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Syntheses and Structures of Titanocene, Zirconocene, and Vanadocene Dichloride Complexes with Two Ethanediyl Bridges[1]

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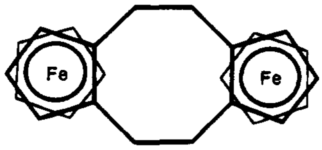
A bis(cyclopentadienyl) ligand containing two ethanediyl bridges is obtained by Skattebøl rearrangement of the bis(dibromocarbene) adduct of 1,2,5,6-tetramethylenecyclooctane. Reactions of its dilithium salt with $TiCl_3(THF)_3$, $ZrCl_4$, and $VCl_3(THF)_3$ afford, after appropriate workup, the corresponding doubly bridged metallocene dichlorides. X-ray diffraction studies give space group $P2_1/n$ for all three of the complexes $(C_2H_4)_2(C_5H_3)_2TiCl_2$, $(C_2H_4)_2(C_5H_3)_2ZrCl_2$, and $(C_2H_4)_2(C_5H_3)_2VCl_2$.

Introduction

C_2-symmetrical *ansa*-metallocenes of group IV transition metals have found applications as chiral homogeneous catalysts, e.g. for α-olefin polymerizations[2] or hydrogenations.[3] The conformational stability of the *ansa*-metallocene ligand framework is generally considered an important feature of these complexes. Several types of bridges[4] have been developed to attain a reduced flexibility.[5] Highly rigid chiral zirconocene complexes result from the introduction of two silanediyl bridges;[6] these complexes were observed to degrade, however, when incubated with the cocatalyst methylalumoxane, probably due to the unusually large angle between the cyclopentadienyl rings caused by two adjacent Me_2Si bridges.[6] Metallocenes with two adjacent ethanediyl bridges are an alternative with a less strained but still highly rigid ligand framework. Here, we describe a synthetic route to doubly ethanediyl-bridged ligands and the preparation and crystal structures of novel, doubly bridged titanocene, zirconocene, and vanadocene complexes.

Results and Discussion

The dimeric *cis*- and *trans*-[2.2]ferrocenophanes (**1**)[7] contain the required bis(ethanediyl)-bridged ligand. Since the preparation of **1** is cumbersome, we have developed a more general access to ligand **4**. The synthesis of **4** and of the corresponding metallocenes **5**−**7** is outlined in Scheme 1. The key step in this procedure is a Skattebøl rearrangement[8] of the addition product of dibromocarbene to a 1,3-diene system. This synthetic method has proven useful for the preparation of several polycyclic mono- and bis(cyclopentadienyl) derivatives.[9]



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1,2,5,6-Tetramethylenecyclooctane (**2**) was used as the starting material for our synthetic route. This compound is available by a two-step reaction from 2,3-dimethylbutadiene in 15% yield, but it still contains about 20% of linear impurities, which are difficult to separate.[10] **2** was treated with 2 equiv of ^tBuOK and bromoform in pentane to yield the two dibromocarbene adducts **3A** and **3B**. As **3** could not be freed from the impurities in the starting material, by either crystal-

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Scheme 1

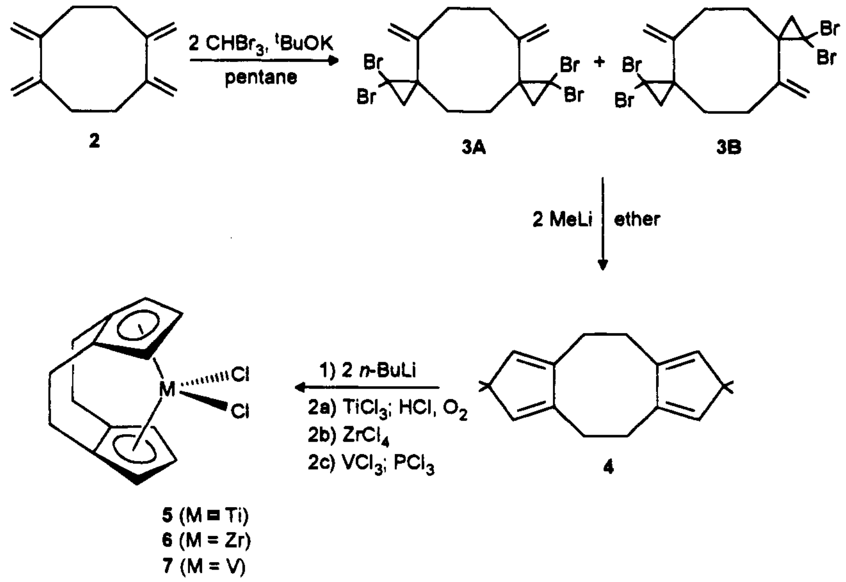

Table 1. ^{1}H NMR Data for Bis(ethanediyl)-Bridged Metallocenes 5 and 6 (CDCl$_3$, 250 MHz, δ in ppm, 25 °C)

5	6	assignt
3.42 (m, 4H)	3.30 (m, 4H)	CH$_2$CH$_2$
6.15 (t, 1H, J = 3.3 Hz)	6.00 (t, 1H, J = 3.3 Hz)	CHC*H*CH
6.59 (d, 2H, J = 3.3 Hz)	6.42 (d, 2H, J = 3.3 Hz)	C*H*CHC*H*

lization or chromatography, the crude product mixture was used without further workup. Skattebøl rearangement,[8] induced by the action of MeLi, gave the doubly ethanediyl-bridged bis(cyclopentadienyl) system **4**. Deprotonation by ^{n}BuLi in THF resulted in a dark red reaction mixture. The dilithium salt was isolated by replacement of THF with pentane and subsequent filtration. The dianion of **4** was reacted with TiCl$_3$(THF)$_3$ in THF, followed by oxidation with HCl in air. After workup (see Experimental Section), the titanium complex **5** was obtained in about 20% yield based on **2** (of ca. 80% purity). Reaction of lithiated **4** with ZrCl$_4$ in toluene afforded the corresponding *ansa*-zirconocene dichloride **6** in 12% yield. Treatment of the deprotonated ligand **4** with VCl$_3$(THF)$_3$ in THF yielded, after oxidation with PCl$_3$,[11] 13% of the vanadocene complex **7**.

The ^{1}H-NMR spectra of the two diamagnetic compounds **5** and **6** (Table 1) are in accord with expectation. The C$_2$H$_4$-bridge signals are found at 3.2 ppm, similar to those of singly ethanediyl-bridged metallocene dichlorides.[12] The titanium complex **5** shows a somewhat larger coupling of the two diastereotopic ethano protons, probably due to smaller dihedral angles C(1)—C(11)—C(12)—C(6) and C(2)—C(13)—C(14)—C(7) (21.7 and 23.6°) compared to the zirconium congener **6** (23.6 and 27.2°). Of particular interest are the chemical shifts of the C$_5$-ring protons: Of these, the two lateral protons have their signals at lower field, while that of the central proton is found at higher field in CDCl$_3$ solution. For singly bridged titanocene and zirconocene dihalides, on the other hand, the low-field signals had been assigned to the β-protons and the high-field signals to the α-protons.[13] Combining the results for both types of complexes, we can now identify C$_5$-ring sectors associated with high- and with low-field shifts of the cyclopentadienyl protons relative to the respective average shift value (Figure 1). A similar shift pattern, which is apparently connected with the magnetic anisotropy of the M—Cl bonds, is also observed for the ^{13}C signals of the lateral and central C atoms in **5** and **6** (see Experimental Section).

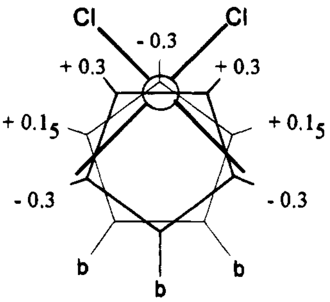

Figure 1. Chemical shifts of C$_5$-ring protons in singly and doubly bridged metallocene dichlorides, relative to the respective average value (+ = low-field shift, − = high-field shift; b = bridge).

The crystal structures of complexes **5**–**7** are likewise in accord with expectations; they exhibit approximate C_2 molecular symmetry (Figure 2; Table 2). The axes bisecting the Cl—M—Cl angles deviate only by 2–3° from the vector connecting the metal with the centroid of the four bridging atoms C(11)–C(14).[14] As in all bridged metallocenes, the two C$_5$ rings are nearly eclipsed. Distortions from ideal C_{2v} symmetry, indicated by dissymmetric rotational angles[5] of θ = 4–5° for each of the cyclopentadienyl units, are comparable to those of θ = 6° for complexes with a single ethano bridge. The angles between the mean planes of the two C$_5$ rings, 57, 62, and 53°, respectively, are likewise only marginally larger than those of the corresponding complexes with a single ethano bridge.[12,15] As mentioned above,

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[14] For complex **7** this deviation is much smaller (3.4°) than for singly bridged (CH$_3$)$_4$C$_2$(C$_5$H$_4$)$_2$VCl$_2$,[15b] where the axis bisecting the Cl—V—Cl angle deviates by ca. 12° from the axis connecting the V atom with the midpoint of the ethano bridge.

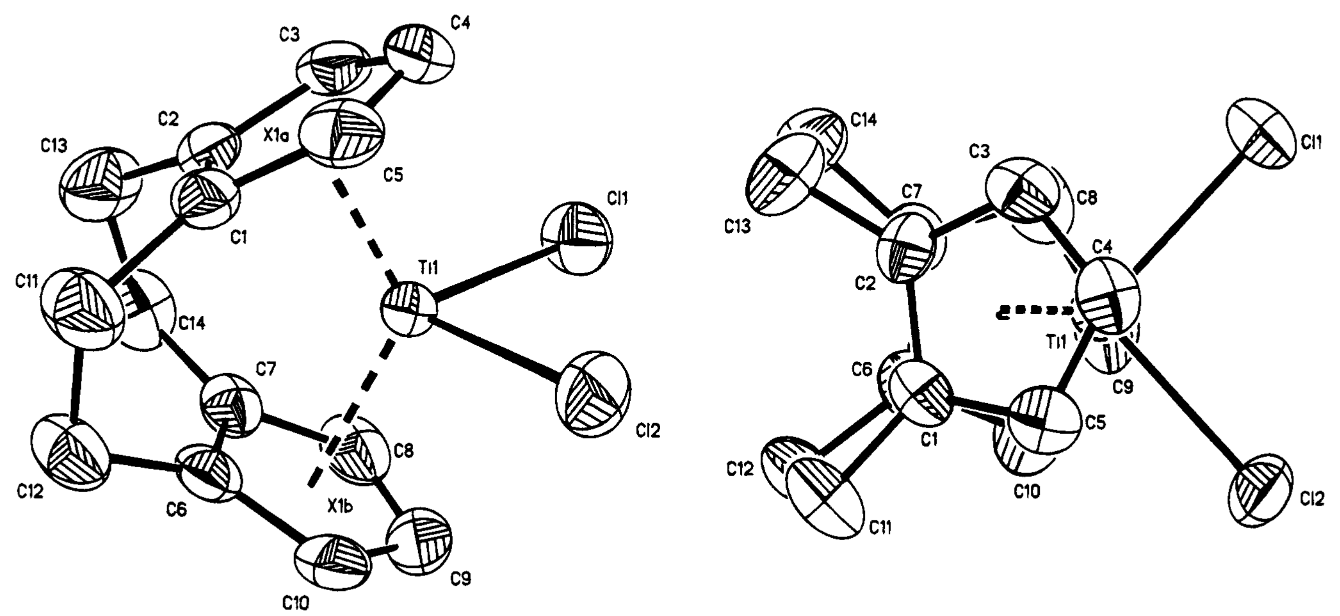

Figure 2. Molecular structure of complex **5** (left) and its projection on the $TiCl_2$ plane (right). The same connectivities and numbering schemes apply to complexes **6** and **7**.

Table 2. Selected Distances (pm) and Angles (deg) for Complexes 5–7

	5 (M = Ti)	6 (M = Zr)	7 (M = V)
M(1)–Cl(1)	235.8(1)	244.6(2)	239.6(2)
M(1)–Cl(2)	235.4(1)	243.5(2)	239.8(2)
M(1)–C(1)	234.6(3)	246.5(5)	229.4(3)
M(1)–C(2)	237.0(3)	248.8(5)	232.0(3)
M(1)–C(3)	238.3(3)	250.6(5)	229.7(3)
M(1)–C(4)	238.7(3)	251.4(5)	228.2(3)
M(1)–C(5)	238.0(3)	249.1(5)	230.5(3)
M(1)–C(6)	237.4(3)	249.0(5)	231.0(3)
M(1)–C(7)	235.1(3)	246.8(5)	230.2(3)
M(1)–C(8)	237.2(3)	250.0(5)	229.4(3)
M(1)–C(9)	239.5(4)	252.1(6)	228.9(3)
M(1)–C(10)	239.6(3)	250.9(5)	231.1(3)
M(1)–CR(1)[a]	205.5	218.7	196.4
M(1)–CR(2)	205.6	219.2	196.5
Cl(1)–M(1)–Cl(2)	94.8(1)	97.8(1)	87.2(1)
CR(1)–M(1)–CR(2)	124.5	120.0	126.3
CP(1)–CP(2)[b]	57.8	62.5	52.9
C(1)–C(11)–C(12)–C(6)	21.7	23.6	22.0
C(2)–C(13)–C(14)–C(7)	23.6	27.2	23.6

[a] CR(1) and CR(2) are the centroids of C atoms numbered 1–5 and 6–10, respectively. [b] CP(1) and CP(2) are the mean planes of the corresponding C_5 rings.

complexes with two dimethylsilyl bridges show substantially larger angles (72–73°) between their cyclopentadienyl rings.[6] As in these latter compounds, the two ethano bridges keep the cyclopentadienyl rings of **5**–**7** in a conformation which places one CH unit of each C_5 ring close to the meridional plane bisecting the Cl—metal—Cl angle. While substitution in this central position will lead to achiral complexes,[16] chiral complexes with a substituent orientation different from that accessible in singly bridged metallocenes are to be expected when additional substituents are placed in the lateral positions of the doubly bridged C_5 rings.

Experimental Section

General Information. 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 was distilled from CaH_2. NMR spectra were recorded on a Bruker WM 250-MHz spectrometer with TMS as internal standard.

Crystal Structure Determinations. Crystals of **5**–**7** were obtained by slow crystallization from $CHCl_3$ or CH_2Cl_2 solutions. Space groups, unit cell dimensions, and diffraction intensities were determined on a Syntex/Siemens-P3 four-circle diffractometer. Table 3 summarizes the crystallographic data, and Tables 4–6 the atomic positional parameters. Additional data are recorded in the supplementary material.

Bis(1,2-ethanediyl)bis(1,2-cyclopentadiene) (4). A 1.6 g (10 mmol) amount of 1,2,5,6-tetramethylenecyclooctane[10] (**2**) was added to a suspension of 2.59 g of ^{t}BuOK (23 mmol) in 50 mL of pentane. A solution of 1.98 mL (22 mmol) of bromoform in 20 mL of pentane was added dropwise over 2 h to the mixture at −20 °C. After it was stirred overnight, the light brown supension was hydrolyzed with 150 mL of water. The resulting mixture was diluted with 100 mL of diethyl ether, and the layers separated. The water layer was extracted three times with 50 mL portions of ether, and the combined organic layers were washed twice with water. After removal of the solvent under reduced pressure, the resulting orange oil was coevaporated twice with 30 mL of toluene to remove any water. The remaining oil was dissolved in 100 mL of ether and cooled to −78 °C. A 37.5 mL amount of a 1.6 M solution of MeLi in diethyl ether was added dropwise over 2 h. The resultant orange mixture was stirred for 1 h at room temperature and then slowly hydrolyzed, under cooling with an ice bath, with small amounts of crushed ice and extracted with ether. The combined organic layers were washed three times with small amounts of water and dried over $MgSO_4$. After filtration, the solvent was removed and the residual oil taken up in 200 mL of pentane. This mixture was filtered over a small plug of Florisil, yielding a light yellow oil after evaporation of the solvent. The product was dissolved in 50 mL of THF and cooled to −78 °C. On addition of 15 mL of 1.6 M *n*-BuLi in hexane the reaction mixture turned bright red. The solution was slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue mixed with 50 mL of pentane. The resulting light red suspension was filtered and the white residue washed several times with pentane to yield, after drying in vacuo, 0.96 g (61% based on **2**) of the white dilithium salt of **4**.

[Bis(1,2-ethanediyl)bis(1,2-cyclopentadienyl)]titanium Dichloride (5). A 0.96 g (4.88 mmol) amount of the

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Table 3. Crystallographic and Experimental Data for the Complexes $(C_2H_4)_2(C_5H_3)_2TiCl_2$ (5), $(C_2H_4)_2(C_5H_3)_2ZrCl_2$ (6), and $(C_2H_4)_2(C_5H_3)_2VCl_2$ (7)[a]

	5	6	7
formula	$C_{14}H_{14}TiCl_2$	$C_{14}H_{14}ZrCl_2$	$C_{14}H_{14}VCl_2$
fw	301.1	344.4	304.1
color, habit	red, rhombohedron	yellow rhombohedron	green needle
cryst size	0.3 × 0.3 × 0.5	0.2 × 0.2 × 0.3	0.3 × 0.3 × 0.5
space group[b]	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	8.0250(10)	8.131(2)	7.872(5)
b, Å	11.690(2)	11.834(3)	11.503(8)
c, Å	13.395(2)	13.401(4)	13.490(7)
β, deg	91.460(10)	91.73(2)	92.32(5)
V, Å^3	1256.3(4)	1288.9(6)	1220.6(13)
density (calcd), g/cm^3	1.592	1.775	1.655
abs coeff (μ), cm^{-1}	1.075	1.231	1.201
temp, K	299	233	294
weighting scheme	$\sigma^2(F) + 0.0003F^2$	$\sigma^2(F) + 0.0002F^2$	$\sigma^2(F) + 0.0003F^2$
2θ range, deg	4.0−47.0	4.0−47.0	4.0−50.0
scan speed, deg/min[c]	1.50−14.65	1.50−14.65	1.50−14.65
scan range, deg	0.60	0.70	0.80
no. of rflns collected	2257	1944	2438
no. of indep rflns	1977	1680	2146
no. of obsd rflns ($F > 4\sigma(F)$)	1635	1678	2143
soln (SHELXTL PLUS)	direct methods	Patterson	direct methods
no. of params refined	154	154	154
R_F,[d] %	3.35	4.44	4.25
R_{wF},[e] %	4.10	4.33	3.93
goodness of fit	1.52	1.84	1.32
residual density, 10^{-6} e pm^{-3}	0.37	0.56	0.37

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

Table 4. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Complex 5

	x	*y*	*z*	U_{eq}[a]
Ti(1)	−2767(1)	−7623(1)	−5039(1)	30(1)
Cl(1)	−2093(1)	−8940(1)	−3758(1)	51(1)
Cl(2)	−5479(1)	−7267(1)	−4485(1)	53(1)
C(1)	−1848(4)	−5834(2)	−5599(2)	37(1)
C(2)	−398(3)	−6508(3)	−5417(2)	37(1)
C(3)	−302(4)	−6726(3)	−4390(2)	43(1)
C(4)	−1643(4)	−6203(3)	−3932(2)	42(1)
C(5)	−2571(4)	−5634(2)	−4674(2)	42(1)
C(6)	−2889(4)	−7571(2)	−6811(2)	38(1)
C(7)	−1530(4)	−8295(2)	−6499(2)	39(1)
C(8)	−2209(5)	−9254(3)	−6030(2)	53(1)
C(9)	−3937(5)	−9137(3)	−6037(3)	61(1)
C(10)	−4358(4)	−8104(3)	−6518(2)	51(1)
C(11)	−2505(5)	−5446(3)	−6601(2)	56(1)
C(12)	−2734(4)	−6435(3)	−7328(2)	49(1)
C(13)	784(4)	−6886(3)	−6205(3)	61(1)
C(14)	286(4)	−8047(3)	−6630(3)	55(1)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Complex 6

	x	*y*	*z*	U_{eq}[a]
Zr(1)	2144(1)	2349(1)	63(1)	24(1)
Cl(1)	2923(2)	1011(1)	1386(1)	43(1)
Cl(2)	−645(2)	2730(1)	583(1)	45(1)
C(1)	3108(6)	4184(4)	−564(4)	29(2)
C(2)	4547(6)	3535(4)	−369(4)	29(2)
C(3)	4686(6)	3362(4)	674(4)	33(2)
C(4)	3381(7)	3906(4)	1119(4)	33(2)
C(5)	2406(6)	4419(4)	363(4)	32(2)
C(6)	2089(7)	2392(4)	−1796(3)	32(2)
C(7)	3425(7)	1688(4)	−1478(3)	32(2)
C(8)	2762(8)	707(5)	−1038(4)	43(2)
C(9)	1050(8)	805(5)	−1071(4)	50(2)
C(10)	647(7)	1838(5)	−1539(4)	43(2)
C(11)	2417(8)	4520(5)	−1576(4)	46(2)
C(12)	2230(7)	3528(4)	−2298(4)	41(2)
C(13)	5688(7)	3113(5)	−1164(4)	47(2)
C(14)	5230(7)	1950(5)	−1556(4)	48(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

ligand salt was dissolved in 50 mL of THF and the solution frozen in liquid nitrogen. A 1.81 g (4.88 mmol) amount of $TiCl_3(THF)_3$ was added at once and the resultant mixture slowly warmed to room temperature. After it was stirred overnight, the dark brown solution was oxidized with 30 mL of 6 M HCl in the presence of air. The two layers were separated and the water layer extracted twice with CH_2Cl_2/ether (1:4). The red solution was dried over $MgSO_4$ and filtered and the solvent removed in vacuo. The residue was washed with methanol, taken up in chloroform, and then filtered. The filtrate was concentrated to a small volume and ethyl acetate added. The precipitating red powder was filtered and dried. Recrystallizations from chloroform/ethyl acetate yielded 505 mg of **5** (21% based on **2**). ^1H NMR: see Table 1. ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.8 (CH_2), 113.8 (cyclopentadienyl CHCHCH), 127 (cyclopentadienyl CH*C*HCH), 136.3 (cyclopentadienyl bridgehead). Anal. Calcd for $C_{14}H_{14}TiCl_2$: C, 55.85; H, 4.69. Found: C, 55.71; H, 4.86. MS (EI): *m/z* 300 (M^+, 94%), 264 ($M^+ - HCl$, 100%).

[Bis(1,2-ethanediyl)bis(1,2-cyclopentadienyl)]zirconium Dichloride (6). After mixing 0.96 g (4.88 mmol) of the dianion of **4** with 1.14 g (4.88 mmol) of $ZrCl_4$, 50 mL of toluene was added. The yellow suspension was stirred for 1 day at room temperature and then filtered. The filtrate was evaporated to dryness and the pink residue extracted with hot ether for 3 days. The extract was concentrated to a small volume, and 1 mL of acetone was added. The resulting mixture was allowed to stand at −30 °C for 1 day and filtered, and recrystallization from diethyl ether/pentane was carried out to give 330 mg of ^1H NMR spectrally pure **6** as a white powder (12% based on **2**). ^1H NMR: see Table 1. ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.7 (CH_2), 110.2 (cyclopentadienyl CHCHCH), 121.4 (cyclopentadienyl CH*C*HCH), 131.8 (cyclopentadienyl bridgehead). Anal. Calcd for $C_{14}H_{14}ZrCl_2$: C, 48.83; H, 4.1. Found: C, 47.62; H, 4.44. MS (EI): *m/z* 343 (M^+, 100%), 306 ($M^+ - HCl - H$, 95%).

[Bis(1,2-ethanediyl)bis(1,2-cyclopentadienyl)]vanadium Dichloride (7). After 1.82 g (4.88 mmol) of $VCl_3(THF)_3$

Table 6. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for Complex 7

	x	*y*	*z*	U_{eq}[a]
V(1)	2675(1)	2379(1)	117(1)	26(1)
Cl(1)	2150(1)	1037(1)	−1219(1)	43(1)
Cl(2)	5455(1)	2650(1)	−509(1)	46(1)
C(1)	1839(3)	4182(2)	637(2)	32(1)
C(2)	332(3)	3506(2)	471(2)	33(1)
C(3)	226(3)	3211(2)	−538(2)	35(1)
C(4)	1615(3)	3707(2)	−1002(2)	37(1)
C(5)	2575(3)	4326(2)	−288(2)	38(1)
C(6)	2859(3)	2447(2)	1830(2)	32(1)
C(7)	1444(3)	1723(2)	1532(2)	33(1)
C(8)	2086(4)	758(2)	1033(2)	43(1)
C(9)	3853(4)	871(3)	1014(2)	49(1)
C(10)	4326(4)	1906(3)	1515(2)	44(1)
C(11)	2540(4)	4597(2)	1621(2)	48(1)
C(12)	2750(4)	3593(2)	2356(2)	42(1)
C(13)	−861(4)	3174(3)	1264(2)	49(1)
C(14)	−389(4)	1985(3)	1690(2)	45(1)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

was mixed with 0.96 g (4.88 mmol) of the dilithium salt of **4**, 100 mL of toluene was added. The dark brown-green reaction mixture was stirred for 1 day at room temperature. After removal of the solvent in vacuo, the residue was taken up in 150 mL of ether and filtered. On addition of 0.42 mL (4.88 mmol) of PCl_3 to the filtrate, a light green powder precipitated. The solid was filtered and, after drying in vacuo, extracted with CH_2Cl_2 for 3 days. The extract was reduced to a small volume, and 40 mL of ether was added. The resulting green precipitate was filtered and washed with a small portion of THF and then acetone. After recrystallization from methylene chloride/toluene and drying, 316 mg of **7** (13% based on **2**) was obtained. IR (Nujol): 3121 (m), 3111 (m), 3093 (m), 1438 (s), 1104 (m), 1044 (m) 835 (m), 811 (s) cm^{-1}. MS (EI): *m/z* 303 (M^+, 42%), 268 ($M^+ - Cl$, 100%). Anal. Calcd for $C_{14}H_{14}VCl_2$: C, 55.29; H, 4.64. Found: C, 54.63; H, 4.68. MS (EI): *m/z* 300 (M^+, 94%), 264 ($M^+ - HCl$, 100%).

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Supplementary Material Available: Tables of crystal data and details of the data collection, solution, and refinement, atomic coordinates and U_{eq} values, bond lengths and angles, and anisotropic displacement coefficients for compounds **5**–**7** and a figure showing the ^1H NMR spectrum of **6** (25 pages). Ordering information is given on any current masthead page.

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