

Ring-Slipped (2,2'-Bipyridine)(η^3 -cyclopentadienyl)(η^5 -cyclopentadienyl)-vanadium(II) and Its Oxidation to (2,2'-Bipyridine)bis(η^5 -cyclopentadienyl)-vanadium(III) Tetraphenylborate

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Reaction of vanadocene(II) (**4**) with 2,2'-bipyridine (**5**) leads to (2,2'-bipyridine)vanadocene(II) (**6**), exhibiting a η^3, η^5 -metallocene unit, proved by X-ray diffraction. By selective one-electron oxidation employing $[\text{Cp}_2\text{Fe}]\text{BPh}_4$ salts, the cationic (2,2'-bipyridine)vanadocene(III) derivative **7** is formed. It is characterized by a classical bent bis(η^5 -cyclopentadienyl)va-

nadium(III) structure. Characteristic structural details comparing changes in the oxidation states are discussed. The ring-slip parameters are compared to those of tungsten and other vanadium complexes.

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Introduction

Since the synthesis and characterization of ferrocene by Fischer and Wilkinson in 1952 the cyclopentadienyl unit has become one of the most important ligands in organometallic chemistry.^[1,2] In addition to the common η^5 -coordination mode (a), η^3 - (b), η^1 - (c), ionic (d) and bridging forms (e) are known (Figure 1).^[3]

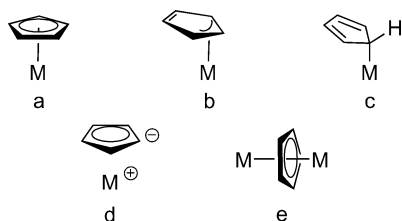


Figure 1. The most common of about ten bonding modes of the Cp ligand: (a) η^5 , (b) η^3 , (c) η^1 , (d) ionic, (e) bridging.

Bonding modes of special interest are η^3 -Cp and η^1 -Cp due to their interconversion chemistry, the so-called “ring slippage”.^[3] Whereas the first η^1 -Cp transition-metal complex was reported only three years after the characterization of ferrocene,^[4] the η^3 -coordination mode was discussed for several years. Generally, Cp-ligand isomerizations often play a significant role in the chemistry of their metal complexes.^[5] Prominent examples of ring-slipped compounds are given in the case of complexes exhibiting an electron excess (> 18) like dicarbonyl(η^3 -cyclopentadienyl)(η^5 -cyclopentadienyl)tungsten (**1**),^[6] or particularly for indenyl complexes such as those shown in Figure 2.^[7]

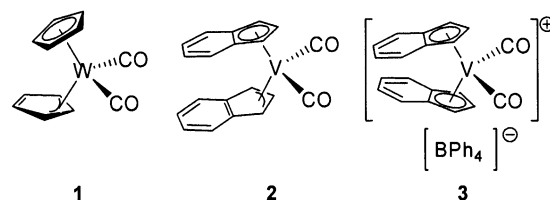


Figure 2. Prominent examples of structurally characterized ring-slipped complexes: dicarbonyl(η^3 -cyclopentadienyl)(η^5 -cyclopentadienyl)tungsten (**1**),^[6] dicarbonyl(η^3 -indenyl)(η^5 -indenyl)vanadium(II) (**2**)^[7a] and the oxidized “non-slipped” form dicarbonylbis(η^5 -indenyl)vanadium(III) tetraphenylborate (**3**).^[7b]

On the other hand, due to their electronic and steric versatility, aromatic *N*-heterocycles play an important role as classical ligands in coordination chemistry,^[8] as bridging ligands in binuclear derivatives^[9] and as building blocks for supramolecular compounds.^[10] Beyond their capability to connect metal centres by forming ligand-to-metal bonds, they provide the opportunity of π -backbonding and thereby may affect delocalization and transport of electrons.^[11] We have investigated the behaviour of bis(azine)s in the coordination sphere of low-valent titanium complexes, leading to bi-,^[12] tri-,^[12a,13] tetra-,^[12a,14] and up to octanuclear derivatives,^[12a] accompanied by spontaneous C–C coupling reactions resulting from the strong reducing properties of titanium(II).^[12a,13] Here we wish to report an example of the behaviour of 2,2'-bipyridine in the coordination sphere of vanadium(II) and vanadium(III). Floriani et al. described the formation of a $[\text{Cp}_2\text{V}(2,2'\text{-bipyridine})]$ derivative. However, because of the lack of structural data the authors assumed a monodentate coordination mode for the 2,2'-bipyridine ligand ($17e^-$ complex) (Figure 3).^[15]

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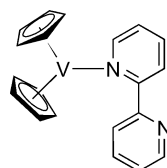
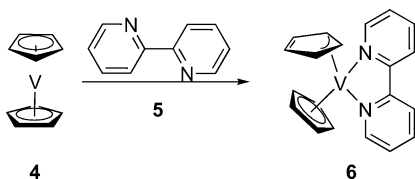


Figure 3. Assumed structure of $[\text{Cp}_2\text{V}(2,2\text{-bipyridine})]$ by Floriani et al.^[15]

Results and Discussion

First at all, we reproduced the reaction of vanadocene(II) (**4**) and 2,2'-bipyridine (**5**)^[15] extended by the structural characterization of the reaction product **6**. In contrast to the proposed monodentate structure, the 2,2'-bipyridine ligand was found to act as a typical chelating unit. Additionally, one of the Cp rings exhibit an η^3 -coordination mode (ring slippage) (Scheme 1). Upon oxidation of complex **6** by ferrocenium tetraphenylborate, the Cp ring flips back to η^5 -coordination to form (2,2'-bipyridyl)bis(η^5 -cyclopentadienyl) vanadium(III) tetraphenylborate (**7**) (Scheme 2). A number of slip parameters were applied to these structures, and the results were compared with given examples of ring-slipped complexes such as **1** and **2**.



Scheme 1. Formation and structure representation of compound **6**.

Synthesis and Characterization of (2,2'-Bipyridine)(η^3 -cyclopentadienyl)(η^5 -cyclopentadienyl)vanadium(II) (**6**)

Vanadocene(II) (**4**) and 2,2'-bipyridine (**5**) were dissolved in *n*-hexane, and the solution was stirred at room temperature overnight. The colour of the solution changed immediately from violet to black. The solution was cooled to -70°C , and complex **6** precipitated in form of black crystals (53%).

Suitable crystals for X-ray diffraction became available by crystallization at -16°C . Complex **6** crystallizes in the space group $R\bar{3}$; the trigonal unit cell contains 18 molecules of the compound. X-ray diffraction of these black flat prisms confirmed the bidentate chelate ligation of the 2,2'-bipyridine (**5**). However, one of the Cp rings offered only η^3 -coordination. This should be necessary to confirm the $18e^-$ rule in **6**. If both Cp rings were η^5 -coordinated, the complex would contain 19 electrons. With one η^3 -coordinated Cp ring, the preferred $17e^-$ structure of **6** was formed. The ORTEP plot (Figure 4) significantly shows the slippage of one Cp ring with respect to the other.

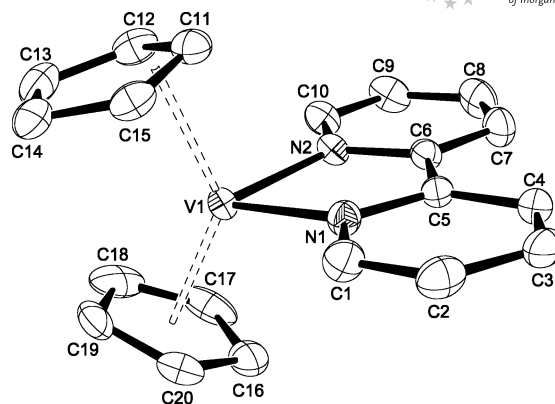


Figure 4. ORTEP plot of the solid-state molecular structure of compound **6**. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: V1–N1 2.036(1), V1–N2 2.053(1), C5–C6 1.423(2), V1–Ct 2.01, N–V–N 76.89(5).

Furthermore the C11 atom slightly turns out of the plane formed by C12–C15 to distort the otherwise rather aromatic planar Cp ring to an envelope-like conformation. The angle Ω between plane C12–C13–C14–C15 and plane C11–C12–C15 is 8.3° and is defined by Faller, Crabtree and Habib as one of a number of slip parameters (Figure 5).^[16]

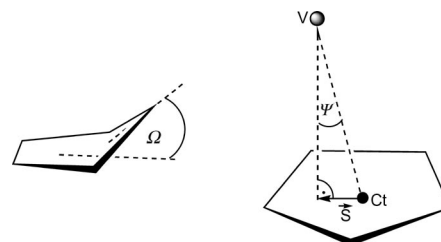


Figure 5. Graphical definition of the dihedral angle Ω , the slip vector $\vec{S}$, whose norm is the slip distortion A , and the angle slip Ψ , which is the angle between the plane normal and the centroid-metal vector.

This distortion seems to be typical for η^3 -coordinated cyclopentadienyl ligands, as can be seen in Table 1.^[6,16] In contrast to that, the η^5 -coordinated Cp ring shows an angle Ω of only 1.2° between plane C17–C18–C19–C20 and plane C16–C17–C20, leading to the expected planarity of a Cp ring.

From the average of the M–C distances a further slip parameter, $\overline{\Delta\text{M}-\text{C}}$, can be calculated.^[16] This parameter is a direct verification for the η^3 -coordinated Cp ligand. While every carbon atom is almost equidistant from the metal in η^5 -Cp, so that $\overline{\Delta\text{M}-\text{C}}$ is very small, in η^3 -Cp two carbons have a significantly elongated distance to the metal centre. This confirms the molecular structure of **6** in which $\Delta\text{M}-\text{C}$ of the η^5 -Cp is $0.04\text{ \AA}$, whereas the η^3 -Cp has a much higher value of $0.56\text{ \AA}$. Also the slip distortion A and the angle slip Ψ (Figure 5) show clear indications for η^3 -coordination modes.^[16]

For the 2,2'-bipyridine complex **6** and comparable derivatives (**1**,^[6]**2**^[7a]) selected structural ring-slip parameters are summarized in Table 1.

Table 1. Slip parameters (see Figure 5) for compounds **6** and **7** and similar complexes.

Compound		Slip parameters				Ref.
		$\Delta = \mathbf{S} $ [Å]	Ψ [°]	$\overline{\Delta M-C}$ [Å]	Ω [°]	
1	$[\eta^3]$	0.928	23.4	0.62	19.7	[6,16]
	$[\eta^5]$	0.076	2.2	0.10	(4.9) ^[a]	
2	$[\eta^3]$	0.798	20.9	0.56	—	[7a]
	$[\eta^5]$	0.157	4.6	0.13	—	
6	$[\eta^3]$	0.876	21.9	0.56	8.3	[c]
	$[\eta^5]$	0.063	1.5	0.04	1.2	
7 ^[b]	$[\eta^3]$	0.110	3.2	0.03	0.1	[c]
	$[\eta^5]$	0.110	3.2	0.03	0.1	

[a] The uncertainty for this value is large. [b] Slip parameters of only one Cp were calculated because of the disordering of the others. [c] This work.

The V–N bonds of **6** are shortened relative to the only known (2,2'-bipyridine)vanadocene complex (2,2'-bipyridine)bis(η^5 -cyclopentadienyl)vanadium(IV) ditriflate (**8**) of Ghosh et al.,^[17] but the shortening of the C5–C6 bond of the 2,2'-bipyridine (**5**) in the complex relative to the free **5**^[18] is more significant (Table 2). This shortening suggests the reduced nature of the ligand in complex **6**. In the neutral vanadium(II) complex **6** and the cationic vanadium(III) derivative **7** the bipyridine ligand is nearly located in the equatorial plane (N–V–N) with a deviation of 5.35° (**6**) and 2.25° (**7**), respectively. These values are significantly lower than the corresponding value of 23.09° in [(Cp)₂Ti(2,2'-bipyridine)].^[19]

Table 2. Selected bond lengths [Å] for **5**, **6**, **7** and **8**.

	5	6	7	8
V1–N1	—	2.036(2)	2.161(2)	2.129(2)
V1–N2	—	2.053(1)	2.165(2)	2.128(2)
C5–C6	1.490(3)	1.423(3)	1.466(4)	1.465(4)

Synthesis and Characterization of (2,2'-Bipyridine)bis(η^5 -cyclopentadienyl)vanadium(III) Tetraphenylborate (**7**)

Direct oxidation of **6** with ferrocenium tetraphenylborate leads to products that are insoluble in common solvents. So recrystallization of red-violet ionic complex **7** was not successful. In contrast to that, vanadocenium tetraphenylborate (**9**), prepared by the reaction of **4** with ferrocenium tetraphenylborate,^[20] is passably soluble in thf. But when **5** was added directly to **9**, an amorphous powder precipitated, too.

A successful procedure is layering of an *n*-hexane solution of **5** on a thf solution of **9** to form large red-violet needles of **7**, which were suitable for X-ray diffraction, in 44% yield at the phase interface (Scheme 2). The ionic compound crystallizes in the monoclinic space group *P*2₁/*c*; the unit cell contains eight ion pairs and there are two independent ion pairs in the asymmetric unit. Three of four Cp rings in an asymmetric unit are disordered; however, both rings in the cation are η^5 -coordinated as can be seen in the ORTEP plot in Figure 6.

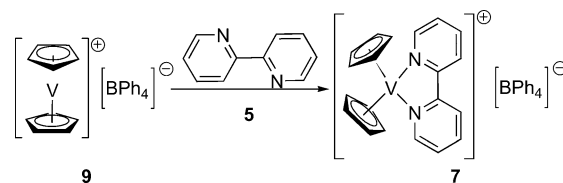
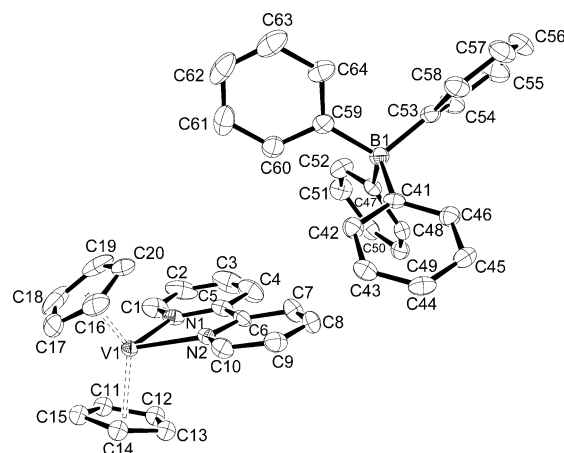
Scheme 2. Formation of compound **7**.

Figure 6. ORTEP plot of the solid-state molecular structure of **7** showing one ion pair of the asymmetric unit with idealized Cp rings, which are disordered in two positions and refined with isotropic coupled displacement parameters. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: V1–N1 2.161(2), V1–N2 2.165(2), C5–C6 1.466(4), V1–Ct 1.95, B1–C 1.66, Ct–V1–Ct 135.4, N1–V1–N2 74.2.

Because of the disordering, the slip parameters for only one Cp ring, which is not disordered, were calculated (Table 1). The parameters are in good accordance with the slip parameters of the η^5 -coordinated Cp rings of the other compounds in Table 1.

The V–Ct distances are insignificantly shorter than those in complex **6** (1.95 Å), but the V–N bonds as well as the connecting C5–C6 bond between the two heterocycles are lengthened relative to those in complex **6** (Table 2). In this case the heterocyclic ligand is not reduced by the metal centre. The V–N bond of **7** is a little longer relative to that in compound **8**, but the C5–C6 bond is almost equal in length (Table 2).^[17]

Conclusions

The reaction of **4** with **5** formed the 17e[−] chelate complex (2,2'-bipyridine)(η^3 -cyclopentadienyl)(η^5 -cyclopentadienyl)-vanadium(II) (**6**) with one η^3 -slipped Cp ring to avoid a 19e[−] complex formation. Upon formal oxidation of **6**, the Cp ring flipped back to an η^5 -coordination mode, forming the ionic 18e[−] species (2,2'-bipyridine)bis(η^5 -cyclopentadienyl)vanadium(III) tetraphenylborate (**7**). To the best of our knowledge this is one of the rare examples of structurally characterized (cyclopentadienyl)vanadium complexes with a structurally verified η^3 -ring-slippage.

Experimental Section

Reagents and General Techniques: All operations were performed in a nitrogen atmosphere with rigorous exclusion of oxygen and moisture by using glovebox and Schlenk techniques. All chemicals used were of reagent grade or higher purity; they were purified according to standard protocols. Solvents were distilled from Na/K alloy and benzophenone under nitrogen. Chemical ionization (CI) mass spectra were taken with a Finnigan-MAT 95 spectrometer. Isobutane was used as the ionization gas. Electrospray ionization (ESI) mass spectra were recorded with a Finnigan-LCQ spectrometer. High-resolution electrospray ionization (HR-ESI) mass spectra were measured with a Micromass Premier quadrupole-time-of-flight (Q-TOF) instrument. IR spectra were recorded with a Bruker VECTOR 22 spectrometer by using KBr pellets. Elemental analyses were carried out by the Analytische Laboratorien GmbH, Lindlar (Germany). Melting points were determined by using a "Mel-Temp" by Laboratory Devices, Cambridge. 2,2'-Bipyridyl (**5**) was purchased from Merck. Vanadocene (**4**)^[21] and vanadocenium tetraphenylborate (**9**)^[20] were prepared according to literature procedures.

X-ray Diffraction: Single-crystal experiments were carried out with a STOE IPDS diffractometer with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct phase determination and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.^[22] Crystallographic details are given in Table 3. CCDC-649843 (**6**) and -649844 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal structure data for compounds **6** and **7**.

	6	7
Empirical formula	C ₂₀ H ₁₈ N ₂ V	C ₄₄ H ₃₈ BN ₂ V
Formula weight	337.30	656.51
Colour	black	blue-violet
Crystal dimensions [mm]	0.42 × 0.31 × 0.08	0.45 × 0.34 × 0.13
Crystal system	trigonal	monoclinic
Space group	$R\bar{3}$	$P2_1/c$
A [Å]	19.0200(7)	19.1779(10)
B [Å]	19.0200(7)	18.4200(8)
C [Å]	23.3811(11)	19.2887(10)
α [°]	90	90
β [°]	90	95.883(8)
γ [°]	120	90
V [Å ³]	7325.1(5)	6778.0(6)
Z	18	8
$D_{\text{calcd.}}$ [g cm ⁻³]	1.376	1.287
μ [mm ⁻¹]	0.610	0.328
T [K]	153	153
θ range [°]	2.62 to 26.21	2.12 to 26.13
No. of reflections collected	23 607	64 254
No. of independent reflections	3247 [$R(\text{int}) = 0.0525$]	13 354 [$R(\text{int}) = 0.0851$]
No. of reflections [$I > 2\sigma(I)$]	2474	7582
Max., min. transmission	0.9529 and 0.7839	0.9902 and 0.9525
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0274$ $wR2 = 0.0633$	$R1 = 0.0440$ $wR2 = 0.0871$
R indices (all data)	$R1 = 0.0429$ $wR2 = 0.0670$	$R1 = 0.0934$ $wR2 = 0.0977$

Synthesis of (2,2'-Bipyridine)(η^3 -cyclopentadienyl)(η^5 -cyclopentadienyl)vanadium(II) (6**):** A solution of vanadocene (**4**) (181 mg, 1 mmol) and 2,2'-bipyridine (**5**) (190 mg, 1.2 mmol) in *n*-hexane

(20 mL) was stirred at room temperature overnight. The colour of the solution changed immediately from violet to black. Black crystals of **6** were obtained by cooling the solution at -70 °C for several days. They were isolated by decanting the solution, washing with cold *n*-hexane and drying in vacuo. Crystals suitable for X-ray diffraction were obtained by cooling the solution to -16 °C. Yield: 178 mg (53%). M.p.: 86 °C (dec.). MS (CI, isobutane): m/z (%) = 337.2 (46) $[M]^+$, 157.2 (100) $[(2,2'\text{-bpy-H})]^+$. IR (KBr): $\tilde{\nu} = 3044$ (w), 1571 (s), 1504 (s), 1454 (s), 1417 (m), 1354 (w), 1301 (m), 1254 (m), 1147 (m), 1124 (w), 1082 (w), 1015 (m), 955 (m), 818 (m), 806 (m), 784 (m), 764 (m), 741 (s) cm⁻¹. C₂₀H₁₈N₂V (337.30): calcd. C 71.21, H 5.38, N 8.30; found C 70.97, H 5.30, N 8.34.

Synthesis of (2,2'-Bipyridine)bis(η^5 -cyclopentadienyl)vanadium(III) Tetraphenylborate (7**):** A solution of vanadocenium tetraphenylborate (**9**) (61 mg, 0.116 mmol) in thf (40 mL) was layered with an *n*-hexane solution (20 mL) of 2,2'-bipyridine (**5**) (20 mg, 0.127 mmol). After two weeks, complex **7** was obtained by decanting the solution as large red-violet needles, which were suitable for X-ray diffraction. Yield: 35 mg (46%). M.p.: 220–222 °C (dec.). MS (ESI, CH₃CN): pos.: m/z (%) = 337.1 (100), 338.1 (18), 339.3 (2) $[\text{Cp}_2\text{V}(2,2'\text{-bipy})]^+$, 168.7 (83) $[\text{Cp}_2\text{V}(2,2'\text{-bipy})]^{2+}$; neg.: m/z (%) = 318.5 (24), 319.3 (100), 320.3 (24) $[\text{BPh}_4]^-$. HR-MS (ESI-Q-TOF, CH₃CN): pos.: m/z (%) = 337.0906 (100) $[\text{Cp}_2\text{V}(2,2'\text{-bipy})]^+$, 168.5456 (42) $[\text{Cp}_2\text{V}(2,2'\text{-bipy})]^{2+}$. IR (KBr): $\tilde{\nu} = 3053$ (m), 2963 (m), 1601 (m), 1477 (m), 1442 (m), 1425 (m), 1261 (s), 1242 (s), 1155 (s), 1103 (br), 1017 (br), 945 (m), 802 (br), 769 (m), 733 (s), 703 (s), 657 (m), 610 (m) cm⁻¹. C₄₄H₃₈BN₂V (656.51): calcd. C 80.49, H 5.83, N 4.27; found C 79.86, H 5.85, N 4.83.

Acknowledgments

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