Organometallics **1999,** *18,* 1663−1668

Unexpected Competition between Vanadium and Zinc in the Synthesis of Sterically Bulky Metallocenes

Jason S. Overby, Kumudini C. Jayaratne, Nathan J. Schoell, and Timothy P. Hanusa*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

Received August 18, 1998

Attempts to form $(Cp^{3i})_2V$ and $(Cp^{4i})_2V$ ($Cp^{ni} = C_5(iPr)_nH_{5-n}$) from the reaction of zinc-reduced VCl_3 and $K[Cp^{ni}]$ in THF at room temperature produces the corresponding zincocenes $(Cp^{3i})_2Zn$ and $(Cp^{4i})_2Zn$ instead. In refluxing THF, the same reactions generate the expected $(Cp^{ni})_2V$ vanadocenes. The latter are also formed from the reaction of aluminum-reduced VCl_3 with $K[Cp^{ni}]$ at room temperature. Reaction of 3 equiv of $K[Cp^{3i}]$ or $K[C_5Ph_4H]$ with VCl_3 in THF produces $(Cp^{3i})_2V$ and $(C_5Ph_4H)_2V$, respectively, whereas the equivalent reaction with $K[Cp^{4i}]$ generates $(Cp^{4i})_2VCl$. These experiments suggest that zincocenes are intermediates whenever vanadocenes are synthesized from zinc-reduced VCl_3 but that zinc complexes will be isolated only when certain cyclopentadienyl rings and temperature conditions are used. A single-crystal X-ray diffraction study of $(Cp^{3i})_2V$ found the metal to reside on a crystallographically imposed inversion center, with an average V−C(ring) distance of 2.274(9) Å; the isopropyl groups orient themselves to minimize unfavorable steric interactions between the rings.

Introduction

Owing to its convenient physical properties and commercial availability, vanadium trichloride serves as a common entry point into low-valent vanadium chemistry. It is easily reduced by metallic zinc in THF to form a material at one time thought to contain "$VCl_2(thf)_2$"[1,2] but was later shown to consist of the vanadium−zinc species $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$.[3,4] The latter is a useful source of the V(II) ion in organovanadium synthesis and has been used to generate a number of vanadocenes and related compounds (eq 1; M = Li, Na, K; Cp′ = Cp, Cp*, C_5Ph_4H, $Me_2C_5H_5$).[1,3,5−7] With other ligands, the final

$$2\,VCl_3 + Zn \xrightarrow{4MCp'} 2Cp'_2V + ZnCl_2 + 4MCl \quad (1)$$

products from reactions using VCl_3/Zn have been shown to contain both vanadium and zinc, such as $[VZnH_2(BH_4)(PMePh_2)_2]_2$[8] and $[VZnO(C_6H_5CO_2)_3(thf)]_4{\cdot}2thf$.[9]

In the present study of vanadium metallocenes containing the "encapsulating" triisopropylcyclopentadienyl (Cp^{3i}) and tetraisopropylcyclopentadienyl (Cp^{4i}) rings,[10,11] we have found that solutions of zinc-reduced VCl_3 may function as a source not only of V(II) but also of Zn(II) alone. Our investigation into the conditions under which the latter occurs suggest that zinc serves as more than a reducing agent for trivalent vanadium in the production of other vanadocenes, including the parent Cp_2V.

Experimental Section

General Considerations. All manipulations were performed with the rigorous exclusion of air and moisture using high-vacuum, Schlenk, or drybox techniques. Proton NMR spectra were obtained on a Bruker NR-300 spectrometer at 300 MHz and were referenced to the residual proton resonances of C_6D_6 (δ 7.15). Infrared data were measured with KBr pellets as previously described.[12] Solution magnetic susceptibility data were obtained in C_6D_6 using the Evans NMR method.[13−16] Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, the University of Illinois Microanalytical Laboratory, or Desert Analytics, Tucson, AZ.

Materials. Vanadium(III) chloride, iron(II) chloride, zinc iodide, and zinc powder were purchased from Aldrich and were used as received. Aluminum powder was used as received from Acros Organics. $K[Cp^{3i}]$,[12] $K[Cp^{4i}]$,[12] $K[C_5Ph_4H]$,[6] and Cp_2Zn[17] were prepared by literature methods. Solvents for reactions were distilled under nitrogen from sodium or potassium

---

[1] Köhler, F. H.; Prössdorf, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1026−1029.

[2] Hall, V. M.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 69−76.

[3] Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715−2718.

[4] Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913−917.

[5] Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedridge, R. W.; Newbound, T. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4860−4869.

[6] Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 1703−1712.

[7] Wilson, D. R.; Ju-Zheng, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 1120−1122.

[8] Bansemer, R. L.; Huffman, J. C.; Caulton, K. C. *J. Am. Chem. Soc.* **1983**, *105*, 6163−6164.

[9] Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4042−4045.

[10] Burkey, D. J.; Hays, M. L.; Duderstadt, R. E.; Hanusa, T. P. *Organometallics* **1997**, *16*, 1465−1475.

[11] Overby, J. S.; Schoell, N. J.; Hanusa, T. P. *J. Organomet. Chem.* **1998**, *560*, 15−19.

[12] Williams, R. A.; Tesh, K. F.; Hanusa, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 4843−4851.

[13] Evans, D. F. *J. Chem. Soc.* **1959**, 2003−2005.

[14] Grant, D. H. *J. Chem. Educ.* **1995**, *72*, 39−40.

[15] Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169−173.

[16] Shubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.

[17] Fischer, B.; Wijkens, P.; Boersma, J.; van Koten, G.; Smeets, W. J. J.; Spek, A. L.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1989**, *376*, 223−233.

10.1021/om980691w CCC: $18.00

benzophenone ketyl. NMR solvents were vacuum-distilled from Na/K (22/78) alloy and stored over 4A molecular sieves.

Attempted Synthesis of Bis(triisopropylcyclopentadienyl)vanadium(II), $(Cp^{3i})_2V$. A THF solution of $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$ was prepared by refluxing VCl_3 (0.10 g, 0.65 mmol) in THF followed by reduction with zinc powder (0.05 g, 0.76 mmol).[3,4] To this solution was added $K[Cp^{3i}]$ (0.30 g, 1.3 mmol), whereupon the solution turned purple. After the mixture was stirred overnight at room temperature, the THF was removed by rotary evaporation. The residue was extracted with hexanes (45 mL), and the resulting dark solution was evaporated to a solid. A ^1H NMR spectrum indicated that the only identifiable species present was the zinc metallocene $(Cp^{3i})_2Zn$.[18]

Synthesis of Bis(triisopropylcyclopentadienyl)vanadium(II), $(Cp^{3i})_2V$. Method A. In the dark, a 125 mL Erlenmeyer flask was charged with a magnetic stirring bar, VCl_3 (0.23 g, 1.5 mmol), and $K[Cp^{3i}]$ (1.0 g, 4.3 mmol). To this was added 25 mL of THF, at which time the resulting solution turned dark brown-purple. This mixture was stirred for 48 h; subsequently the solution was evaporated to dryness and extracted with 30 mL of hexane. The hexane extract was filtered through a medium-porosity glass frit to remove precipitated KCl. The filtrate was evaporated to dryness and the remaining solid fractionally sublimed (100−120 °C, 10^{-6} Torr) to give purple $(Cp^{3i})_2V$ (0.51 g, 1.2 mmol) in 80% yield, mp 85−87 °C. Anal. Calcd for $C_{28}H_{46}V$: C, 77.56; H, 10.69. Found: C, 77.29; H, 10.28. Principal IR bands (KBr, cm^{-1}): 2964 (vs), 2871 (s), 1460 (s), 1380 (s), 1276 (m), 1180 (m), 1102 (m), 1029 (s), 816 (s), 420 (m). Magnetic susceptibility: $\mu_{corr} = 3.83\ \mu_B$. X-ray-quality crystals of $(Cp^{3i})_2V$ were grown by slow evaporation of a hexane solution.

Method B. A solution of $VCl_3(thf)_3$ prepared by refluxing VCl_3 (0.10 g, 0.64 mmol) in THF overnight, was placed into a 125 mL Erlenmeyer flask containing a magnetic stirring bar. Excess aluminum powder was added (0.021 g, 0.78 mmol) along with KH (0.01 g). After it was stirred for several hours, the mixture turned blue-green, indicating the presence of the $[V_2Cl_3(thf)_6]^+$ cation. To this was added $K[Cp^{3i}]$ (0.30 g, 1.3 mmol), and a purple solution developed within 10 min. After this mixture was stirred at room temperature for several hours, the solution was evaporated to dryness and the residue extracted with hexanes (50 mL). Filtration through a medium-porosity glass frit, followed by removal of the solvent, produced a purple solid. This crude material was fractionally sublimed as described above to give $(Cp^{3i})_2V$ (0.25 g, 0.58 mmol) in 89% yield.

Method C. A THF solution of $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$ was prepared by refluxing VCl_3 in THF followed by reduction with zinc powder (0.05 g, 0.76 mmol). To this solution was added $K[Cp^{3i}]$ (0.30 g, 1.3 mmol), whereupon the mixture turned purple. After the mixture was refluxed and stirred overnight, the THF was removed by rotary evaporation. The residue was extracted with hexanes (45 mL), and the resulting dark solution was reduced to dryness to give dark purple $(Cp^{3i})_2V$ in 85% yield, identified by its magnetic susceptibility and IR spectrum.

Attempted Synthesis of Bis(tetraisopropylcyclopentadienyl)vanadium(II), $(Cp^{4i})_2V$. A THF solution of $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$ was prepared by refluxing VCl_3 (0.10 g, 0.64 mmol) in THF followed by reduction with zinc powder (0.05 g, 0.76 mmol). To this solution was added $K[Cp^{4i}]$ (0.35 g, 1.5 mmol), whereupon the solution turned purple. After the mixture was stirred overnight at room temperature, the THF was removed by rotary evaporation. The residue was extracted with hexanes (45 mL), and the resulting solution was evaporated to leave a pink solid. A ^1H NMR spectrum indicated that the only identifiable species present was the zinc metallocene, $(Cp^{4i})_2Zn$;[18] in addition, a crystal obtained from the solid was examined with X-ray diffraction and found to have unit cell dimensions matching those reported for $(Cp^{4i})_2Zn$.[18]

Synthesis of Bis(tetraisopropylcyclopentadienyl)vanadium(III) Chloride, $(Cp^{4i})_2VCl$. As in the procedure used for $(Cp^{3i})_2V$ (method A), a 125 mL Erlenmeyer flask was equipped with a magnetic stirring bar and charged with VCl_3 (0.10 g, 0.64 mmol) and $K[Cp^{4i}]$ (0.53 g, 1.9 mmol). THF (30 mL) was added, and the resulting solution was stirred in the dark for 48 h. The mixture was evaporated to dryness and the residue extracted with 30 mL of hexane. Filtration of the hexane extract through a medium-porosity glass frit removed precipitated KCl. The filtrate was evaporated, leaving a brownish oily material. Fractional sublimation (140−160 °C, 10^{-6} Torr) of this using a Kugelrohr apparatus gave an extremely viscous brown material. Upon prolonged standing (>1 week), brown-black $(Cp^{4i})_2VCl$ solidified (0.21 g, 0.38 mmol) in 60% yield. Anal. Calcd for $C_{34}H_{58}ClV$: C, 73.82; H, 10.57. Found: C, 74.04; H, 10.84. Principal IR bands (KBr, cm^{-1}): 2964 (vs), 2877 (s), 1457 (m), 1370 (m), 1323 (w), 1263 (m), 1175 (m), 1095 (m), 1029 (m), 801 (m). Magnetic susceptibility: $\mu_{corr} = 2.92\ \mu_B$.

Synthesis of Bis(tetraisopropylcyclopentadienyl)vanadium(II), $(Cp^{4i})_2V$. Method A. A solution of $VCl_3(thf)_3$ prepared by refluxing VCl_3 (0.10 g, 0.64 mmol) in THF overnight, was placed into a 125 mL Erlenmeyer flask containing a magnetic stirring bar. Excess aluminum powder (0.021 g, 0.78 mmol) was added, along with KH (0.01 g). After it was stirred for several hours, the mixture turned blue-green, indicating the presence of the $[V_2Cl_3(thf)_6]^+$ cation. To this was added $K[Cp^{4i}]$ (0.35 g, 1.3 mmol), and a purple solution developed within 10 min. After this mixture was stirred for several hours, the solution was evaporated to dryness and the residue extracted with hexanes (50 mL). Filtration through a medium-porosity glass frit followed by removal of the solvent produced a purple solid. This crude material was fractionally sublimed using a Kugelrohr apparatus (140−160 °C/10^{-6} Torr) to give purple $(Cp^{4i})_2V$ (0.24 g, 0.46 mmol) in 72% yield, mp 152−156 °C. Anal. Calcd for $C_{34}H_{58}V$: C, 78.87; H, 11.29. Found: C, 77.71; H, 11.21. Principal IR bands (KBr, cm^{-1}): 2967 (vs), 2875 (vs), 1460 (s), 1374 (s), 1176 (m), 1070 (s), 1015 (s), 915 (w), 862 (m), 808 (m), 637 (w), 538 (w). Magnetic susceptibility: $\mu_{corr} = 3.91\ \mu_B$.

Method B. A THF solution of $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$ was prepared by refluxing VCl_3 in THF followed by reduction with zinc powder (0.05 g, 0.76 mmol). To this solution was added $K[Cp^{4i}]$ (0.35 g, 1.5 mmol), whereupon the mixture turned purple. After the mixture was refluxed and stirred overnight, the THF was removed by rotary evaporation. The residue was extracted with hexanes (45 mL), and the resulting dark solution was reduced to dryness to give a dark purple solid. This solid was identified as $(Cp^{4i})_2V$ (0.25 g, 0.48 mmol) (64%) by comparison of its magnetic susceptibility measurement and IR spectrum to those of previously prepared material.

Reaction of Cp_2Zn with $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$. A THF solution of $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$, prepared as described above (VCl_3, 0.32 g, Zn, 0.065 g), was placed into a 125 mL Erlenmeyer flask containing a magnetic stirring bar. To this solution was added Cp_2Zn (0.50 g, 2.6 mmol). The mixture turned purple-gray and was stirred overnight. Removal of the THF by rotary evaporation left a purple-gray solid. Fractional sublimation as described in the literature[19] yielded Cp_2V (60%), identified by its magnetic susceptibility[20] and IR spectrum.[21]

Reaction of $K[Cp^{3i}]$ with $FeCl_2/ZnI_2$. To a 125 mL Erlenmeyer flask containing a magnetic stirring bar was added $FeCl_2$ (0.082 g, 0.65 mmol) and ZnI_2 (0.21 g, 0.66 mmol),

---

[18] Burkey, D. J.; Hanusa, T. P. *J. Organomet. Chem.* **1996**, *512*, 165−173.

[19] King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1.

[20] König, E.; Desai, V. P.; Kanellakopulos, B.; Dornburger, E. *J. Organomet. Chem.* **1980**, *187*, 61−67.

[21] Fritz, H. P. *Chem. Ber.* **1959**, *92*, 780−791.

Table 1. Crystal Data and Summary of X-ray Data Collection for $(Cp^{3i})_2V$

formula	$C_{28}H_{46}V$
fw	433.61
color of cryst	purple
cryst dimens, mm	$0.85 \times 0.33 \times 0.35$
space group	$P\bar{1}$
a, Å	9.178(4)
b, Å	9.429(8)
c, Å	8.797(2)
α, deg	99.26(6)
β, deg	116.96(2)
γ, deg	77.22(7)
V, Å^3	660.8(7)
Z	1
D(calcd), g/cm^3	1.089
radiation type	Cu Kα
abs coeff, cm^{-1}	32.10
transmissn factors	0.57−1.00
scan speed, deg/min	4.0
scan width	$1.63 + 0.30 \tan \theta$
limits of data collcn (deg)	$20 \le 2\theta \le 120$
tot. no. of rflns	2099
no. of unique rflns	1958
no. of rflns with $I > 3.0\sigma(I)$	1742
$R(F)$	0.060
$R_w(F)$	0.080
goodness of fit	3.29
max Δ/σ in final cycle	0.03
max/min peak (final diff peak) (e/Å^3)	0.37, −0.61

followed by THF (40 mL). The solution was stirred until the solids had dissolved. K[Cp^{3i}] (0.30 g, 1.3 mmol) was added, and the mixture immediately turned deep yellow; within minutes, the mixture had become orange-brown. After this mixture was stirred for 2 h, the solvent was removed by rotary evaporation and the solid extracted with hexanes (40 mL). Rotary evaporation of this solution gave an orange-red solid identified as $(Cp^{3i})_2Fe$ by ^1H NMR spectroscopy;[22] no $(Cp^{3i})_2Zn$ was detected.

X-ray Crystallography of $(Cp^{3i})_2V$. A suitable crystal of $(Cp^{3i})_2V$ was located and sealed in a glass capillary tube. All measurements were performed on a Rigaku AFC6S diffractometer with graphite-monochromated Cu Kα ($\lambda = 1.541\,78$ Å) radiation. Relevant crystal and data collection parameters for the present study are given in Table 1.

Cell constants and an orientation matrix for data collection were obtained from systematic searches of limited hemispheres of reciprocal space; sets of diffraction maxima were located whose setting angles were refined by least squares. The space group $P\bar{1}$ was chosen from a consideration of unit cell parameters and statistical analysis of intensity distributions. Subsequent solution and refinement of the structure confirmed the choice.

Data collection was performed using continuous $\omega-2\theta$ scans with stationary backgrounds (peak/background counting time 2/1). Data were reduced to a unique set of intensities and associated σ values in the usual manner. The structure was solved by direct methods (SHELXS-86, DIRDIF) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted in calculated positions on the basis of packing considerations and $d(C-H) = 0.95$ Å. The positions were fixed for the final cycles of refinement. Final difference maps were featureless. Selected bond distances and angles are listed in Table 2.

Results

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(Cp^{3i})_2V^a$

V(1)−C(2)	2.284(4)	C(2)−C(3)	1.422(6)
V(1)−C(3)	2.267(4)	C(2)−C(6)	1.405(6)
V(1)−C(4)	2.279(4)	C(3)−C(4)	1.421(6)
V(1)−C(5)	2.278(4)	C(4)−C(5)	1.426(5)
V(1)−C(6)	2.262(4)	C(5)−C(6)	1.411(6)
V(1)−ring centroid	1.928	C(ring)−CH (av)	1.51(1)
$CH-CH_3$ (av)	1.50(2)		

$CH_3-CH-CH_3$ (av)	111.4(9)
ring centroid−V(1)−ring centroid	180
ring normal−V(1)−ring normal	180

[a] The rings are planar to within 0.002 Å. The average displacement of the methine carbon from the ring plane is 0.063 Å.

Synthesis of Isopropylated Vanadocenes. An overview of the reactions conducted in this study is provided in Scheme 1. In attempts to synthesize isopropylated vanadocenes, we initially used a zinc-reduced solution of vanadium(III) chloride in THF, which has previously been shown to yield the heterobimetallic complex $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$.[3,4] Subsequent reaction of this solution with the $[Cp']^-$ anion usually forms the corresponding vanadocenes.[1,3,5,6]

Unexpectedly, upon workup of the room-temperature reactions of VCl_3/Zn with the $[Cp^{3i}]^-$ and $[Cp^{4i}]^-$ anions, no vanadium-containing compounds were isolated, and the corresponding *zincocenes* $(Cp^{3i})_2Zn$ and $(Cp^{4i})_2Zn$[18] were recovered instead. However, mildly forcing conditions (THF reflux) generated the isopropylated vanadocenes from the $VCl_3/Zn/[Cp^{ni}]^-$ mixtures (eq 2). Hexanes extraction of the reaction mixture yielded crude $(Cp^{3i})_2V$ as a purple solid. Fractional sublimation of the solid produced analytically pure material that is extremely air- and moisture-sensitive despite the presence of bulky substituents on the rings. The ring substituents are able to block interaction with larger reagents, however; no reaction is observed between $(Cp^{3i})_2V$ and diphenylacetylene, for example, unlike the adduct formed with Cp_2V.[23] The corresponding purple $(Cp^{4i})_2V$ must be handled with slightly greater care but, with a Kugelrohr apparatus, can be purified by sublimation as for $(Cp^{3i})_2V$.

$$\text{“VCl}_2\text{”} + 2K[Cp^{ni}] \xrightarrow[\text{reflux}]{\text{THF}} (Cp^{ni})_2V + 2KCl\downarrow \qquad (2)$$

A series of reactions was conducted in order to investigate the origin of the zinc complexes isolated from the room-temperature $VCl_3/Zn/[Cp^{ni}]^-$ experiments. The possibility that $(Cp^{ni})_2V$ species were in fact the initially formed products but that they subsequently reacted in the presence of Zn(II) to generate zincocenes is unlikely from the failure of separately prepared $(Cp^{3i})_2V$ to react with Zn(II) (supplied by soluble ZnI_2) (i.e., eq 3).

$$(Cp^{3i})_2V + Zn(II) \xrightarrow[\text{room temp, 1 h}]{\text{THF}} \text{no reaction} \qquad (3)$$

Conversely, we find that it is possible for zincocene to transfer its rings to V(II) (generated from VCl_3/Zn), as in eq 4.

$$\text{“VCl}_2\text{”} + Cp_2Zn \rightarrow Cp_2V + ZnCl_2 \qquad (4)$$

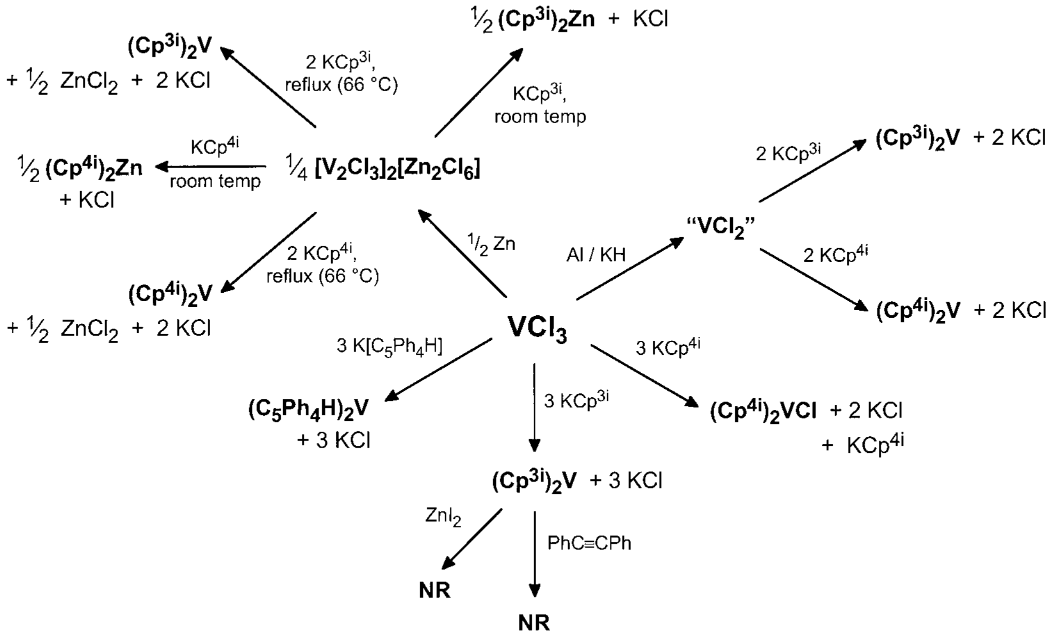
If aluminum powder and a small amount of KH are used to reduce VCl_3, both $(Cp^{ni})_2V$ vanadocenes are

---

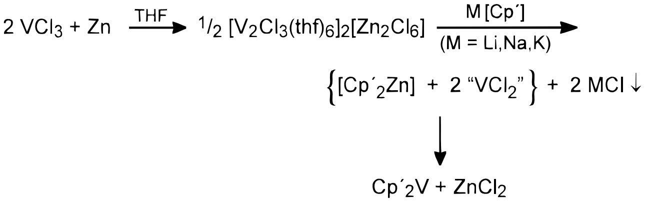
[22] Sitzmann, H. J. *J. Organomet. Chem.* **1988**, *354*, 203-214.

[23] Petersen, J. L.; Griffith, L. *Inorg. Chem.* **1980**, *19*, 1852−1858.

Scheme 1. Summary of the Reactions Conducted in This Study



Scheme 2. Proposed Route for the Formation of Vanadocenes from VCl$_3$/Zn Mixtures[a]



[a] Zincocenes are likely intermediates, although they are not always detected.

formed at ambient temperature (eq 5).

$$\mathrm{VCl_3 + Al + KH \xrightarrow[\text{THF}]{2K[Cp^{ni}]} (Cp^{ni})_2V + 2KCl\downarrow} \quad (5)$$

As a further check on the intermediacy of organozinc species in these reactions, a VCl$_3$/Zn/K[Cp^{4i}] reaction in THF was stopped after the mixture was stirred overnight, and an aliquot of the solution was removed and dried and the residue extracted with hexanes. Only (Cp^{4i})$_2$Zn was present in the sample (^{1}H NMR). When the same reaction was then continued with refluxing overnight, (Cp^{4i})$_2$V was isolated upon hexanes extraction of the reaction.

An alternate route to vanadocenes that requires the addition of a third equivalent of [Cp′]$^-$ as the reducing agent was also investigated; it has been previously employed to prepare Cp$_2$V,[19] (MeCp)$_2$V,[24] and Cp*$_2$V.[25] We find that it works equally well with both [Cp^{3i}]$^-$ and the bulky [C$_5$Ph$_4$H]$^-$ (eq 6). If 3 equiv of K[Cp^{4i}] is

$$\mathrm{3K[Cp^{3i},C_5Ph_4H] + VCl_3 \xrightarrow{THF} (Cp^{3i},C_5Ph_4H)_2V + 3KCl\downarrow} \quad (6)$$

allowed to react with VCl$_3$, however, reduction of the vanadium does not occur, and instead (Cp^{4i})$_2$VCl is isolated in 60% yield as a brown-black viscous oil that solidifies after standing for 1 week.

Magnetic Properties. The magnetic moments of the vanadium complexes were measured using the Evans NMR method in C$_6$D$_6$ solution.[13−16] The experimentally determined values for (Cp^{3i})$_2$V (3.83 μ_B) and (Cp^{4i})$_2$V (3.91 μ_B) are close to the spin-only value of 3.87 μ_B expected for complexes with three unpaired electrons. This value is typical of other vanadocenes, e.g.: Cp$_2$V, 3.78 μ_B;[20] Cp*$_2$V, 3.78 μ_B;[25] (C$_5$Ph$_4$H)$_2$V, 3.74 μ_B.[6] The experimentally determined value for (Cp^{4i})$_2$VCl of 2.82 μ_B corresponds well to the expected value of 2.83 μ_B for a d^2 configuration with two unpaired electrons; it compares favorably with those found for Cp*$_2$VCl (2.78 μ_B) and Cp*$_2$VI (2.79 μ_B).[25]

Solid-State Structure of (Cp^{3i})$_2$V. Owing to the initial difficulty in forming (Cp^{3i})$_2$V, we were interested in determining whether its structure was in any way atypical for a vanadocene. Crystals of (Cp^{3i})$_2$V were grown by slow evaporation of a hexanes solution. The molecule displays a classic sandwich geometry, with rigorously parallel rings by virtue of a crystallographically imposed inversion center at the vanadium atom. Crystals of (Cp^{3i})$_2$V are isomorphous with all other structurally characterized bis(triisopropyl)cyclopentadienyl complexes of the first-row transition metals (Cr−Co).[10,11,26] An ORTEP view of the molecule displaying the numbering scheme used in the tables is provided in Figure 1.

The average vanadium−carbon distance of 2.274(8) Å is indistinguishable from the 2.269(6) and 2.268(4) Å V−C distances in Cp$_2$V[27] and (C$_5$Ph$_4$H)$_2$V,[6] respectively. The range of V−C distances in (Cp^{3i})$_2$V (2.262(4)−2.284(4) Å (Δ = 0.022 Å)) is also similar to that in Cp$_2$V (2.260(1)−2.278(1) Å (Δ = 0.018 Å)); (C$_5$HPh$_4$)$_2$V dis-

---

(24) Rettig, M. F.; Drago, R. S. *J. Am. Chem. Soc.* **1969**, *91*, 1361−1370.

(25) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739−1748.

(26) Hays, M. L.; Burkey, D. J.; Overby, J. S.; Hanusa, T. P.; Yee, G. T.; Sellers, S. P.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 5521−5527.

(27) Antipin, M. Y.; Lyssenko, K. A.; Boese, R. *J. Organomet. Chem.* **1996**, *508*, 259−262.

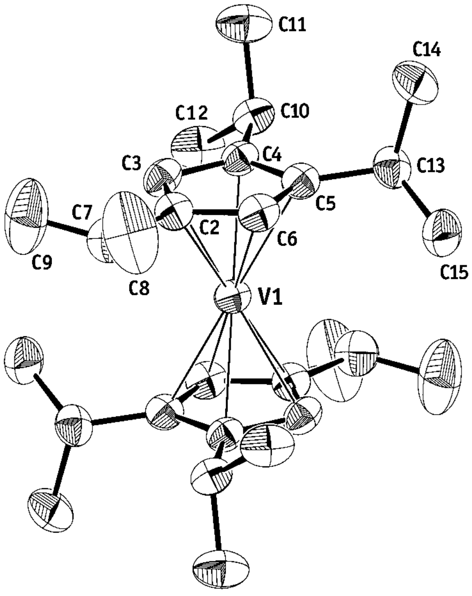


Figure 1. ORTEP diagram of the non-hydrogen atoms of $(Cp^{3i})_2V$, giving the numbering scheme used in the text. Thermal ellipsoids are shown at the 30% level.

plays a slightly larger range of 2.234(4)−2.282(4) Å (Δ = 0.048 Å). The large effective size of V(II) (0.93 Å)[28] may contribute to the small differences among the V−C lengths, despite the varying kinds and numbers of substituents on the cyclopentadienyl rings.

The rings in $(Cp^{3i})_2V$ adopt a perfectly staggered orientation, with the isopropyl groups exhibiting angles of 15.2, 71.3, and 65.2° (involving C(2), C(4), and C(5), respectively) with respect to the cyclopentadienyl ring plane. The closest inter-ring contact involving the isopropyl groups is 4.14 Å (between C(9) and C(15′)), which is outside the sum of the van der Waals radii for two methyl groups (4.0 Å).[29] The isopropyl methine carbons are bent out of the ring plane by an average displacement of 0.063 Å. The long V−C bonds coupled with judicious arrangement of the isopropyl substituents serve to make the molecule essentially strain-free.

Discussion

Under sufficiently forcing conditions (refluxing THF), vanadocenes are reliably formed from $VCl_3/Zn/Cp'$ mixtures regardless of the Cp′ ring involved (Cp*,[5] Cp^{3i}, Cp^{4i}, C_5Ph_4H,[6] etc.). When the temperature is lowered, differences begin to appear, and at room temperature $(Cp^{ni})_2V$ species are not formed. Although zinc-containing products have been isolated from reactions with $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$,[8,9] zincocenes have not been previously reported from $VCl_3/Zn/[Cp']^-$ mixtures. The isolation of the $(Cp^{ni})_2Zn$ complexes raises two questions about the reactions. (1) Are Cp'_2Zn species involved in other vanadocene syntheses using the Zn/VCl_3 route? (2) If so, why do $(Cp^{3i})_2Zn$ and $(Cp^{4i})_2Zn$ not readily transfer their rings to form vanadocenes?

The answer to the first question requires an estimation of the relative rates of transfer of the [Cp′] anion from Na^+/K^+ to V(II) and Zn(II). Rapid $[Cp']^-$ ring transfer could occur from Na^+/K^+ to the similarly ionic but more highly charged Zn(II) center, followed by a shift to the V(II) center. The results of the experiments in eqs 3 and 4 indicate that Cp_2Zn is an efficient cyclopentadienyl ring transfer agent to V(II) but that the converse reaction with $(Cp^{3i})_2V$ and Zn(II) does not occur. These results are consistent with previous studies that have established the high thermodynamic[30] and kinetic[31,32] stability of the V−Cp bond. It is reasonable to expect that zincocenes are previously undetected intermediates in the synthesis of other vanadocenes (Scheme 2).

That heat is necessary to drive the reactions with $VCl_3/Zn/Cp^{ni}$ to form the vanadocenes suggests that the isopropylated zincocenes reside in a local thermodynamic well along the potential energy surface of the reaction profile, a minimum that is missing or is less pronounced with other zincocene intermediates. Owing to the stability of the $(Cp^{ni})_2Zn$ complexes, the temperature of the reaction mixtures serves as a "switch" that determines which metal eventually appears in the product. Presumably, however, if the syntheses of other vandocenes were conducted at sufficiently low temperatures, zincocenes could be isolated (or at least detected) from their reaction mixtures.

Despite the greater amount of slippage of the rings in $(Cp^{4i})_2Zn$ relative to other structurally characterized zincocenes,[18] the fact that the substituted zincocenes are isolated instead of the vanadocenes is consistent with enhanced thermodynamic stability for the former. This hypothesis is supported by the failure to detect any organoaluminum products when reactions are conducted using aluminum metal as the reductant. If these reactions followed the same path proposed for the zinc-reduced reactions, organoaluminum complexes (e.g., "$(Cp^{ni})_2AlCl$") would serve as intermediates. Compounds of this type are likely to have σ-bonded, labile ligands,[33] and should readily react with the $[V_2Cl_3]^+$ moiety to generate the more covalent $(Cp^{ni})_2V$ complexes.

The role of steric interactions in determining the outcome of these reactions is not easily analyzed. The reaction given in eq 6, which employs an extra equivalent of the cyclopentadienyl salt as the reducing agent for V(III), forms $(Cp^{3i})_2V$ and $(C_5Ph_4H)_2V$ but not $(Cp^{4i})_2V$; the bis(cyclopentadienyl) chloride $(Cp^{4i})_2VCl$ is isolated instead. Electronically, it is not obvious why $[Cp^{3i}]^-$ and $[C_5Ph_4H]^-$ should reduce V(III) but $[Cp^{4i}]^-$ will not. Nevertheless, it is not entirely reasonable that steric effects should hinder the formation of $(Cp^{4i})_2V$ but that the generation of the comparably encumbered $(C_5Ph_4H)_2V$ is unimpeded.

It is worth noting that related difficulties are encountered in forming $(Cp^{3i})_2Cr$ and $(Cp^{4i})_2Cr$ using a zinc-reduced solution of $CrCl_3$; as with the vanadium reactions, the zincocenes $(Cp^{ni})_2Zn$ are the sole products isolated.[11] In contrast to the vanadocenes, however, no difficulty is encountered in preparing $(Cp^{3i})_2Cr$ or $(Cp^{4i})_2Cr$ when starting from a solution of $CrCl_2$ in THF. Steric

---

[28] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

[29] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[30] Chipperfield, J. R.; Sneyd, J. C. R.; Webster, D. E. *J. Organomet. Chem.* **1979**, *178*, 177−189.

[31] Switzer, M. E.; Rettig, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 687−688.

[32] Borisov, Y. A. *Zh. Strukt. Khim.* **1977**, *18*, 29−32; *Chem. Abstr.* **1977**, *87*, 52580e.

[33] Fisher, J. D.; Budzelaar, P. H. M.; Shapiro, P. J.; Staples, R. J.; Yap, G. P. A.; Rheingold, A. L. *Organometallics* **1997**, *16*, 871−879.

effects apparently do not impede the use of the Cr(II)/Cp^{ni} combination, even though metallocene Cr−Cp′ bonds are usually shorter than analogous V−Cp′ bonds, and the crowding should be somewhat greater in the chromocenes.

Conclusions

It is now apparent that $[V_2Cl_3(thf)_6]_2(Zn_2Cl_6)$, generated from the zinc reduction of VCl_3, can function as a source of V(II) alone, V(II) and Zn(II) together,[8,9] or Zn(II) alone. The isolation of $(Cp^{ni})_2Zn$ from VCl_3/Zn solutions is not simply a consequence of the steric bulk of the ligands or of the encapsulation of the metal center usually provided by $[Cp^{ni}]^-$ ($[Cp^{4i}]_2Zn$ displays a highly slipped structure).[18] As the zincocenes are also formed in the course of reactions with $CrCl_3$/Zn, their formation is not a consequence of some peculiarity of the VCl_3/Zn mixture. The isopropylated zincocenes evidently possess a higher degree of stability than might be expected from the lability of other zincocenes.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Funds for the X-ray diffraction facility at Vanderbilt University were provided through NSF Grant CHE-8908065.

Supporting Information Available: Listings of atom fractional coordinates and *U* values, bond distances and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980691W