

Ansa-vanadocene complexes with short interannular bridges

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Abstract

The new *ansa*-vanadocene complexes with short interannular bridges $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) were prepared, characterized by spectroscopic methods and X-ray structural analysis. It was shown, that connection of cyclopentadienyl rings by dimethylmethane bridge affects the structural parameters. The behavior *ansa*-vanadocene dichloride in aqueous solution in presence of bio-ligands was studied by EPR spectroscopy.

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1. Introduction

Bent metallocene complexes of the type Cp_2MX_2 ($\text{M} = \text{Ti}, \text{V}$; $\text{X} = \text{halide}$) are currently largely investigated owing to the pronounced antitumor activity [1–6] and low toxic side effects [7]. Past research in our group has been focused on the aqueous chemistry vanadocene dichloride [8–11] due to the large stability of $[\text{Cp}_2\text{V}]^{2+}$ fragment [12]. An EPR spectroscopy was appeared as very efficient method for investigation of such paramagnetic d^1 -complexes. This method should be used at concentration range that is used in biological experiments [13].

Earlier predominates the theory, that ring-substituted and *ansa*-bridged derivatives are much lower active than unsubstituted derivatives or quite inactive [14]. However, recently some published works showed that water-soluble ring-substituted [15,16] and *ansa*-bridged [17–19] metallocene dihalides show antitumor properties comparable or better than their unsubstituted counterparts.

Previously some efficient routes for preparation of *ansa*-vanadocene complexes were developed by Brintzinger et al. [20–22]. Such studies were focused particularly on the

catalytic properties of *ansa*-metallocenes toward polymerization of α -olefins. Hence important study about redox properties and structure of *ansa*-metallocene compounds of vanadium(III) and vanadium(IV) was achieved.

The aim of this study is the synthesis of new *ansa*-vanadocene complexes and their investigation as potential antitumor agents. So we focused on structure investigation of *ansa*-vanadocene complexes, their ligand-exchange reactivity in aqueous media and interaction with bio-ligands compared to unsubstituted vanadocene dichloride.

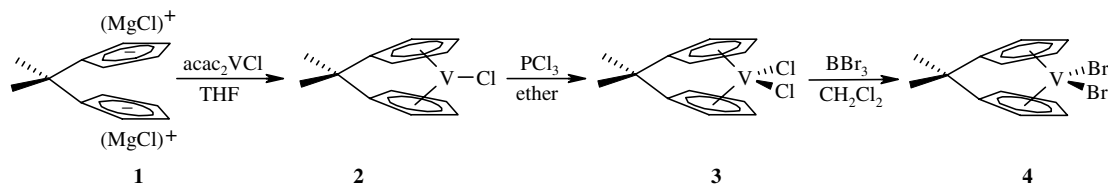
2. Results and discussion

2.1. Preparation and characterization

The *ansa*-vanadocene complex $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VCl}_2$ (**3**) is formed by oxidation of monochloride complex (**2**), which was prepared by the reaction of $(\text{acac})_2\text{VCl} \cdot \text{THF}$ with the Grignard reagent $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4\text{MgCl})_2$ (**1**), see Scheme 1. This method was previously successfully used for preparation of tetramethylethano- [21] and biphenyl-bridged vanadocene dichlorides [22].

The relatively low yield of this reaction (6%) is probably caused by strained geometry of forming metallocene complex. Previously reported one-carbon bridged *ansa*-titanocene complexes were also synthesized in yields about

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Scheme 1. Preparation of *ansa*-vanadocene halides.

3–5% [23]. The bromide complex (**2**) was prepared from chloride (**1**) by ligand-exchange reaction with boron tribromide in good yield (92% isolated).

Ansa-vanadocene dihalides (**3** and **4**) are air-stable dark green solids that are soluble in polar organic solvents such as CH_2Cl_2 , acetone, DMSO, etc. Both compounds were characterized by spectroscopic measurements. Their structures were determined by single crystal X-ray diffraction analysis.

Infrared and Raman spectra of compounds **3** and **4** have similar pattern. They show bands characteristic for ring-substituted bent metallocenes. Both, infrared (IR) and Raman spectra of compounds **3** and **4** show absorption bands typical for η^5 -bonded cyclopentadienyl ring. The bands of medium to strong intensity in IR and Raman spectra at $\sim 3100\text{ cm}^{-1}$ correspond to C–H stretching ($\nu_{\text{C-H}}$, Cp), strong IR bands at $\sim 1450\text{ cm}^{-1}$ to C=C stretching ($\nu_{\text{C=C}}$, Cp), strong IR bands at $\sim 1060\text{ cm}^{-1}$ to C–H bending in the plane ($\delta_{\text{C-H}}$, Cp) and very strong IR bands at $\sim 830\text{ cm}^{-1}$ to out of plane ($\gamma_{\text{C-H}}$, Cp). The bands at $\sim 2950\text{ cm}^{-1}$ in IR and Raman spectra can be assigned to C–H stretching modes of methyl groups.

EPR spectra of dichloromethane solutions of **3** and **4** at ambient temperature show the expected eight lines due to the interaction of the unpaired electron with ^{51}V ($I = 7/2$; 99.8%) nucleus. Isotropic hyperfine coupling (HFC) constants of both *ansa*-vanadocene halides (**3**: $|A_{\text{iso}}| = 65.58 \times 10^{-4}\text{ cm}^{-1}$; **4**: $|A_{\text{iso}}| = 59.97 \times 10^{-4}\text{ cm}^{-1}$) are significantly lower and isotropic g -factors are higher (**3**: $g_{\text{iso}} = 1.9924$; **4**: $g_{\text{iso}} = 2.0257$) than were found for corresponding unbridged vanadocenes (**3a**: $|A_{\text{iso}}| = 69.68 \times 10^{-4}\text{ cm}^{-1}$, $g_{\text{iso}} = 1.9890$; **4a**: $|A_{\text{iso}}| = 63.60 \times 10^{-4}\text{ cm}^{-1}$, $g_{\text{iso}} = 2.0238$). This trend was further proved on the series of vanadocene compounds with and without dimethylmethane bridge (see Table 1 and Fig. 1).

The strong super-hyperfine coupling (S-HFC) was observed in solution EPR spectrum of phosphate complex $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VO}_2\text{PO}_2\text{H}$ (**8**). This splitting is caused by one nucleus of ^{31}P ($I = 1/2$; 100%) that is positioned at C_2 -axis. In contrary to splitting caused by vanadium, S-HFC is not affected by interannular bridging. Both bridged (**8**) and unbridged compound (**8a**) show the same $|a_{\text{iso}}(\text{P})|$ value of $27.19 \times 10^{-4}\text{ cm}^{-1}$.

2.2. X-ray diffraction analysis

The structures of compounds **3** and **4** are shown in Figs. 2 and 3, respectively. The important structural

Table 1

Isotropic HFC constants (in 10^{-4} cm^{-1}) and isotropic g -factors of *ansa*-vanadocene compounds compared to their unsubstituted counterparts

X_2	$(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VX}_2$		$(\text{C}_5\text{H}_5)_2\text{VX}_2$	
	$ A_{\text{iso}} $	g_{iso}	$ A_{\text{iso}} $	g_{iso}
Cl_2	65.58	1.9924	69.68	1.9890
Br_2	59.97	2.0257	63.60	2.0238
$(\text{CN})_2$	54.79	1.9972	56.65	1.9948
$(\text{H}_2\text{O})_2$	68.74	1.9847	73.95	1.9790
CO_3	55.09	1.9884	58.40	1.9861
PO_4H	59.30	1.9880	63.05	1.9862
gly ^a	59.78	1.9885	62.88	1.9850
ala ^b	59.68	1.9882	62.61	1.9850
val ^c	59.84	1.9889	62.73	1.9848

^a $[(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{V}(\text{gly})]\text{Cl}$.

^b $[(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{V}(\text{ala})]\text{Cl}$.

^c $[(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{V}(\text{val})]\text{Cl}$.

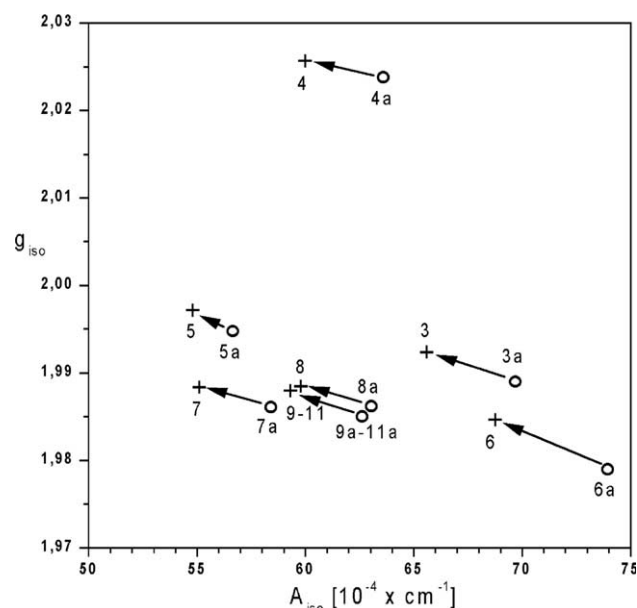


Fig. 1. Isotropic HFC constant versus isotropic g -factor of *ansa*-vanadocene and unbridged complexes (labeled by a). The arrows show the shift of EPR parameters caused by bridging.

parameters are summarized in the Tables 2 and 3. Typical *ansa*-metallocene structure was found for compounds **3** and **4**, in which two η^5 -Cp rings (linked by dimethylmethane bridge) and two halides occupy the pseudotetrahedral

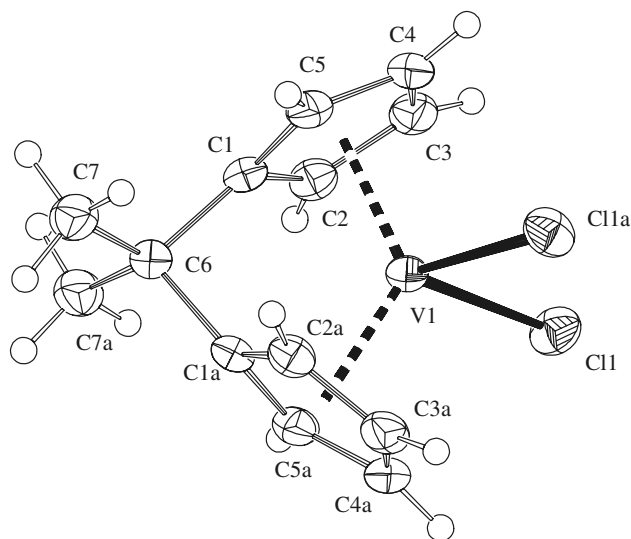


Fig. 2. ORTEP drawing of the molecular structure of compound **3** showing 50% probability displacement ellipsoids and atom numbering scheme.

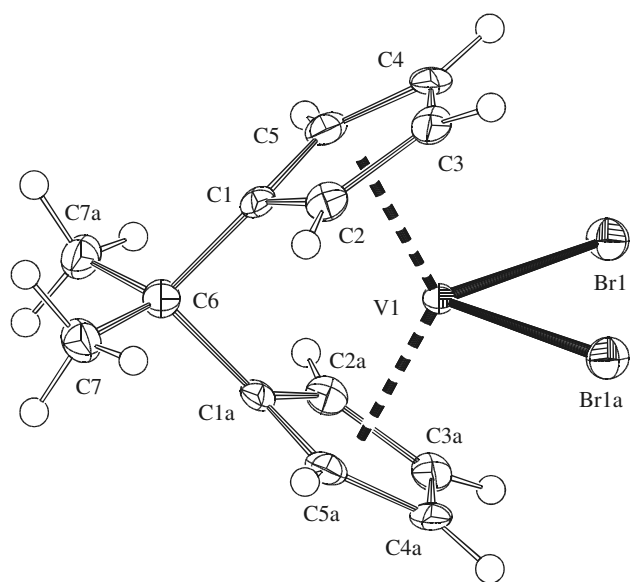


Fig. 3. ORTEP drawing of the molecular structure of compound **4** showing 50% probability displacement ellipsoids and atom numbering scheme.

Table 2
The selected bond lengths and angles of compounds **3** and **4** (Å, °)

	3	4
Cg–V ^a	1.9650(9)	1.9574(12)
V–X	2.3830(6)	2.5451(5)
Cg–V–Cg ^a	124.35(4)	124.58(6)
X–V–X	89.43(2)	88.89(2)

^a Cg – centroid of cyclopentadienyl ring.

coordination sites around the vanadium(IV) center. Molecules of compounds **3** and **4** have rigorous overall C₂ symmetry (approximately C_{2v}) and their crystal lattices are

isomorphous. The most of structural parameters of compounds **3** and **4** are similar (see Table 2), only, as expected, the vanadium-halide bond lengths are much longer for bromine derivative [V–Cl = 2.3830(6) Å, V–Br = 2.5451(5) Å].

The short interannular bridges cause some significant distortions toward unsubstituted vanadocene dichloride or *ansa*-vanadocene dichloride with longer interannular bridges (see Table 3). The most affected parameters are the bond angle Cg–V–Cg (Cg is the centroid of the cyclopentadienyl ring) being the lowest one and the angle between planes of Cp rings (α) being the largest for compounds **3** and **4**. The parameter α is even more affected because cyclopentadienyl rings are tilted (see parameter δ in Table 3). The further large distorted parameter is angle ϕ . Hence, the bridging atom is displaced out of the Cp-ring plane about 15°.

The Cp–V bond distances in chloride derivative **3** [1.9650(9) Å] are comparable to those in Cp₂VCl₂ [from 1.9676(14) to 1.9770(13) Å] [24] and *ansa*-complex with two-carbon bridge [from 1.962(4) to 1.972(4) Å] [20] and are shorter than in ring-substituted compounds (RC₅H₄)₂VCl₂ [R = Me 1.991 Å, *i*-Pr 1.995(6) Å, *t*-Bu 1.985(4) Å] [25,26]. The bromide compound (**4**) has the Cg–V bond lengths [1.9574(12) Å] barely shorter than compound **3**.

2.3. Aqueous chemistry

Ansa-vanadocene dichloride **3** dissolved in water splits off immediately both chloride ligands forming aqua complex **6**, similarly to the unbridged counterpart (**3a**) [27]. The aqua complex (**6**) interacts with Na₂CO₃ and K₂HPO₄ at neutral pH giving chelate complexes (CH₃)₂C(C₅H₄)₂VO₂CO (**7**) and (CH₃)₂C(C₅H₄)₂VO₂PO₂H (**8**), respectively (Scheme 2). The presence of compounds **6–8** in reaction mixture was unambiguously detected by EPR spectroscopy. In Table 1 EPR parameters of **6–8** are summarized. The hydrolytic properties of compound **3** and its interaction with carbonate anion were studied, because chelate carbonate complex **7a** is formed in human blood immediately after application of **3a**, as it was previously reported [9]. The phosphate complex **8a** was recently described as a product of **3a** interaction with phosphate buffered saline (PBS) that is used at preclinical tests [8].

Further complexes that can play important role in the mechanism of antitumor effect are complexes of α -amino acids. Vanadocene dichloride (**3a**) forms chelate complexes with α -amino acids [11]. The same type of coordination was proved for dimethylmethano-bridged vanadocene by EPR spectroscopy. Chelate complexes **9–11** were detected by EPR spectroscopy immediately after addition of appropriate α -amino acid (glycine, L-alanine, L-valine) to aqueous solution of **3** at neutral pH (for EPR parameters see Table 1).

Table 3
Important structural parameters of some vanadocene dihalides (°)

	α^a	ϕ^b	δ^c	Cg–M–Cg	X–M–X	Reference
(C ₅ H ₅) ₂ VCl ₂ (3a)	49.31(17)	–	88.14(13) 89.32(13)	131.92(5)	87.2(3)	[24]
(CH ₃) ₂ C(C ₅ H ₄) ₂ VCl ₂ (3)	63.26(12)	15.58(11)	86.20(9)	124.35(4)	89.43(2)	This work
(CH ₃) ₂ C(C ₅ H ₄) ₂ VBr ₂ (4)	62.89(16)	15.54(16)	86.26(12)	124.58(6)	88.89(2)	This work
(CH ₃) ₄ C ₂ (C ₅ H ₄) ₂ VCl ₂ ^d	50.9(1)	4.0(5) 1.8(5)	88.8(4) 88.4(4)	130.2(1)	88.0(1)	[20]
(CH ₃) ₄ C ₂ (C ₅ H ₄) ₂ VCl ₂ ^e	49.5(1)	2.6(6) 1.9(5)	89.1(4) 88.6(4)	131.0(1)	87.4(1)	[20]

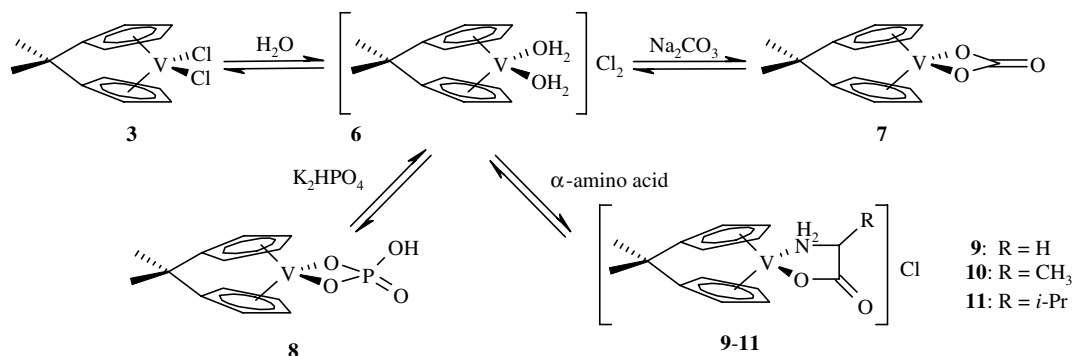
^a α – Angle between Cp rings.

^b ϕ – Angle between bridgehead carbon vector and ring plane.

^c δ – Angle between the ring plane and the metal-ring centroid vector.

^d Molecule A in the unit cell.

^e Molecule B in the unit cell.



Scheme 2. Aqueous chemistry of complex **3**.

3. Conclusions

The air-stable vanadocene complexes **3** and **4** with short interannular bridges were prepared, characterized by spectroscopic methods and by X-ray structural analysis. On the basis of EPR spectra measurements, the stability of *ansa*-metallocene moiety in water was proved. The forming of chelate complexes with carbonate, phosphate and α -amino acids at physiological pH was observed. These complexes (**7–11**) apparently play the important role in mechanism of antitumor effect.

It was shown, that connection of cyclopentadienyl rings by short interannular bridge affects the structural parameters and some parameters in EPR spectra. Nevertheless, the hydrolysis and ligand exchange reactions go on similarly to unbridged vanadocene counterpart.

4. Experimental section

4.1. Methods and materials

All operations were performed under argon by using conventional Schlenk-line techniques. The solvents were purified and deoxygenated by standard methods. Water was deionised, double distilled and saturated with argon.

BBr₃ (Aldrich) was used without further purification. (CH₃)₂C-(C₅H₅)₂ [28], (acac)₂VCl·THF [29] and unbridged vanadocene compounds **3a–6a** [12,30,31] were prepared according literature procedures. **3a**: EPR (CH₂Cl₂ solution) $|A_{\text{iso}}| = 75.04$ G, $g_{\text{iso}} = 1.9890$; **4a**: EPR (CH₂Cl₂ solution) $|A_{\text{iso}}| = 67.32$ G, $g_{\text{iso}} = 2.0238$; **5a**: EPR (aqueous solution) $|A_{\text{iso}}| = 60.83$ G, $g_{\text{iso}} = 2.0238$; **6a**: EPR (aqueous solution) $|A_{\text{iso}}| = 80.04$ G, $g_{\text{iso}} = 1.9790$; **7a**: EPR (aqueous solution) $|A_{\text{iso}}| = 62.98$ G, $g_{\text{iso}} = 1.9861$; **8a**: EPR (aqueous solution) $|A_{\text{iso}}| = 68.00$ G, $|a_{\text{iso}}(^{31}\text{P})| = 29.32$ G, $g_{\text{iso}} = 1.9862$; **9a**: EPR (aqueous solution) $|A_{\text{iso}}| = 67.85$ G, $g_{\text{iso}} = 1.9850$; **10a**: EPR (aqueous solution) $|A_{\text{iso}}| = 67.56$ G, $g_{\text{iso}} = 1.9850$; **11a**: EPR (aqueous solution) $|A_{\text{iso}}| = 67.70$ G, $g_{\text{iso}} = 1.9848$.

4.2. Measurements

EPR spectra were measured on an ERS 221 (ZWG Berlin) apparatus in microwave X-band (~ 9.5 GHz). The apparatus was calibrated with DPPH ($g = 2.0036 \pm 2$). The samples were measured in flat quartz cuvettes (width 0.3 mm) at room temperature. The EPR spectra obtained were computer-simulated using EPR simulation software SimFonia v.1.2 (Bruker).

IR spectra of prepared complexes were recorded in the 4000–350 cm^{-1} region on a Perkin–Elmer 684 station as KBr pellets.

Raman spectra of solid samples in quartz capillaries were recorded on a Bruker IFS 55s with extension FRA 106 at 50–3500 cm^{-1} region.

4.3. Synthesis of $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VCl}_2$ (**3**)

To a solution of $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_5)_2$ (5.5 g, 32 mmol) in THF (100 ml) was added dropwise 64 mmol of *n*-BuMgCl (etheral solution). The mixture was stirred for 30 min at room temperature and then ether was distilled off. The formed THF solution of $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4\text{MgCl})_2$ (**1**) was slowly added via cannula to the suspension of $(\text{acac})_2\text{VCl} \cdot \text{THF}$ (11.3 g, 32 mmol) and 100 ml THF that was cooled at dry ice temperature. The color of the green suspension changed to brown. After stirring for 2 h at room temperature, the volatiles were removed in vacuo. The brown solid was extracted by ether on the frit. The brown extract containing the *ansa*-vanadocene monochloride (**2**) was oxidized with PCl_3 (4.4 g, 32 mmol) to *ansa*-vanadocene dichloride (**3**), which precipitated and was collected on the frit. The green solid was washed with ether (2×20 ml) and small amount of cold CH_2Cl_2 and then was recrystallized from dichloromethane (yield: 0.52 g, 5.6%). The single crystals of **1** suitable for X-ray analysis were obtained by careful layering of CH_2Cl_2 solution with double volume of hexane. Calc. for $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{V}$ (MW 292.08): C, 53.5; H, 4.8; Cl, 24.3. Anal. Found: C, 53.3; H, 4.8; Cl, 14.2. EPR (CH_2Cl_2 solution): $|A_{\text{iso}}| = 70.16$ G, $g_{\text{iso}} = 1.9924$. IR (KBr pellet, cm^{-1}): 3137 (s), 3105 (m), 3083(s), 2977 (s), 1904 (m), 1475 (s), 1455(s), 1417 (s), 1281 (s), 1152 (m), 1082 (s), 1050 (s), 941 (m), 875 (m), 857 (m), 840 (vs), 830 (s), 814 (vs), 726 (s), 706 (m), 606 (m), 471 (m), 429 (m), 360 (m), 347 (m). Raman (quartz capillary, cm^{-1}): 3300 (<1), 3240 (<1), 3134 (3), 3106 (3), 3089 (3), 3081 (4.5), 2974 (2), 2947 (1), 2924 (1), 2874 (<1), 1456 (<1), 1418 (<1), 1281 (1), 1147 (2), 1086 (1), 1069 (<1), 1051 (<1), 880 (1), 847 (<1), 726 (<1), 552 (<1), 469 (1.5), 430 (2), 379 (2), 358 (<1), 340 (<1), 268 (10), 225 (2), 183 (<1), 150 (2), 143 (2), 120 (<1).

4.4. Synthesis of $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VBr}_2$ (**4**)

Compound **3** (0.05 g, 0.17 mmol) was dissolved in dichloromethane (50 ml) and BBr_3 (0.17 g, 0.68 mmol) was added through septum. The color of the light green solution immediately changed to dark green. After stirring for 20 min at room temperature, the volatiles were removed in vacuo. The dark green solid was washed with hexane and then was recrystallized from dichloromethane (yield: 0.06 g, 92%). The single crystals of **4** suitable for X-ray analysis were obtained by careful layering of CH_2Cl_2 solution with double volume of hexane. Calc. for $\text{C}_{13}\text{H}_{14}\text{Br}_2\text{V}$ (MW 381.00): C, 41.0; H, 3.7; N, 4.8; Cl, 12.2. Anal. Found: C, 40.8; H, 3.6. EPR (CH_2Cl_2 solution): $|A_{\text{iso}}| = 63.41$ G,

$g_{\text{iso}} = 2.0257$. IR (KBr pellet, cm^{-1}): 3130 (m), 3104 (m), 3081 (m), 2963(s), 2257 (m), 1454 (s), 1421 (m), 1261 (s), 1194 (m), 1095 (s), 1025 (s), 891 (m), 821 (vs), 803 (s), 723 (m), 650 (m), 549 (m), 393 (m).

4.5. Reactivity of **3**

The compounds $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{VX}_2$ [$\text{X} = \text{CN}$ (**5**); $\text{X}_2 = \text{CO}_3$ (**7**), PO_4H (**8**)] and $[(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4)_2\text{V}(\text{aa})]\text{Cl}$ [$\text{aa} = \text{gly}$ (**9**), ala (**10**), val (**11**)] were prepared in small amount from compound **3** (5 mg) in similar way to their unbridged counterparts according to literature procedures [8,11,31]. These compounds were characterized in solution by EPR spectroscopy. **5**: $|A_{\text{iso}}| = 58.76$ G, $g_{\text{iso}} = 1.9972$, **7**: $|A_{\text{iso}}| = 59.30$ G, $g_{\text{iso}} = 1.9901$; **8**: $|A_{\text{iso}}| = 63.90$ G, $g_{\text{iso}} = 1.9880$, $|a_{\text{iso}}(^{31}\text{P})| = 29.32$ G; **9**: $|A_{\text{iso}}| = 64.40$ G, $g_{\text{iso}} = 1.9885$; **10**: $|A_{\text{iso}}| = 64.30$ G, $g_{\text{iso}} = 1.9882$; **11**: $|A_{\text{iso}}| = 64.45$ G, $g_{\text{iso}} = 1.9880$.

4.6. X-ray diffraction analyses

The X-ray data for **3** and **4** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and ω scan mode. Data reductions were performed with DENZO-SMN [32]. The absorption was neglected for **3** ($\mu(\text{Mo K}\alpha) = 1.236$ mm^{-1}). For data of **4** the absorption correction was carried on using Gaussian integration from

Table 4
Crystal data of **3** and **4**, measurement and refinement details^a

Compound	3	4
Formula	$\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{V}$	$\text{C}_{13}\text{H}_{14}\text{Br}_2\text{V}$
Crystal system	Monoclinic	Monoclinic
Space group	$\text{C}2/c$ (No. 15)	$\text{C}2/c$ (No. 15)
T (K)	240	150
a (Å)	12.4100(4)	12.9880(5)
b (Å)	10.2750(3)	9.8010(4)
c (Å)	10.0960(3)	10.6050(5)
β (°)	110.9800(18)	112.230(2)
Z	4	4
D_{calc} (g cm^{-3})	1.614	2.025
Crystal size (mm)	$0.25 \times 0.12 \times 0.08$	$0.35 \times 0.25 \times 0.2$
Crystal shape	Green prism	Green prism
μ (mm^{-1})	1.236	7.157
θ Range (°)	1–27.5	1–27.5
h k l range	–16/16, –13/13, –13/13	–15/15, –11/11, –12/12
Reflections measured	10471	6471
Independent (R_{int}) ^a	1384(0.041)	1148(0.0583)
Observed [$I > 2\sigma(I)$]	1169	1071
No. of parameters	75	76
R , wR ^b	0.0291, 0.0725	0.026, 0.077
GOF ^c	1.060	1.081
$\Delta\rho$ (e Å^{-3})	0.375, –0.342	0.436, –0.562

^a $R_{\text{int}} = \sum |F_o^2 - F_{o,\text{mean}}^2| / \sum F_o^2$.

^b $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed data, $wR(F) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$ for all data.

^c $\text{GOF} = [\sum (w(F_o^2 - F_c^2)^2) / (N_{\text{diffs}} - N_{\text{params}})]^{1/2}$ for all data.

crystal shape [33] ($\mu(\text{Mo K}\alpha) = 7.157 \text{ mm}^{-1}$, $T_{\text{min}} = 0.246$, $T_{\text{max}} = 0.394$). Structures were solved by direct methods SIR92 [34] and refined by full matrix least-square based on F^2 [35].

Crystal data are summarized in Table 4. Hydrogen atoms in both structures were calculated into ideal positions, riding during refinement on the respective pivot atom. The isotropic displacement parameters of hydrogen atoms were set to $1.2U_{\text{eq}}$ of the attached atom or $1.5U_{\text{eq}}$ for methyl moiety.

5. Supplementary material

Full crystallographic data for the structures of reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 268033 and 268034 for **3** and **4**, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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