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ansa-VANADOCENE COMPLEXES – SYNTHESES, STRUCTURES AND LIGAND EXCHANGE REACTIONS*

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

Tetramethylethano-bridged vanadocene dichlorides $(CH_3)_4C_2(3\text{-}R\text{-}C_5H_3)_2VCl_2$ with R = H, Me, *t*-Bu are obtained by reacting the corresponding ligand MgCl salts with vanadium(III) acetylacetonato compounds, followed by oxidation with PCl_3 or AgCl. Smooth ligand exchange reactions of these *ansa*-vanadocene dichlorides afford acetylacetonato cations and binaphtholate complexes; from these, the dichlorides are regenerated by exposure to $MgCl_2$ in THF solution. Separation of *meso* and *rac* isomers (as well as enantiomer separation) is achieved *via* corresponding binaphtholate complexes; conversion to the vanadium(III) diisonitrile cations $(CH_3)_4C_2(3\text{-}R\text{-}C_5H_3)_2V(CNt\text{-}Bu)_2^+$ allows an assessment of diastereoisomer ratios by ^1H NMR. Lewis-acidic bistriflate derivatives of these *ansa*-vanadocene complexes are obtained from the dichlorides by reaction with silver triflate.
Key words: *ansa*-Metallocenes; Vanadium; Acetylacetonato complex; Chiral; Enantioseparation.

Structures, electronic properties and reactivities of a great diversity of titanocene complexes have been admirably elucidated over the last three decades in more than eighty publications by Karel Mach and his coworkers[2]. That comparable insights are largely lacking in regard to related vanadocene and chromocene complexes is undoubtedly connected with the generally more difficult access to this class of metallocenes, especially to their ring-bridged representatives[1,3]. In order to open up this field to more incisive investigations, also with regard to possible application to asymmetric catalysis, we have tried to develop improved methods for the synthesis of *ansa*-vanadocene compounds. In an earlier publication, we have reported[3] that the synthesis of ethano-bridged vanadocene chlorides suffers from the reduction of VCl_4 by the dianionic ligand compound $(CH_3)_4C_2(C_5H_4Li)_2$, and that improved yields are obtained by reaction of VCl_4 or – prefereably – of VCl_3 with the dimagnesium salt $(CH_3)_4C_2(C_5H_4MgCl)_2$ (**1a**).

* Part XXXVII in the series on *ansa*-Metallocene Derivatives; Part XXXVI: see ref.[1].

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Further studies with bis(acetylacetonato)vanadium dichloride[4], $(acac)_2VCl_2$, showed that this compound is less easily reduced than VCl_4 ($E_p((acac)_2VCl_2) = -0.18$ V, $E_p(VCl_4(THF)_2) = -0.06$ V in THF solution), but that even this starting material produces only the vanadium(III) monochloride complex $(CH_3)_4C_2(C_5H_4)_2VCl$ (**2a**). Control experiments showed that $(acac)_2VCl_2$ is reduced to $(acac)_2VCl$ when reacted with half an equivalent of the cyclopentadienyl magnesium compound **1a**. The reduced acetylacetonato compound, $(acac)_2VCl$, thus appeared to be an even more suitable starting material for *ansa*-vanadocene syntheses; in the following we report applications of this concept to syntheses of unsubstituted and ring-substituted, tetramethylethano-bridged vanadocene complexes $(CH_3)_4C_2(3\text{-}R\text{-}C_5H_3)_2VCl_2$ (**3**) with R = H (**3a**), Me (**3b**) or *t*-Bu (**3c**).

RESULTS AND DISCUSSION

ansa-Vanadocene Syntheses

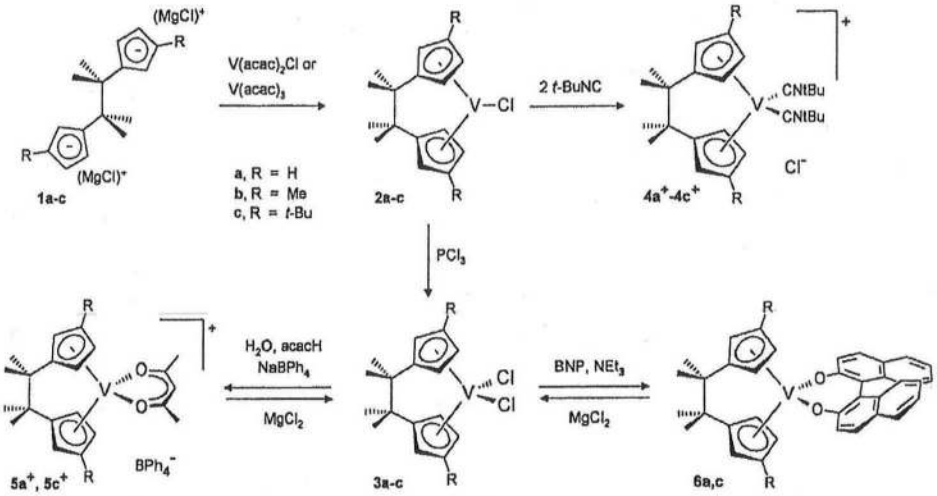
Reaction of the vanadium(III) compound $(acac)_2VCl$ with one equivalent of cyclopentadienyl potassium leads to substitution of the chloride ligand under formation of KCl and $C_5H_5V(acac)_2$ (previously prepared by reaction of $CpVCl_2(PMe_3)_2$ with acetylacetone[5]). Additional amounts of C_5H_5K give only unidentified reduction products; no dicyclopentadienyl vanadium species are observed in this reaction system. With C_5H_5MgCl, however, either $(acac)_2VCl$ or $(C_5H_5)V(acac)_2$ react to give vanadocene monochloride, $(C_5H_5)_2VCl$, from which $(C_5H_5)_2V(CN\textit{t}\text{-}Bu)_2^+Cl^-$ is formed by excess *tert*-butyl isonitrile in near-quantitative yield[6]. Apparently, the relative affinities of Mg(II) and V(III) for the ligands available in these reaction systems are such that acetylacetonate is completely scavenged by Mg(II) while V(III) will take up two cyclopentadienyl and one chloride ligand.

In accord with these preferences, we find that $(acac)_2VCl$ reacts with the dimagnesium compound $(CH_3)_4C_2(C_5H_4MgCl)_2$ (**1a**) to give, under substitution of the acetylacetonato ligands, the blue *ansa*-vanadocene monochloride **2a** (Scheme 1). *In situ* oxidation of the latter with PCl_3 affords the green dichloride **3a** in a total yield of 79%. The trisacetylacetonate $V(acac)_3$ reacts with $(CH_3)_4C_2(C_5H_4MgCl)_2$ (**1a**) to give the monochloride **2a** in similar yields, as documented by the isolation of the diisonitrile complex $(CH_3)_4C_2(C_5H_4)_2V(CN\textit{t}\text{-}Bu)_2^+Cl^-$ (**4a**$^+Cl^-$) in 75% yield upon addition of two equivalents of *tert*-butyl isonitrile to the product mixture.

Co-Ligand Exchange Reactions

An increased oxophilicity of the V(IV) center of the *ansa*-vanadocene dichloride $(CH_3)_4C_2(C_5H_4)_2VCl_2$ (**3a**) – relative to the V(III) center of **2a** – is documented by the observation that exposure to acetylacetone in water converts **3a** to the acetylacetonato

cation $(CH_3)_4C_2(C_5H_4)_2V(acac)^+$ (**5a**$^+$), which is isolated (as described for its unbridged analog[7]) by precipitation with tetraphenyl borate. Even cation **5a**$^+$, however, exchanges its acetylacetonato ligand for two Cl^- ligands completely – albeit slowly – when **5a**$^+B(C_6H_5)_4^-$ is stirred with excess $MgCl_2$ in THF solution: IR-spectrometrically, this ligand exchange reaction is found to be complete after 48 h; after this reaction period, the dichloride complex **3a** is quantitatively recovered. The relative oxophilicity of Mg(II) thus appears to exceed even that of the V(IV) center of **3a**.



SCHEME 1

When **5a**$^+B(C_6H_5)_4^-$ is reacted with $MgCl_2$ in the presence of the reducing agent $(Me_2N)_2C = C(NMe_2)_2$, however, the blue monochloride **2a** arises instantaneously. The V(III) acetylacetonate **8a** formed by reduction of **5a**$^+B(C_6H_5)_4^-$ thus appears much more reactive toward ligand exchange with Mg(II): Complex **8a**, for which a high-spin d^2 configuration is to be expected, is likely to bind its acetylacetonate in a monodentate manner only and is thus easily attacked by $MgCl_2$. A similar ligand exchange occurs with 1,1′-bi-2-naphtholate: Reaction of **3a** with one equivalent of binaphthol and two equivalents of triethylamine gives the *ansa*-vanadocene binaphtholate complex **6a**; this complex is reconverted to the dichloride **3a** by reaction with $MgCl_2$ in THF in the course of one hour. Conversion of the dichloride **3a** to the bis(triflate) complex $(CH_3)_4C_2(C_5H_4)_2V(O_3SCF_3)_2$ (**7a**), finally, is brought about, in analogy to the corresponding titanocene system[8], by reaction with two equivalents of silver triflate in THF solution.

Chiral ansa-Vanadocene Complexes

In order to synthesize the chiral complex $(CH_3)_4C_2(C_5H_3\text{-}3\text{-}Me)_2VCl_2$ (**3b**), the dimagnesium ligand salt **1b** was reacted with $V(acac)_3$ in THF solution. From this reaction, the ring-substituted *ansa*-vanadocene compound **2b** arises as a mixture of *meso*- and racemic diastereoisomers. To determine the ratio of these diastereoisomers, typical product mixtures were converted to the diisonitrile complexes *rac*- and *meso*-**4b**$^+Cl^-$. The racemic and *meso* isomers can be distinguished by the *tert*-butyl signals of their isonitrile ligands, which are homotopic for the racemic complex and diastereotopic for the *meso* isomer. A *rac/meso* ratio of close to 1 : 1 was thus obtained. In this case, we were not able to separate the diastereomers. Oxidation of the product mixture with PCl_3 gave the dichloride **3b** as a mixture of *rac* and *meso* diastereomers in a total yield of 76%.

For the synthesis of the *tert*-butyl substituted complex $(CH_3)_4C_2(C_5H_3\text{-}3\text{-}t\text{-}Bu)_2VCl_2$ (**3c**), reactions of the corresponding dimagnesium ligand salt **1c** with a number of different vanadium(III) starting compounds were conducted at various temperatures and the ensuing *rac/meso* ratios studied by conversion of the respective product mixtures to the diamagnetic diisonitrile complexes *rac*- and *meso*-**4c**$^+Cl^-$ (Table I). Higher *rac/meso* ratios (6 : 1) were achieved with $V(acac)_3$ than with $V(acac)_2Cl$ or VCl_3 as starting materials. With $V(acac)_2Cl$, higher reaction temperatures led to a stronger preference for the racemic product, as previously observed in other cases[9]. With the chiral reactant tris(*R,S*-hydroxymethylene camphorate) V(III), *rac*-**3c** was again the preferred product, but with a *rac/meso* ratio of only 3.5 : 1. Oxidation of the *tert*-butyl substituted monochloride complex **2c** with PCl_3 proved to be very sluggish; in this case, oxidation of the product mixture with AgCl gave the dichloride **3c** in the course of 12 h in a yield of 74%.

TABLE I
Yields and *rac/meso* ratios for compound **3c**

Reactant	Temperature, °C	Yield, %	*rac/meso*
$VCl_3(THF)_3$	–78	38	1/1
$VCl_3(THF)_3$	20	35	3/1
$VCl_3(THF)_3$	65	34	4/1
$(acac)_2VCl(THF)$	–78	61	1/1.3
$(acac)_2VCl(THF)$	20	62	3/1
$(acac)_2VCl(THF)$	65	61	5/1
$V(acac)_3$	20	59	6/1

Finally, complex **3c** was also converted to the red binaphtholate derivative **6c** by reaction with *rac*-1,1′-bi-2-naphthol and triethylamine. After chromatography on silanized silica gel, complex **6c** was isolated in *ca* 70% yield. Reduction with tetrakis(*N*,*N*-dimethylamino)ethylene and conversion to the diisonitrile complex **4c**$^+$Cl$^-$ showed that only the racemic binaphtholate derivative, *rac*-**6c**, was obtained. The fate of the *meso* isomer remains to be clarified; conceivable are either its conversion to the racemic isomer during complex formation with the binaphtholate anion or its irreversible fixation to the chromatography column.

Reaction of complex **3c** with one half equivalent of (*R*)-(+)-binaphthol and one equivalent of triethylamine and subsequent removal of unreacted dichloride **3c** by chromatography on silanized silica gel afforded an optically active binaphtholate complex, presumably the isomer of **6c** with 1-*R* configuration at the bridgehead carbon atom, in which the *tert*-butyl groups are farthest from the binaphtholate ligands. Rather than by chromatography, unreacted dichloride *S*-**3c** can also be removed from the product mixture by its selective conversion to the acetylacetonate cation upon extraction with water and acetylacetone. The tetraphenylborate of the acetylacetonato complex, **5a**$^+$B(C_6H_5)$_4^-$,

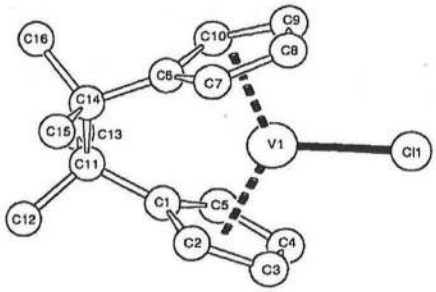


FIG. 1
Crystal structure of complex **2a**

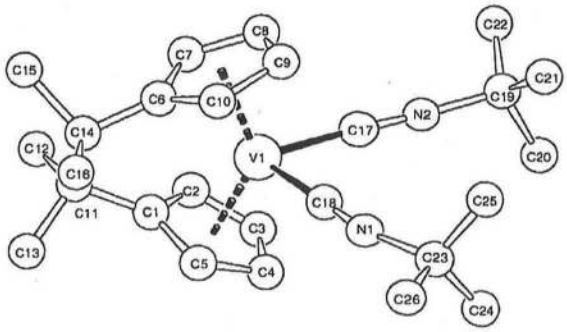


FIG. 2
Structure of cation **4a**$^+$ in crystalline **4a**$^+$Cl$^-$

was thus obtained in form of green crystals suitable for a diffractometric structure determination.

The bis(triflate) complexes **7a** and *R*-**7c** (obtained from the chiral dichloride *R*-**3c** in a manner analogous to that described above for **7a**) proved to be useful catalysts for Lewis-acid induced Diels–Alder and other C–C coupling reactions; these observations are to be reported in a separate communication.

Crystal Structures

The molecular structures of complexes **2a**, **4a**$^+$Cl$^-$, **5a**$^+$B$(C_6H_5)_4^-$ and **5c**$^+$B$(C_6H_5)_4^-$ were determined by crystal structure analysis (Figs 1–4). Characteristic bond lengths and angles are summarized in Tables II and III.

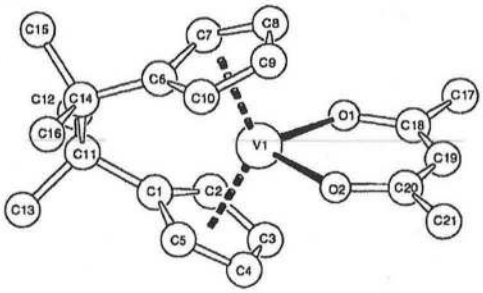


FIG. 3
Structure of cation **5a**$^+$ in crystalline **5a**$^+$B$(C_6H_5)_4^-$

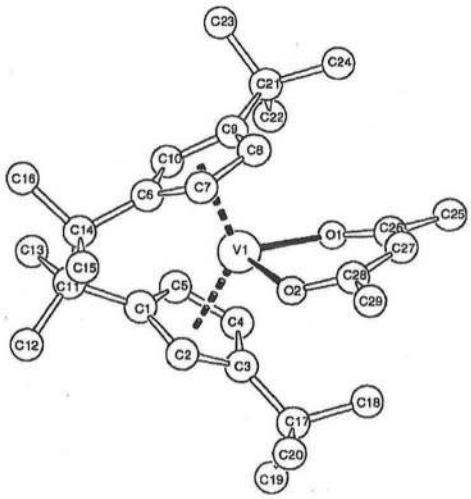


FIG. 4
Structure of cation **5c**$^+$ in crystalline **5c**$^+$B$(C_6H_5)_4^-$

In the vanadium(III)–monochloro complex **2a**, the VCl distance is about 7 ppm shorter than in the dichloro complex **3a**. The vanadium–Cp-centroid distance is likewise shortened by *ca* 3 pm. As in the corresponding unbridged vanadocene mono- and di-

TABLE II
Selected bond distances (ppm) and angles (°) for complex **2a** and of the cation $\mathbf{4a}^+$ in crystalline $\mathbf{4a}^+Cl^-$

Atoms	Distances, angles	Atoms	Distances, angles
2a		$\mathbf{4a}^+$	
V1–C1	238.0(1)	V1–C17	202.4(14)
V1–C1	226.4(3)	V1–C18	195.8(14)
V1–C2	226.0(4)	V1–C1	226.2(13)
V1–C3	227.9(4)	V1–C2	226.5(15)
V1–C4	228.5(4)	V1–C3	230.4(16)
V1–C5	227.8(4)	V1–C4	224.6(13)
V1–C6	227.0(4)	V1–C5	221.3(14)
V1–C7	227.3(4)	V1–C6	222.3(13)
V1–C8	227.5(4)	V1–C7	229.3(13)
V1–C9	227.3(4)	V1–C8	230.8(14)
V1–C10	226.1(4)	V1–C9	224.1(14)
V1–CCR1[a]	193.2	V1–C10	222.1(14)
V1–CR2[a]	192.8	C17–N2	114.3(18)
		C18–N1	116.6(18)
CR1–V–CR2[a]	136.7	C19–N2	148.0(16)
CP1–CP2[b]	44.6	C23–N1	150.1(19)
		V1–CR1[a]	191.7
		V1–CR2[a]	191.7
		CR1–V1–CR2[a]	134.2
		C17–V1–C18	82.4(6)
		C17–N2–C19	172.0(13)
		C18–N1–C23	167.3(13)
		CP1–CP2[b]	46.6

[a] CR1, CR2 centroids of C atoms numbered 1–5 and 6–10, respectively. [b] CP1, CP2 mean planes of corresponding C_5 rings.

chlorides[10], the decreased VCl bond distance is likely to result from the reduced coordination number. Due to the shortened centroid–vanadium distances, the bridgehead–bridgehead distance is only about 268 pm. As a consequence, the centroid–V–centroid angle is widened by *ca* 6° relative to that in the dichloride **3a**. The V–Cl bond deviates by only 3° from the C_2-axis of the ligand framework.

The centroid–V–centroid angle in the diamagnetic vanadium(III) cation **4a**$^+$ is intermediate between that of the monochloride **2a** and the dichloride **3a**. The V–centroid

TABLE III
Selected bond distances (ppm) and angles (°) for cationic complexes **5a**$^+$ and **5c**$^+$ in their crystalline BPh_4^- salts

Atoms	Distances, angles	Atoms	Distances, angles
5a$^+$		**5c**$^+$	
V1–O1	201.5(4)	V1–O1	199.7(3)
V1–O2	201.0(3)	V1–O2	200.8(3)
V1–C1	228.8(5)	V1–C1	230.0(4)
V1–C2	223.9(5)	V1–C2	230.9(4)
V1–C3	226.2(6)	V1–C3	238.3(4)
V1–C4	232.2(7)	V1–C4	232.8(4)
V1–C5	228.5(6)	V1–C5	228.7(4)
V1–C6	229.2(5)	V1–C6	227.4(5)
V1–C7	228.1(5)	V1–C7	227.1(4)
V1–C8	231.4(5)	V1–C8	231.6(5)
V1–C9	228.5(5)	V1–C9	240.3(5)
V1–C10	224.2(5)	V1–C10	231.9(5)
C18–O1	127.7(7)	C26–O1	127.3(6)
C20–O2	127.4(6)	C28–O2	128.0(6)
V1–CR1[a]	194.4	V1–CR1[a]	198.4
V1–CR2[a]	194.7	V1–CR2[a]	197.8
CR1–V–CR2[a]	131.9	CR1–V–CR2[a]	130.1
O1–V1–O2	86.5(1)	O1–V1–O2	86.3(1)
CP1–CP2[b]	49.3	CP1–CP2[b]	53.4

[a] CR1, CR2 centroids of C atoms numbered 1–5 and 6–10, respectively. [b] CP1, CP2 mean planes of corresponding C_5 rings.

distance of 191 pm is shorter here than in any of the other vanadium complexes studied. The bisector of the diisonitrile vanadium fragment deviates by 21° from the C_2 axis of the ligand fragment; distortions of this kind were previously observed also in other *ansa*-metallocene complexes[11].

In the vanadium(IV)acetylacetonato cation **5a**$^+$, bond distances and angles of the ligand framework are similar to those in the dichloride[3] **3a**. The acetylacetonato ligand is practically planar; its geometry is comparable to those of other vanadium(IV) acetylacetonato compounds[12]. The bisector of the V(acac) fragment deviates from the C_2 axis of the ligand framework by only 7°, compared to a deviation of 16° for the VCl_2 fragment in the dichloro complex[3] **3a**.

The geometry of the cation **5c**$^+$, finally, documents the racemic configuration of this *tert*-butyl substituted *ansa*-vanadocene complex. Compared to its unsubstituted analog **5a**$^+$, the V(acac) fragment deviates from the C_2 axis of the ligand framework by a substantially larger angle of *ca* 20°; this is undoubtedly caused by the increased steric interactions. As generally observed with related metallocene structures, the metal–centroid distances are also increased by introduction of the bulky ring substituents.

EXPERIMENTAL

General

Moisture- and air-sensitive compounds were handled under an argon atmosphere using Schlenk techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl, pentane from CaH_2. NMR spectra were recorded on Bruker WM-250 and Bruker AC-250 FT spectrometers. $(acac)_2VCl(THF)$ (ref.[13]), $V(acac)_3$ (ref.[14]) and $(CH_3)_4C_2(C_5H_3R)_2(MgCl)_2(THF)_4$ (R = H, Me, *t*-Bu) (refs[2,15,16]) were prepared as described in the literature.

Bis(acetylacetonato)cyclopentadienylvanadium(III) A solution of 0.42 g (4 mmol) cyclopentadienyl potassium dissolved in 50 ml THF was slowly added to 0.71 g (2 mmol) $(acac)_2VCl(THF)$ in 150 ml THF. After stirring the reaction mixture for 16 h at room temperature, the precipitated potassium chloride was removed by filtration. The filtrate was freed from solvent *in vacuo* and the remaining solid taken up in 50 ml ether. After filtration, the solution was concentrated to a small volume, 30 ml of pentane were added and the mixture cooled to –80 °C. The brown precipitate was isolated by filtration and dried *in vacuo* to give 440 mg (*ca* 70% yield) of a brown air-sensitive powder consisting of essentially pure $CpV(acac)_2$, which presumably still contains a small amount of $(acac)_2VCl(THF)$ as judged by its IR spectrum. IR spectrum (Nujol, KBr, cm^{-1}): 3 079 (w), 1 576 (s), 1 521 (s), 1 457 (s), 1 424 (m), 1 420 (m), 1 381 (s), 1 364 (s), 1 275 (m), 1 018 (m), 931 (w), 798 (m). Mass spectrum (EI, 70 eV, 50 °C), $C_{10}H_{19}OV$ (314 g/mol): *m/z* 348 ($V(C_5H_7O_2)_3$, 3%), 314 (M^+, 26%), 249 ($M^+ - C_5H_5$, 100%), 215 ($M^+ - C_5H_7O_2$, 3%), 166 ($M^+ - C_5H_5 - C_5H_8O$, 37%).

Tetramethylethanediylbis(cyclopentadienyl)vanadium dichloride (**3a**). To 0.71 g (2 mmol) $(acac)_2VCl(THF)$ in 60 ml THF, 2 mmol of $(CH_3)_4C_2(C_5H_4)_2(MgCl)_2(THF)_4$ (**1a**) dissolved in 100 ml THF were slowly added. After stirring the reaction mixture for 20 h, the solvent was removed *in vacuo*. The residue was taken up in ether and the resulting blue suspension filtered to remove insoluble inorganic products. From the filtrate, $(CH_3)_4C_2(C_5H_4)_2VCl$ (**2a**) was obtained as an air-sensitive blue solid. IR spectrum (Nujol, KBr): 3 079 (w), 1 452 (m), 1 043 (w), 804, 795 (s) cm^{-1}. Mass spectrum (EI, 70 eV, 170 °C), $C_{16}H_{20}VCl$ (298.7 g/mol): *m/z* 298 (M^+, 54%), 258 ($M - C_3H_4$, 45%), 192

($M^+ - C_8H_{10}$, 23%), 156 ($M^+ - HCl - C_8H_{10}$, 100%). Alternatively, the filtrate, which contained the monochloride **2a**, was oxidized with 0.17 ml (2 mmol) of PCl_3 to the green *ansa*-vanadocene dichloride **3a** which precipitated and was isolated by filtration. The green solid was dissolved in 20 ml methylene chloride, filtered and the filtrate concentrated to a small volume (*ca* 1–2 ml). Ether (40 ml) was added and the resulting suspension cooled to –30 °C. The green solid was collected by filtration and dried *in vacuo* to yield 528 mg (79%) $(CH_3)_4C_2(C_5H_4)_2VCl_2$ (**3a**). IR spectrum (Nujol, KBr): 3 093 (w), 1 420 (m), 1 051 (w), 823 (s). For $C_{16}H_{20}Cl_2V$ (334.2) calculated: 57.51% C, 6.03% H; found: 58.04% C, 6.23% H. Mass spectrum (EI, 70 eV, 250 °C): *m/z* 333 (M^+, 15%), 298 ($M^+ - Cl$, 22%), 258 ($M^+ - Cl - C_3H_4$, 19%), 191 ($M^+ - Cl - C_9H_{10}$, 100%), 156 ($M^+ - 2\ Cl - C_9H_{10}$, 45%).

Tetramethylethanediylbis(cyclopentadienyl)vanadiumbis(t-butylisonitrile) chloride (**4a**$^+Cl^-$). To 0.97 g (2.8 mmol) $V(acac)_3$ in 100 ml THF were added dropwise 2.8 mmol of the magnesium ligand salt **1a**, dissolved in 100 ml THF. After stirring the mixture for 24 h at room temperature, the solvent was removed *in vacuo*. The residue was taken up in 200 ml of ether and filtered. On addition of 0.63 ml (4.6 mmol) of *t*-butylisonitrile to the filtrate, the color changed from blue to brown and the brown product **4a**$^+Cl^-$ precipitated. The solid was isolated by filtration and recrystallization from CH_2Cl_2–ether to yield 0.98 g $[(CH_3)_4C_2(C_5H_4)_2V(C_4H_9NC)_2]Cl$ (**4a**$^+Cl^-$) (75% yield). IR spectrum (Nujol, KBr, cm^{-1}): 2 137, 2 102 (ν(CN)). ^1H NMR spectrum ($CDCl_3$, 250 MHz): δ 1.02 s, 12 H (CH_3-bridge); 1.38 s, 18 H ($C(CH_3)_3$-NC); 5.0 m, 4 H (β-C_5H_4); 5.13 m, 4 H (α-C_5H_4). The ^1H NMR signals of α and β cyclopentadienyl protons of these complexes were assigned by means of a ROESY experiment; as in other metallocene complexes with 18-electron configuration[2,17], the protons in α-position are shifted to lower fields than those in β-position. ^{13}C NMR spectrum (63 MHz, $CDCl_3$): δ 27.33 ($C(CH_3)_2$-bridge); 30.39 ($(CH_3)_3C$-NC); 44.65 ($C(CH_3)_2$-bridge); 58.91 ($(CH_3)_3C$-NC); 86.60 (α-C_5H_4); 98.26 (β-C_5H_4); 128.89 (bridgehead-(1)-C_5H_4). For $C_{26}H_{38}ClNV$ (465.0) calculated: 6.02% N, 8.24% H; found: 6.09% N, 8.26% H.

Tetramethylethanediylbis(cyclopentadienyl)acetylacetonatovanadium tetraphenylborate (**5a**$^+B(C_6H_5)_4^-$). Compound $(CH_3)_4C_2(C_5H_4)_2VCl_2$ (**3a**) (150 mg, 0.45 mmol) was suspended in 20 ml H_2O. On addition of 90 mg acetylacetone (0.91 mmol), the solid dissolved and the color changed from green to brown. After stirring for one hour at room temperature, the reaction mixture was filtered and the filtrate, which contained the cation $[(CH_3)_4C_2(C_5H_4)_2V(C_5H_7O_2)]^+$ (**5a**$^+$), mixed with 170 mg (0.5 mmol) $Na(B(C_6H_5)_4)$ in 10 ml water to precipitate an olive green solid. This was collected by filtration and washed with water. Coevaporation of the green powder with toluene and drying *in vacuo* gave 260 mg $[(CH_3)_4C_2(C_5H_{42}V(C_5H_7O_2)]B(C_6H_5)_4$ (**5a**$^+B(C_6H_5)_4^-$ (85% yield). IR spectrum (Nujol, KBr, cm^{-1}): 3 107 (w), 3 050 (m), 3 037 (w), 3 025 (m), 1 582 (s), 1 561 (s), 1 521 (s), 1 512 (s), 1 463 (s), 1 426 (w), 1 344 (w), 1 279 (w), 1 147 (w), 1 031 (w), 935 (w), 846 (w), 831 (m), 744 (m), 736 (m), 728 (m). For $C_{45}H_{47}BO_2V$ (681.6) calculated: 79.3% C, 6.95% H; found: 79.53% C, 7.05% H.

Tetramethylethanediylbis(cyclopentadienyl)vanadium binaphtholate (**6a**). To a solution of 0.47 g (1.41 mmol) $(CH_3)_4C_2(C_5H_4)_2VCl_2$ (**3a**) and 0.4 g (1.41 mmol)binaphthol in 50 ml THF were added 0.39 ml (2.81 mmol) of triethylamine in one portion. After stirring for one hour, the green solution slowly turned red. After stirring for 14 h, THF was exchanged for toluene. The colorless precipitate was removed by filtration and the solution filtered over a small plug of silylated silica gel. The filtrate was evaporated *in vacuo*, the residue suspended in a small volume of ether and cooled to –30 °C. The red orange solid was isolated by filtration and dried *in vacuo* to give 0.66 g (86%) $(CH_3)_4C_2(C_5H_4)_2V(C_{20}H_{12}O_2)$ (**6a**). IR spectrum (Nujol, KBr, cm^{-1}): 3 107 (w), 3 083 (w), 1 610 (w), 1 587 (w), 1 499 (w), 1 354 (m), 1 277 (m), 1 246 9s), 1 124 (m), 1 071 (m), 826 9s), 817 9s), 745 (m). For $C_{44}H_{48}O_2V$ (547.8) calculated: 78.94% C, 5.89% H; found: 78.13% C, 6.01% H. Mass spectrum (EI, 70 eV, 280 °C): *m/z* 547 (M^+, 13%), 412 ($M^+ - C_8H_{10}$, 2%), 335 ($M^+ - C_{16}H_{19}$, 10%), 261 ($M^+ - C_{20}H_{14}O_2V$, 100%).

Tetramethylethanediylbis(cyclopentadienyl)vanadium bistriflate (**7a**). 0.23 g (0.69 mmol) of the *ansa*-vanadocene dichloride **3a** and 0.35 g (1.38 mmol) silver triflate were mixed and 50 ml of THF

added. After 10 h the precipitated silver chloride was removed by filtration and the filtrate evaporated to dryness. The residue was recrystallized twice from CH_2Cl_2–ether mixture to give 0.3 g $(CH_3)_4C_2(C_5H_4)_2V(O_3SCF_3)_2$ (**7a**) as a blue-green powder in 78% yield. IR spectrum (Nujol, KBr, cm^{-1}): 3 123 (w), 1 454 (w), 1 327 (m), 1 284 (w), 1 232 (m), 1 206 (s), 1 191 (s), 1 090 (m), 1 041 (s), 1 020 (m), 860 (w), 845 (w), 801 (w). For $C_{18}H_{20}F_6O_6S_2V$ (561.4) calculated: 38.51% C, 3.59% H; found: 38.21% C, 3.73% H. Mass spectrum (EI, 70 eV, 220 °C): *m/z* 561 (M^+, 31%), 412 ($M^+ - SO_3CF_3$, 70%), 305 ($M^+ - SO_3CF_3 - C_8H_{11}$, 100%), 261 ($M^+ - 2\ HSO_3CF_3$, 36%).

Tetramethylethanediylbis(3-methylcyclopentadienyl)vanadium dichloride (**3b**). The same procedure and the same molar ratios used to synthesize **3a** were used to give 76% $(CH_3)_4C_2(3\text{-}(CH_3)\text{-}C_5H_3)_2VCl_2$ (**3b**) starting from $V(acac)_3$. IR spectrum (Nujol, KBr, cm^{-1}): 3 117 (w), 3 081 (w), 1 502 (w), 1 455 (s), 1 367 (s), 1 261 (w), 1 092 (m), 1 073 (m), 1 060 (m), 1 029 (m), 865 (m), 841 (w), 824 (w), 801 (m). For $C_{18}H_{24}Cl_2V$ (362.2) calculated: 59.69% C, 6.68% H; found: 58.89% C, 6.72% H. Mass spectrum (EI, 70 eV, 170 °C): *m/z* 361 (M^+, 20%), 326 ($M^+ - Cl$, 39%), 288 ($M^+ - 2\ HCl - H$, 27%), 205 ($M^+ - C_9H_{13}$, 100%), 170 ($M^+ - C_9H_{13} - Cl$, 45%).

Tetramethylethanediylbis(3-t-butylcyclopentadienyl)vanadium dichloride (**3c**). 0.54 g (1.55 mmol) of $V(acac)_3$ were reacted with 1.55 mmol of the dimagnesium salt **1c** in 150 ml of THF. After stirring for 16 h, the solvent was removed *in vacuo*. The remaining solid was stirred in 5 ml of methylene chloride and then 100 ml of pentane were added. The mixture was filtered and the filtrate freed from solvent. The solid residue was taken up in THF and 1.6 mmol AgCl added. After stirring for 12 h, the suspension was filtered and solvent removed from the filtrate. The residue was extracted with hexane in a Soxhlet apparatus. The extract was cooled to –80 °C and the yellow-green solid isolated by filtration to give 74% $(CH_3)_4C_2(3\text{-}((CH_3)_3C)\text{-}C_5H_3)_2VCl_2$ (**3c**). IR spectrum (Nujol, KBr, cm^{-1}): 3 135 (m), 3 117 (m), 1 497 (s), 1 399 (w), 1 382 (m), 1 375 (m), 1 365 (s), 1 358 (m), 1 242 (m), 1 169 (w), 1 076 (m), 877 (m), 824 (m). For $C_{24}H_{36}Cl_2V$ (446.4) calculated: 64.58% C, 8.13% H; found: 64.1% C, 8.08% H. Mass spectrum (EI, 70 eV, 200 °C): *m/z* 445 (M^+, 27%), 410 ($M^+ - Cl$, 100%), 373 ($M^+ - 2\ HCl$, 1%), 233 ($M^+ - Cl - C_{12}H_{19}$, 76%).

Tetramethylethanediylbis(3-t-butylcyclopentadienyl)vanadiumbis(t-butylisonitrile) chloride (**4c**$^+Cl^-$). To a solution of 1 mmol of the vanadium(III) starting material in 50 ml of THF, 1 mmol of ligand salt **1c** in 50 ml THF was added dropwise. After stirring for 6 h at the temperature given in Table I, the reaction mixture was stirred at room temperature for another 10 h. The solvent was removed *in vacuo*, the residue stirred in 5 ml of methylene chloride; then 100 ml of pentane were added. The suspension was filtered and the solution reduced to a small volume. Addition of 0.23 ml (2 mmol) of *t*-butylisonitrile resulted in a slow color change from blue to brown. After 16 h, the solvent was removed *in vacuo* and the remaining solid examined by ^1H NMR spectroscopy. Purification of the brown solid was achieved by recrystallization from CH_2Cl_2–ether (yields and diastereoisomer ratios, see Table I). IR spectrum (Nujol, KBr, cm^{-1}): ν(CN): 2 125, 2 112, 2 102; *rac*-**4a**$^+Cl^-$: ^1H NMR spectrum ($CDCl_3$, 250 MHz): δ 0.99 s, 6 H (**CH**$_3$-bridge, Me next to C(2)); 1.05 s, 6 H (**CH**$_3$-bridge, Me next to C(5)); 1.23 s, 18 H ($(\mathbf{CH_3})_3$C-cp); 1.43 s, 18 H ($(\mathbf{CH_3})_3$C-NC); 4.68 m, 2 H (β-(4)-$C_5\mathbf{H}_3$); 4.90 m, 2 H (α-(2)-$C_5\mathbf{H}_3$); 4.95 m, 2 H (α-(5)-$C_5\mathbf{H}_3$). ^1H NMR spectrum ($(CD_3)_2CO$, 250 MHz): δ 1.07 s, 6 H (**CH**$_3$-bridge, Me next to C(2)); 1.15 s, 6 H (**CH**$_3$-bridge, Me next to C(5)); 1.34 s, 18 H ($(\mathbf{CH_3})_3$C-cp); 1.54 s, 18 H ($(\mathbf{CH_3})_3$C-NC); 5.04 m, 2 H (β-(4)-$C_5\mathbf{H}_3$); 5.22 m, 2 H (α-(2)-$C_5\mathbf{H}_3$); 5.33 m, 2 H (α-(5)-$C_5\mathbf{H}_3$). ^{13}C NMR spectrum (63 MHz, $CDCl_3$): δ 25.37 (C(**CH**$_3)_2$-bridge, Me next to C(5)); 28.12 ((C(**CH**$_3)_2$-bridge, Me next to C(2)); 29.54 (C(**CH**$_3)_3$-NC); 30.46 (C(**CH**$_3)_3$-cp); 31.49 (C(**CH**$_3)_3$-cp); 43.81 (**C**(CH$_3)_2$-bridge); 65.03 (**C**(CH$_3)_3$-NC); 81.51 (α-(2)-**C**$_5$H$_3$); 82.19 (α-(5)-**C**$_5$H$_3$); 95.85 (β-(4)-**C**$_5$H$_3$); 128.96 (β-(3)-**C**$_5$H$_3$); 133.44 (bridgehead-(1)-**C**$_5$H$_3$). *meso*-**4c**$^+Cl^-$: ^1H NMR ($(CD_3)_2CO$, 250 MHz): δ 1.06, 1.29 2 s, 12 H (**CH**$_3$-bridge); 1.25 s, 18 H ($(\mathbf{CH_3})_3$C-cp); 1.59, 1.56 2 s, 18 H ($(\mathbf{CH_3})_3$C-NC); 4.86, 5.26, 5.67 m, 6 H ($C_5\mathbf{H}_3$).

TABLE IV
Crystallographic and experimental data for complexes **2a**, **4a**$^+$Cl$^-$, **5a**$^+$BPh$_4^-$ and **5c**$^+$BPh$_4^-$

Parameter	**2a**	**4a**$^+$Cl$^-$	**5a**$^+$BPh$_4^-$	**5c**$^+$BPh$_4^-$
Formula	$C_{16}H_{20}VCl$	$C_{26}H_{38}N_2VCl$	$C_{45}H_{47}BO_2V$	$C_{53}H_{63}BO_2V$
Molecular weight	298.73	464.99	681.62	793.8
Color, habit	blue needles	red cuboid	green needles	green needle
Crystal size	0.2 × 0.2 × 0.4	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.4	0.3 × 0.3 × 0.3
Space group[a]	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a, Å	7.574(2)	12.012(6)	9.669(3)	13.061(5)
b, Å	18.691(4)	12.238(6)	18.088(8)	22.119(5)
c, Å	9.933(2)	17.589(8)	20.981(5)	15.602(6)
β, °	95.33(2)		93.27(2)	92.70(3)
Volume, Å^3	1 400(5)	2 586(2)	3 636(2)	4 502(3)
D_c, g cm^{-3}	1.417	1.194	1.236	1.171
Absorption coefficient (μ), cm^{-1}	0.858	0.489	0.296	0.249
Temperature, K	235	238	235	245
Weighting scheme	$\sigma^2(F) + 0.0004F^2$	$\sigma^2(F) + 0.0002F^2$	$\sigma^2(F) + 0.0003F^2$	$\sigma^2(F) + 0.0004F^2$
2θ range, °	3.0 to 50.0	4.0 to 40.0	4.0 to 45.0	4.0 to 50.0
Scan speed, ° min^{-1}	1.50 to 14.65	1.50 to 14.65	1.50 to 14.65	1.5 to 14.65
Scan range, °	0.85	0.80	0.70	0.60
Reflection collected	1 721	1 430	5 335	8 564
Independent reflections	1 648	1 413	4 796	7 950
Observed reflections ($F > 4\sigma(F)$)	1 362	922	2 909	4 309
Solution (SHELXTL PLUS)	direct methods	Patterson	Patterson	direct method
Number of parameters refined	153	271	442	514
R_F[c], %	3.12	5.92	5.33	5.39
wR_F[d], %	3.88	5.03	4.97	5.48
Goodness-of-fit	1.35	1.39	1.43	1.27
Residual density, 10^{-6} e pm^{-3}	0.32	0.41	0.25	0.32

Conditions: Syntex/Siemens-P3 four-circle diffractometer, MoKα radiation, 71.073 pm, graphite monochromator.
[a] Monoclinic, Z = 4; [b] Wyckoff scan; [c] $R_F = \Sigma||F_o| - |F_c|| / \Sigma|F_c\delta|$; [d] $wR_F = |\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2|^{1/2}$.

Tetramethylethanediylbis(3-t-butylcyclopentadienyl)vanadium-rac-1,1′-bi-2-naphtholate (*rac*-**6c**). To a toluene solution containing 0.41 g (0.92 mmol) of the dichloride **3c** (both diastereoisomers) and 0.26 g (0.92 mmol) *rac*-1,1′-bi-2-naphthol 0.25 ml (1.8 mmol) triethylamine was added. In the course of 2 h the solution turned deep red. After stirring overnight, insoluble triethylammonium hydrochloride was removed by filtration. The filtrate was concentrated *in vacuo* and chromatographed over a column of silanized silica gel with pentane as eluent. Evaporation of the deep red fraction and drying the solid residue *in vacuo* yielded 0.42 g of the racemate of $(CH_3)_4C_2(3\text{-}((CH_3)_3C)\text{-}C_5H_3)_2VC_{20}H_{12}O_2$ (*rac*-**6c**, 69% yield). IR spectrum (Nujol, KBr, cm^{-1}): 1 588 (m), 1 499 (m), 1 419 (m), 1 382 (m), 1 365 (s), 1 280 (m), 1 246 (s), 1 232 (m), 744 (m). For $C_{44}H_{48}O_2V$ (660.0) calculated: 80.08% C, 7.33% H; found: 79.43% C, 7.52% H. Mass spectrum (EI, 70 eV, 175 °C): *m/z* 659 (M^+, 4%), 497 ($M^+ - C_{12}H_{18}$, 2%), 324 ($M^+ - C_{20}H_{12}O_2V$, 42%), 284 ($M^+ - C_{24}H_{36}V$, 100%).

Tetramethylethanediylbis(3-t-butylcyclopentadienyl)vanadium-R-1,1′-bi-2-naphtholate (*R*-**6c**). A procedure analogous to that described above for *rac*-**6c**, but conducted with one half equivalent of *R*-(+)-1,1′-bi-2-naphthol, gave one enantiomer of **6c**, with $[\alpha]_D = 2\ 224$ ° (d = 1, 13.1 mg **6c** in 1.5 ml $CHCl_3$).

Tetramethylethanediylbis(3-t-butylcyclopentadienyl)acetylacetonato vanadium hexafluorophosphate (**5c**$^+PF_6^-$). A reaction mixture containing the binaphtholate **6c** and unreacted dichloride **3c** was freed from triethylammonium hydrochloride by filtration, evaporated to dryness and then stirred with 20 ml water and 1 ml acetylacetone for one hour. After collecting the insoluble binaphtholate **6c** by filtration, addition of 0.3 g (1.6 mmol) of KPF_6 to the green aqueous filtrate gave a precipitate of 0.23 g of **5c**$^+PF_6^-$ (40% theoretical yield, based on dichloride **3c**). IR spectrum (Nujol, KBr, cm^{-1}): 1 581 (s), 1 519 (s), 1 498 (m), 1 403 (m), 1 279 (m), 1 261 (m), 1 021 (m), 878 (m), 836 (s), 771 (m). For $C_{29}H_{43}F_6O_2PV$ (619.6) calculated: 56.22% C, 7.0% H; found: 56.63% C, 7.1% H.

Crystal Structure Determinations

Crystals of complex **2a** were obtained from ether–hexane solutions at 0 °C, crystals of **4a**$^+Cl^-$, **5a**$^+B(C_6H_5)_4^-$ and **5c**$^+B(C_6H_5)_4^-$ were obtained by slow crystallization from CH_2Cl_2–ether solutions. Space groups, unit cell dimensions and diffraction intensities were determined on a Syntex/Siemens-P3 four-circle diffractometer. Table IV summarizes the experimental data for the crystallographic structure determination. Additional data can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen 2, upon quotation of deposit number CSD-59372, the authors and the journal reference for this article.

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