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## *ansa*-Metallocene derivatives

### XXV \*. Synthesis, crystal structure and reactions of a tetramethylethano-bridged vanadocene dichloride, $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$

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#### Abstract

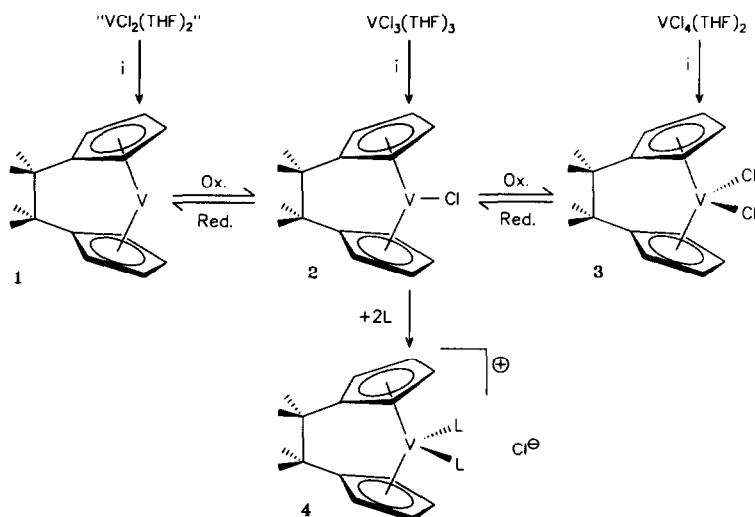
The tetramethylethano-bridged vanadocene complex  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  has been made in two ways: (i) from  $\text{VCl}_3 \cdot 3\text{THF}$  by reaction with  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)\text{MgCl} \cdot 2\text{THF}$  in THF and subsequent oxidation with  $\text{PCl}_3$ , and (ii) from  $\text{VCl}_4 \cdot 2\text{THF}$  by reaction with  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)\text{Li}$  or with  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)\text{MgCl} \cdot 2\text{THF}$  in a toluene/dimethoxyethane mixture. Its crystal structure is in accordance with expectations. Reduction of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  with tetrakis(dimethylamino)ethene in toluene or with  $\text{LiAlH}_4$  in THF yields the monochloride  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$ ; from this  $\text{V}^{\text{III}}$  compound cationic complexes  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VL}_2^+$  with  $\text{L} = \text{CO}$  or  $\text{CN}^t\text{Bu}$  are readily obtained by ligand exchange.  $^1\text{H}$  NMR signals of these diamagnetic complexes have been assigned to H atoms in  $\alpha$  and  $\beta$   $\text{C}_5$ -ring positions by use of selective nuclear Overhauser effects. The ring-bridged  $\text{V}^{\text{II}}$  complex  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}$  could not be prepared. Cyclovoltammetry studies indicate that (in contrast to its unbridged counterpart  $(\text{C}_5\text{H}_5)_2\text{V}$ ) this  $\text{V}^{\text{II}}$  complex decays within seconds after its formation by electrochemical reduction of its chloro derivatives.

#### Introduction

More than thirty years ago it was reported that vanadocene chloride complexes such as  $(\text{C}_5\text{H}_5)_2\text{VCl}_2$  yield catalyst systems capable of polymerizing ethene when combined with a suitable alkyl aluminium halide activator [1,2]. Despite considerable efforts to identify the species present in these reaction systems [3–5], the nature of the vanadocene complexes responsible for this catalysis (and even whether they still contain intact  $(\text{C}_5\text{H}_5)_2\text{V}$  units) remains largely unestablished. It thus seemed to us of interest to prepare chiral *ansa*-vanadocene derivatives with structures similar to those of the more recently described chiral *ansa*-zirconocene

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\* For Part XXIV, see ref. 21.



Scheme 1

derivatives [6–8] and compare the catalytic properties of these Group IV and V transition metal complexes, *e.g.* in methylaluminoxan-activated  $\alpha$ -olefin polymerization [9,10].

To acquire the necessary background information for syntheses of this kind, we investigated which of the alternative routes to vanadocene compounds, starting from either V<sup>II</sup>, V<sup>III</sup> or V<sup>IV</sup> chlorides, would also give access to the corresponding ethano-bridged vanadocene derivatives; in addition, we have studied some redox and ligand exchange reactions typical of *ansa*-vanadocene complexes obtained in this manner (Scheme 1). We describe below the results of such a study on vanadocene derivatives with a tetramethylethano-bridged but otherwise unsubstituted ligand framework.

## Results and discussion

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

Reactions of a VCl<sub>2</sub> adduct, such as VCl<sub>2</sub> · 0.5ZnCl<sub>2</sub> · 3THF, with the Na<sup>+</sup> or Li<sup>+</sup> salts of the corresponding cyclopentadienide anion have been described in the literature as a preferred, high-yield route to normal, unbridged vanadocene derivatives [11,12]. However, from reactions of this VCl<sub>2</sub> adduct with either  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{Li})_2$  or  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl} \cdot 2\text{THF})_2$  [13] in THF, we did not obtain any pentane-soluble or sublimable products, nor did we observe any IR absorptions assignable to carbonyl complexes when the product mixtures were exposed to CO. Apparently, ring-bridged vanadocenes are not accessible, at least by this route, at the V<sup>II</sup> oxidation level. We had previously observed that reaction of CrCl<sub>2</sub> · THF with the ligand derivative  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl} \cdot 2\text{THF})_2$  yields, instead of the *ansa*-chromocene  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{Cr}$ , an insoluble, presumably polymeric, isomer of this complex. Apparently, the C<sub>5</sub>-axial geometry of  $(\text{C}_5\text{H}_5)_2\text{Cr}$  and  $(\text{C}_5\text{H}_5)_2\text{V}$  is not compatible with an interannular ethano bridge.

Attempts to obtain the V<sup>III</sup> complex  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$  (2) by reaction of VCl<sub>3</sub> · 3THF with  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{Li})_2$  or  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{Na})_2$  in THF proved

similarly unsuccessful \*, but this V<sup>III</sup> complex was obtained by reaction of VCl<sub>3</sub> · 3THF with (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>MgCl · 2THF)<sub>2</sub> in THF at -80°C as a very air-sensitive blue precipitate, which was oxidized, without prior purification, to (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> (**3**) by reaction with PCl<sub>3</sub> [14]. Recrystallization from toluene afforded the green dichloride **3** in 37% yield.

The reactions of VCl<sub>4</sub> · 2THF with the bridged ligand dianion are similarly sensitive to the counter-cations and reaction conditions. Thus reaction with (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>Na)<sub>2</sub> in THF solution gave only an orange-red precipitate of VCl<sub>3</sub> · 3THF whereas reaction with (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>Li)<sub>2</sub> in a toluene/dimethoxyethane mixture afforded the dichloride (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> as a green microcrystalline precipitate in ca. 30% yield. Reaction of VCl<sub>4</sub> · 2THF with the Grignard derivative (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>MgCl<sub>2</sub> · 2THF)<sub>2</sub> in this solvent mixture likewise gave (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> in 35–40% yield (see Experimental section) \*\*. Apparently, the dichloride product is protected from reaction with the excess of the ligand dianion by its precipitation from this less polar solvent mixture.

#### *Crystal structure of (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> (**3**).*

Slow crystallization from toluene/dichloromethane (50:1) gave single crystals of (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> suitable for an X-ray structural determination. The resulting atomic coordinates are listed in Table 1, with the numbering scheme shown in Fig. 1.

For both crystallographically independent molecules of **3**, the coordination geometry of the vanadium centre is quite similar to that found for the unbridged (C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>VCl<sub>2</sub> [19]. As in this compound, the Cl–V–Cl angles of ca. 88° are substantially smaller than Cl–Ti–Cl angles of ca. 95° reported for related titanocene complexes [6,7].

As observed for a number of ethano- and etheno-bridged titanocene dichlorides [7,20,21], the structure of **3** deviates from C<sub>2</sub>-axial symmetry: in both molecules, the axis bisecting the Cl–Ti–Cl angle deviates by ca. 12° from the axis connecting the Ti atom with the midpoint of the ethano bridge. As previously discussed for related *ansa*-titanocene and -zirconocene derivatives [21], this distortion indicates that a “consymmetric” rotation of the *ansa*-metallocene framework around the metal-centroid axes has a very shallow, double-minimum energy profile, which is due to intramolecular repulsions between the Cl ligands and the β C–H groups on each C<sub>5</sub>-ring.

#### *Redox and ligand exchange reactions*

The redox properties of (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> were studied by cyclic voltammetry of 1–3 × 10<sup>-3</sup> M solutions in THF containing 0.1 M tetrabutylammonium

\* Reaction of VCl<sub>3</sub> · 3THF with C<sub>5</sub>H<sub>5</sub>Na gives (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>VCl in excellent yields [15]; the more strongly reducing C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>Na, however, is partly consumed by reduction of V<sup>III</sup> to form (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)<sub>2</sub>V<sup>II</sup> [16].

\*\* The preparation of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>VCl<sub>2</sub> by reaction of VCl<sub>4</sub> with C<sub>5</sub>H<sub>5</sub>Na or C<sub>5</sub>H<sub>5</sub>MgCl in THF or dimethoxyethane was described previously [17]. The dimethylsilyl-bridged vanadocene dichloride (CH<sub>3</sub>)<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>VCl<sub>2</sub> has recently been obtained, in ca. 7% yield, by reaction of VCl<sub>4</sub> with (CH<sub>3</sub>)<sub>2</sub>Si(C<sub>5</sub>H<sub>4</sub>Li)<sub>2</sub> in THF/pentane [18].

Table 1

Selected bond lengths (pm) and bond and dihedral angles (deg) for  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  (CR = centroid, PL = mean plane of  $\eta^5\text{-C}_5$  ring)

1		2	
V(1)–Cl(1)	240.5(3)	V(2)–Cl(3)	239.5(3)
V(1)–Cl(2)	240.4(3)	V(2)–Cl(4)	238.8(3)
V(1)–C(1)	230.9(7)	V(2)–C(21)	231.7(7)
V(1)–C(2)	230.3(10)	V(2)–C(22)	229.3(9)
V(1)–C(3)	232.3(9)	V(2)–C(23)	231.4(8)
V(1)–C(4)	232.6(7)	V(2)–C(24)	229.6(7)
V(1)–C(5)	227.3(7)	V(2)–C(25)	226.4(7)
V(1)–C(9)	230.0(7)	V(2)–C(29)	229.9(7)
V(1)–C(10)	230.2(8)	V(2)–C(30)	227.3(8)
V(1)–C(11)	233.9(10)	V(2)–C(31)	228.7(7)
V(1)–C(12)	227.8(7)	V(2)–C(32)	233.9(6)
V(1)–C(13)	227.1(7)	V(2)–C(33)	229.6(7)
C(6)–C(14)	158.8(9)	C(26)–C(34)	157.3(10)
Cl(1)–V(1)–Cl(2)	88.0(1)	Cl(3)–V(2)–Cl(4)	87.4(1)
CR(1)–V(1)–CR(2)	130.2(1)	CR(3)–V(2)–CR(4)	131.0(1)
PL(1)–PL(2)	50.9(1)	PL(3)–PL(4)	49.5(1)
C(1)–C(6)–C(14)–C(9)	–31.5(10)	C(21)–C(26)–C(34)–C(29)	29.0(8)

hexafluorophosphate as a supporting electrolyte at 10°C. The redox properties apparent from the cyclic voltammograms (Fig. 2) are similar in several respects to those of unbridged  $(\text{C}_5\text{H}_5)_2\text{VCl}_2$  [22–24]: a reversible oxidation to  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2^+$  occurs at  $E_p(E') \approx +0.6$  V \*, while reduction at  $E_p(A) \approx -1.5$  V occurs at somewhat lower potentials than that of  $(\text{C}_5\text{H}_5)_2\text{VCl}_2$  ( $E_p(A) \approx -1.2$  V). The corresponding oxidation at  $E_p(D') \approx -0.5$  V indicates that the  $\text{V}^{\text{III}}$  anion  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2^-$  is (like its unbridged counterpart) converted into  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$  by loss of  $\text{Cl}^-$  and reoxidized at peak D' to  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}^+$  (see Scheme 2). Reduction of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$  to the  $\text{V}^{\text{II}}$  state is likewise observed at a potential close to that of the unbridged vanadocene system,  $E_p(B) \approx -2.4$  V (Table 2).

An interesting difference from the behaviour of unbridged vanadocene is apparent, however, in the low-voltage region in Fig. 2. Whereas reduction of  $(\text{C}_5\text{H}_5)_2\text{VCl}$  to  $(\text{C}_5\text{H}_5)_2\text{VCl}^-$  at B is followed by an additional reversible one-electron reduction of  $(\text{C}_5\text{H}_5)_2\text{V}$  (formed from the chloro anion by loss of  $\text{Cl}^-$ ) to  $(\text{C}_5\text{H}_5)_2\text{V}^-$  at  $E_p(C) \approx -3.3$  V [23,24], much less than a full electron equivalent is taken up in this region by the *ansa*-vanadocene system. This shows that  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}$  escapes further reduction at peak C by some decay reaction, which occurs with a half-life of about 1 s \*\*: This lower stability of

\* All peak potentials are relative to  $E_{1/2}$  for the ferrocene/ferrocinium couple (see Experimental section). The appearance of two new, unidentified, peaks after bulk electrolysis at the potential of E' indicates that the cation  $3^+$  is stable only on the cyclovoltammetric time scale.

\*\* Peak C increases in relative height at higher sweep rates, e.g. at 5 V/s, or at temperatures below 0°C; at slower sweep rates, e.g. at 0.1 V/s and 10°C, peak C disappears completely. The corresponding anodic peak C' was undetectable at any of the sweep rates used.

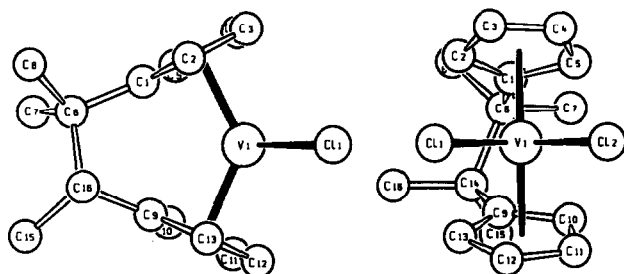


Fig. 1. Structure of molecule 1 of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  (3); projections perpendicular to ring centroid-metal-centroid plane (left) and parallel to Cl-V-Cl bisector axis (right).

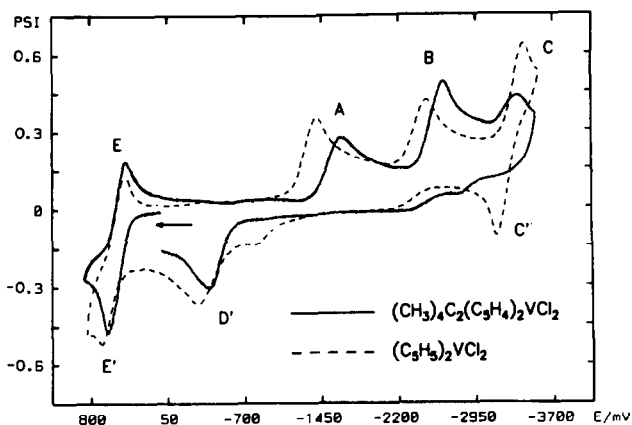
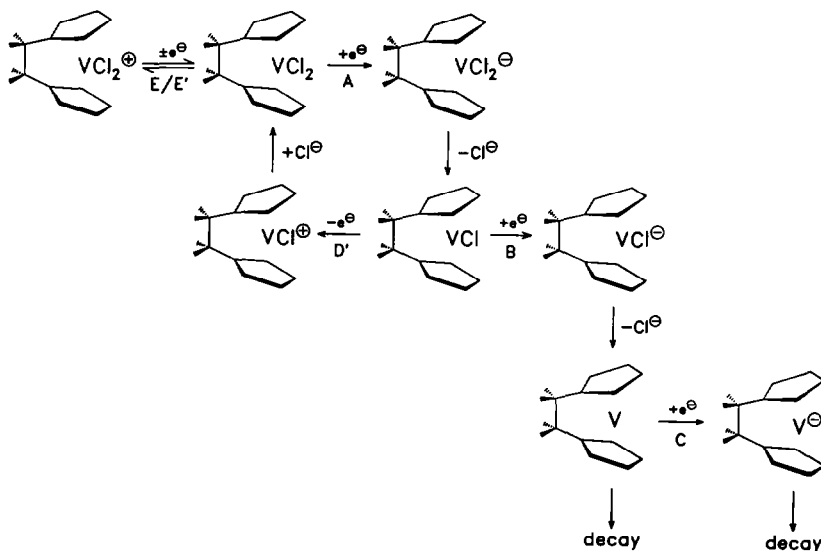


Fig. 2. Cyclovoltammograms of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  (solid line) and of  $(\text{C}_5\text{H}_5)_2\text{VCl}_2$  (broken line), in THF solution at  $10^\circ\text{C}$ ; sweep rate  $\nu = 1.0 \text{ V/s}$  (for further details see Experimental section).



Scheme 2

Table 2

Peaks observed in cyclovoltammograms of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  (**3**) and of  $(\text{C}_5\text{H}_5)_2\text{VCl}_2$  in THF solution at 10°C, sweep rate  $\nu = 0.1$  V/s, potentials (V) vs. ferrocene/ferrocinium couple

Complex	A	B	C	C'	D'	E'	E
<b>3</b>	-1.50	-2.40	-3.32 <sup>a</sup>		-0.54	+0.60	+0.49
$(\text{C}_5\text{H}_5)_2\text{VCl}_2$	-1.15	-2.20	-3.33	-3.20	-0.50	+0.63	+0.49

<sup>a</sup> Not observed at  $\nu = 0.1$  V/s; peak potential for  $\nu = 1.0$  V/s.

$(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}$  than of  $(\text{C}_5\text{H}_5)_2\text{V}$  is in accord with our observation that the *ansa*-vanadocene is not accessible at the V<sup>II</sup> stage by normal synthetic routes.

The synthesis of the V<sup>III</sup> species  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$  (**2**) was achieved by reduction of the dichloride **1**. A very convenient reducing agent for this purpose is tetrakis(dimethylamino)ethene [25,26]; this reagent was previously found to be particularly useful for similar reduction reactions in titanocene systems [27]. Treatment of a toluene solution of the green dichloride **3** with half a molar equivalent of the amino-ethene brings about quantitative reduction to the blue monochloride **2**. The dichloride of the organic cation  $((\text{CH}_3)_2\text{N})_4\text{C}_2^{2+}$  precipitates out and is easily removed from the solution; and after partial evaporation of the solution, and cooling to -80°C the monochloride complex **2** separates as blue microcrystals. This highly air-sensitive compound is readily soluble in diethyl ether but less so in pentane; it sublimes *in vacuo* at 150–160°C. The monochloride **2** can also be obtained by treatment of a THF solution of the dichloride **3** with one equivalent of  $\text{LiAlH}_4$ .

The diamagnetic, low-spin V<sup>III</sup> complex cations **4**,  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VL}_2^+$  with L = CO or CN<sup>t</sup>Bu, are readily obtained from solutions of the monochloride **2**. Reaction of 2 equivalents of *t*-butyl isonitrile in diethyl ether affords the chloride of **4a** as a reddish-brown precipitate. The dicarbonyl cation **4b** is similarly obtained by admission of CO to a THF solution of **2**; the tetraphenylborate salt of **4b** separates as a yellow solid upon addition of an aqueous solution of one equivalent of sodium tetraphenylborate.

The IR spectra of these compounds (Table 3) show C≡O and C=N stretching vibrations at frequencies lower than those observed for their unbridged counterparts [28], and approaching those of the corresponding permethyl vanadocene

Table 3

Ligand stretching vibration frequencies ( $\text{cm}^{-1}$ ) for vanadocene and *ansa*-vanadocene dicarbonyl and bis-isonitrile complexes (Nujol mull)

Complex	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{NR})$	Reference
$(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}(\text{CO})_2^+ \text{B}(\text{C}_6\text{H}_5)_4^-$	1970, 2030		
$(\text{C}_5\text{H}_5)_2\text{V}(\text{CO})_2^+ \text{B}(\text{C}_6\text{H}_5)_4^-$	2000, 2040		28
$(\text{C}_5(\text{CH}_3)_5)_2\text{V}(\text{CO})_2^+ \text{B}(\text{C}_6\text{H}_5)_4^-$	1952, 1995		16
$(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}(\text{CN}^t\text{Bu})_2^+ \text{Cl}^-$		2050, 2083, 2135	
$(\text{C}_5\text{H}_5)_2\text{V}(\text{CN}-\text{C}_6\text{H}_{11})_2^+ \text{Cl}^-$		2130, 2160	28
$(\text{C}_5(\text{CH}_3)_5)_2\text{V}(\text{CN}^t\text{Bu})_2^+ \text{Cl}^-$		2030, 2070, 2100	16

derivatives [16]. Introduction of the ethano bridge thus appears to increase the ability of the vanadium centre to back-donate electrons to  $\pi$  acceptor ligands.

In their  $^1\text{H}$  NMR spectra these diamagnetic cationic *ansa*-vanadocene complexes show, in addition to a singlet for the four methyl groups at the  $\text{C}_2$  bridge, a pair of pseudo-triplets for the  $\alpha$ -H and  $\beta$ -H atoms at the  $\text{C}_5$ -rings. Of these, the low field signal is selectively enhanced in intensity upon irradiation at the resonance frequency of the  $\text{CH}_3$  group at the ethano bridge. This nuclear Overhauser effect allows assignment of the low-field and the high-field signals to the  $\alpha$ -H and  $\beta$ -H atoms, respectively. This assignment is in accord with that for resonances observed for related *ansa*-titanocene and *ansa*-chromocene complexes with 18-valence-electron configuration [29]. The equivalence of all four  $\text{CH}_3$  groups and the pairwise equivalence of  $\alpha$ -H and  $\beta$ -H atoms shows that these complex molecules, like their titanium analogues, undergo rapid interchange between  $\lambda$  and  $\delta$  chelate-ring conformers in the solutions studied.

## Experimental

All reactions were carried out under argon by standard Schlenk techniques. Solvents were thoroughly dried and degassed.

The bifunctional Grignard derivative  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl} \cdot 2\text{THF})_2$  was prepared as described previously [13]. Since we have found that this compound contains varying amounts of  $\text{MgCl}_2$ , the actual amount of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl} \cdot 2\text{THF})_2$  was determined by dissolution of a small sample in 0.1 *M* HCl and back-titration with 0.1 *M* NaOH. In the procedures below, the amount of Grignard compound used is therefore given in mmol. The corresponding sodium and lithium derivatives were obtained by hydrolysis of the Grignard compound to  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_5)_2$  and rearomatization with NaH and with *n*-butyl lithium, respectively.

$\text{VCl}_2 \cdot 3\text{THF} \cdot 0.5\text{ZnCl}_2$ ,  $\text{VCl}_3 \cdot 3\text{THF}$  and  $\text{VCl}_4 \cdot 2\text{THF}$  were prepared according to standard methods [30,31].

### Synthesis of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$ from $\text{VCl}_3 \cdot 2\text{THF}$

Solid  $(\text{C}_6\text{H}_5)_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl} \cdot 2\text{THF})_2$  (8.0 mmol) was added during 1 h to a suspension of 3.0 g (8.0 mmol) of  $\text{VCl}_3 \cdot 3\text{THF}$  in 150 ml THF cooled to  $-50^\circ\text{C}$ . The mixture was then allowed to warm to room temperature, during which the initially violet suspension turned dark brown. After 12 h stirring at room temperature the solvent was removed *in vacuo* and the residue extracted with pentane in a Soxhlet extractor. Evaporation of the pentane solution gave 1.1 g (3.7 mmol, 47% yield) of dark blue  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$ . This was taken up in 100 ml of diethyl ether; upon addition of 6.3 ml (3.7 mmol)  $\text{PCl}_3$ , 1.0 g (3.0 mmol, 37% yield) of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  separated as light green microcrystals. The product was characterized by a mass spectrum, showing peaks at  $m/e$  333, 335 and 337 with the expected isotope distribution. Elemental analysis: Found: 56.89; H 6.14%.  $\text{C}_{16}\text{H}_{20}\text{VCl}_2$  calc.: 57.51; H 6.03%.

### Synthesis of $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$ (3) from $\text{VCl}_4 \cdot 2\text{THF}$

To a solution of 2.8 g of  $\text{VCl}_4 \cdot 2\text{THF}$  (8.3 mmol) in 150 ml of toluene a suspension of 8.3 mmol of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4\text{MgCl} \cdot 2\text{THF})_2$  in 80 ml of

dimethoxyethane was added dropwise at  $-80^{\circ}\text{C}$ . When the mixture warmed to room temperature the initially dark-red solution became brown-green. The mixture was stirred for an additional 12 h. Removal of solvent under reduced pressure, extraction of the residue with pentane and cooling of the filtrate to  $-80^{\circ}\text{C}$  afforded 1.03 g (3.1 mmol, 37% yield) of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  as a light green powder.

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

Tetrakis(dimethylamino)ethane (0.52 ml, 2.25 mmol) was added to a solution of 1.5 g (4.5 mmol) of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  in 120 ml of toluene at room temperature, resulting in an immediate change of colour from green to blue. After 1 h stirring at room temperature the precipitate of  $((\text{CH}_3)_2\text{N})_4\text{C}_2\text{Cl}_2$  was removed by filtration. Evaporation of the filtrate to ca. 40 ml and cooling to  $-80^{\circ}\text{C}$  gave a blue precipitate which was filtered off and dried *in vacuo* to give 0.83 g (2.8 mmol, 62% yield) of the highly air-sensitive monochloride  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$ , which was identified by its mass spectrum, which showed peaks at  $m/e$  298–300 with an isotope distribution as expected for the molecular ion of 2. IR spectra of this complex show out-of-plane cyclopentadienyl C–H vibrations at  $798\text{--}801\text{ cm}^{-1}$ , *i.e.* at a frequency typical of vanadocene complexes at the  $\text{V}^{\text{III}}$  oxidation level [32].

*Synthesis of  $[(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}(\text{CN}'\text{Bu})_2]\text{Cl}$*

To the blue solution of 1.41 g (4.72 mmol) of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}$  in 80 ml of diethyl ether, 1.1 ml (9.73 mmol) of *t*-butyl isocyanide was added at room temperature, resulting in a change of colour to brown and separation of a red-brown solid. After cooling of the mixture to  $-80^{\circ}\text{C}$ , the solid was filtered off, washed with pentane, and dried *in vacuo* to give 1.6 g (3.4 mmol, 72% yield) of  $[(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}(\text{CN}'\text{Bu})_2]\text{Cl}$ . IR spectrum; see Table 3.  $^1\text{H}$  NMR spectrum in acetone- $d_6$  solution ( $\delta$  in ppm): 1.16 (s, 12H,  $(\text{CH}_3)_4\text{C}_2$ ); 1.50 (s, 18H,  $\text{CNC}(\text{CH}_3)_3$ ); 5.32 (pt \*, 4H, H( $\beta$ )); 5.45 (pt, 4H, H( $\alpha$ )).

*Synthesis of  $[(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}(\text{CO})_2]\text{B}(\text{C}_6\text{H}_5)_4$*

$\text{LiAlH}_4$  (0.11 g, 3 mmol) was added to a solution of 1 g (3 mmol) of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  in 60 ml of THF, resulting in a change of colour of the solution from green to blue. The solution was decanted from the precipitate and exposed to CO for 1 h. To the brown solution thus obtained was added a suspension of 1 g of  $\text{NaB}(\text{C}_6\text{H}_5)_4$  in 30 ml of  $\text{H}_2\text{O}$ . A yellow-orange solid separated, and was filtered off, washed with water, and dried *in vacuo*. Recrystallization from acetone afforded 0.92 g (1.44 mmol, 48% yield) of  $[(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{V}(\text{CO})_2]\text{B}(\text{C}_6\text{H}_5)_4$ . IR spectrum; see Table 3.  $^1\text{H}$  NMR spectrum in acetone- $d_6$  solution ( $\delta$  in ppm): 1.32 (s, 12H,  $(\text{CH}_3)_4\text{C}_2$ ); 5.97 (pt, 4H, H( $\beta$ )); 6.13 (pt, 4H, H( $\alpha$ )).

*Cyclovoltammetric measurements*

The compounds studied were handled with strict exclusion of air, either in a glovebox or on a vacuum line. Cyclovoltammetric measurements were made with

\* pt, pseudo-triplet.



$10^{-3}$  to  $3 \times 10^{-3}$  M solutions in anhydrous THF containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBA}^+ \text{PF}_6^-$ ) by use of an electrochemical cell with an internal drying column, as previously described [33]. Peak potentials were measured with full IR compensation against an  $\text{Ag}|\text{AgNO}_3(\text{sat})|\text{TBA}^+ \text{PF}_6^- (0.1 \text{ M})|\text{THF} (25^\circ\text{C})$  reference electrode. All potentials were then referred to the standard potential of the ferrocene/ferrocinium couple,  $E_{1/2} = [E_{\text{pa}}(\text{Cp}_2\text{Fe}) + E_{\text{pc}}(\text{Cp}_2\text{Fe}^+)]/2$  (rather than to the SCE standard), by adding an increment of +0.12 V, obtained from the peak potentials of ferrocene, which were checked after each measurement by adding a small amount of ferrocene to the solution studied.

Table 4

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters  $U_{\text{eq}}^a$  ( $\text{pm}^2 \times 10^{-1}$ )

Atom	x	y	z	$U_{\text{eq}}$
V(1)	4546(1)	9(1)	2429(1)	29(1)
Cl(1)	3864(2)	796(1)	743(2)	53(1)
Cl(2)	4159(2)	964(1)	3483(2)	48(1)
C(1)	5999(5)	-703(4)	2919(7)	34(3)
C(2)	5928(5)	-218(4)	2027(8)	41(3)
C(3)	6041(6)	510(4)	2469(8)	48(3)
C(4)	6170(6)	475(5)	3609(8)	49(3)
C(5)	6110(6)	-265(4)	3895(8)	45(3)
C(6)	6002(6)	-1540(4)	2897(7)	35(3)
C(7)	6354(6)	-1850(4)	4128(7)	54(3)
C(8)	6810(6)	-1789(5)	2477(7)	53(3)
C(9)	4133(5)	-1217(4)	2088(7)	30(3)
C(10)	4034(5)	-1008(4)	3115(7)	34(3)
C(11)	3239(6)	-498(4)	2817(7)	39(3)
C(12)	2870(5)	-354(4)	1621(8)	41(3)
C(13)	3407(5)	-801(4)	1168(7)	34(3)
C(14)	4874(5)	-1790(4)	2024(7)	30(3)
C(15)	4577(6)	-2539(4)	2370(7)	50(3)
C(16)	4731(6)	-1858(4)	772(7)	50(3)
V(2)	412(1)	7634(1)	2263(1)	30(1)
Cl(3)	323(2)	8465(1)	3676(2)	55(1)
Cl(4)	779(2)	8677(1)	1366(2)	52(1)
C(21)	1204(5)	6497(4)	2782(7)	31(3)
C(22)	1629(6)	6883(4)	2125(8)	46(3)
C(23)	2146(6)	7504(5)	2757(9)	61(3)
C(24)	2026(6)	7525(5)	3775(9)	63(3)
C(25)	1424(6)	6919(4)	3787(7)	45(3)
C(26)	623(5)	5762(4)	2445(7)	32(3)
C(27)	1115(6)	5233(4)	3481(7)	48(3)
C(28)	787(6)	5422(4)	1435(7)	45(3)
C(29)	-783(5)	6703(4)	1657(7)	28(3)
C(30)	-1156(5)	7280(4)	2095(7)	36(3)
C(31)	-1306(6)	7903(4)	1384(8)	44(3)
C(32)	-1048(5)	7719(4)	477(7)	40(3)
C(33)	-701(5)	6993(4)	655(6)	31(3)
C(34)	-539(5)	5925(4)	2125(6)	28(3)
C(35)	-1283(6)	5411(4)	1178(7)	49(3)
C(36)	-795(6)	5850(4)	3164(7)	46(3)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

### Crystal structure determination

Space group, cell parameters and X-ray diffraction intensities of suitable crystals of  $(\text{CH}_3)_4\text{C}_2(\text{C}_5\text{H}_4)_2\text{VCl}_2$  were determined on a Syntex P3 four circle diffractometer (Mo- $K_\alpha$ ,  $\lambda = 71.073$  ppm, graphite monochromator, variable scan speed in  $\omega$  with  $\Delta\omega$   $0.7^\circ$  ( $2.89 \leq \dot{\omega} \leq 29.3^\circ/\text{min}$  and  $4.0 \leq 2\theta \leq 52.0^\circ$ )) at 296 K. The crystals were monoclinic, space group  $P2_1/c$  with  $a = 14.444(4)$ ,  $b = 18.186(5)$ ,  $c = 12.732(3)$  Å,  $\beta = 115.80(2)^\circ$ ,  $V = 3011.0(14)$  Å<sup>3</sup>, four crystallographically equivalent sets of two independent molecules per unit cell,  $d_{\text{calc}} = 1.474$  g/cm<sup>3</sup>. For resolution and refinement of the structure, 2890 independent reflections with  $I \geq 2.0\sigma(I)$  were used, without absorption corrections ( $\mu = 0.98$  mm<sup>-1</sup>). The structure was solved by direct methods (SHELXTL). Refinement with an anisotropic model, with all H atoms in calculated positions (riding model), weighting scheme  $w^{-1} = \sigma^2(F) + 0.0002F^2$ , converged at  $R_1 = 0.077$  and  $R_2 = 0.053$  \*; goodness-of-fit 1.24, largest difference peak  $0.6$  e/Å<sup>3</sup>. The resulting atomic coordinates are listed in Table 4; for bond lengths and angles see Table 1. Tables of hydrogen atom coordinates, anisotropic thermal parameters, and structure factors are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, upon quotation of deposit number CSD-55774, the authors and the journal reference for the article.

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\*  $R_1 = (\sum \|F_o\| - |F_c|) / \sum |F_o|$  and  $R_2 = [\sum \omega (|F_o| - |F_c|)^2]^{1/2} / [\sum \omega |F_o|^2]^{1/2}$ .

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