for colloids in PVP. This technique, in which the radial distribution function (RDF) gives the M–M distances, confirms the fcc structure of the particles. Structural characterization of the rhodium colloids by WAXS was consistent in size and structure with a proposed model, a small 55-atom cuboctahedron.[52] The size of the Pd particles shows a mean diameter of about 1.8 nm with a relatively large size distribution. The coherence length can be evaluated to be 2 nm, in agreement with TEM measurements.[53] The same RDF was observed when solids [Rh-PVP] and [Pd-PVP] were treated with O_2 or CO (20 bar, 4 d). With O_2, the RDF gives direct evidence of the absence of significant oxidation of the solid sample, at least in the core of the nanoparticles. The concentration of metal embedded in the polymer can be modulated as a function of the different amounts of PVP added (2% to 13% in M weight).

The catalytic potential of the [Rh-PVP] and [Pd-PVP] nanoparticles, which are soluble in alcoholic solvents as well as in water, has been explored in heterogeneous and biphasic conditions, as well as ionic liquids, for the hydrogenation of different types of substrates (benzene, quinoline, adiponitrile, aromatic nitro compounds, ...).[54]

The main advantage of this [VCp_2] method for reducing chloride-containing organometallic precursors to nanoparticles is the availability of the organometallic complexes $M^I(L)_x$ of groups 8–10. Large-scale synthesis of nanoparticles embedded with PVP can be performed and their use in different catalytic processes from the same batch is possible, thus allowing kinetic measurements under various experimental conditions.

Concluding Remarks

Throughout this review we have mainly reported the isolation and characterization of various vanadocene complexes. Importantly, all pathways have been confirmed by a structural elucidation of the molecules present in the reaction. We have to point, again, this necessity to ensure the chemical nature of the different species when paramagnetism, disproportionation, and redox reactions are possible due to the nature of the vanadium center. Indeed, starting from divalent vanadocene different redox reactions are observed with formation of V^{III} and V^{IV} species. Vanadocene has been shown to react with various poly-ynes, and some similarities were observed with related titanocene or zirconocene chemistry. Their intrinsic reactivity towards small organic molecules has not yet been explored but we can predict a high chemical potential for all these compounds. On the other hand, the incorporation of two paramagnetic centers along a chain constitutes a challenge in the realization of new homodimetallic systems that are able to convey magnetic coupling. The reactivity with nitriles and polynitriles could constitute a new approach to the fascinating area of molecular magnets developed by Miller from TCNE and TCNQ with [$V(CO)_6$] or [$V(C_6H_6)_2$].[55] Indeed, some research on TCNE with **1** in the presence of a borane is in progress in our group.

The role of vanadocene as a source of vanadium carbide (VC) or as a reducing agent for the formation of metal nanoparticles seems an efficient starting point for expending the number of new applications in the ever-growing field of advanced materials chemistry.

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