rameters, thermal parameters, H atom parameters, and the table of observed and calculated structure amplitudes have been deposited.

Registry No. *meso*-1, 97371-16-9; *dl*-1 (isomer I), 97371-17-0; **2**, 81609-97-4; **3**, 97295-68-6; [WCl$_3$(SMe)], 97295-72-2; [WCl$_3$(SEt)], 97295-74-4; [WCl$_3$(SPh)], 97295-76-6; Me$_3$Si(SMe), 3908-55-2; Me$_3$Si(SEt), 5573-62-6; Me$_3$Si(SPh), 4551-15-9; WCl$_6$, 13283-01-7; WCl$_4$(Me$_2$S)$_2$, 53922-82-0; Et$_3$SiH, 617-86-7; [PPN][Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_3$], 97295-69-7; [Ph$_4$As][Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_3$], 97295-70-0; D$_2$, 7782-39-0; W, 7440-33-7.

Supplementary Material Available: Tables containing positional parameters for the non-hydrogen atoms of the cation and solvate molecules in complex **3** (Table SI), thermal parameters for all non-hydrogen atoms for complex **3** (Table SII), positional and isotropic thermal parameters for the hydrogen atoms of complex **3** (Table SIII), and bond distances (Table SIV) and bond angles (Table SV) for the Ph$_4$P$^+$ cation and CH$_2$Cl$_2$ solvate molecules of complex **3**, a view of the unit cell contents of [Ph$_4$P][Cl$_3$W(μ-H)(μ-Me$_2$S)$_2$WCl$_3$]·2CH$_2$Cl$_2$ (**3**) (Figure S1), and a listing of the observed and calculated structure factors and $\sigma(F)$ values for complex **3** (33 pages). Ordering information is given on any current masthead page.

Bimetallic Halides. Crystal Structure of and Ethylene Polymerization by VCl$_2$·ZnCl$_2$·4THF

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The title compound is prepared either by the zinc reduction of VCl$_4$(THF)$_2$ in refluxing THF or by the reaction of [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$ with ZnCl$_2$(THF)$_2$ in THF at 90 °C. The crystal structure indicates discrete molecules of (THF)$_4$V(μ-Cl)$_2$ZnCl$_2$. The six-coordinate environment of vanadium approximates octahedral geometry whereas the four-coordinate zinc geometry is virtually tetrahedral. The octahedron and tetrahedron are linked by two chloride bridges. Crystals belong to the monoclinic space group $P2_1/c$ with cell dimensions (−158 °C) a = 14.732 (5) Å, b = 9.680 (3) Å, c = 16.207 (6) Å, and β = 94.12 (2)° and Z = 4. High catalytic activity was found for ethylene polymerization by the title compound as well as for several other related V/Zn/Cl/THF compounds whose structures have been established. Catalyst activity is greatly enhanced by added halocarbons. Activity of V(II) compounds equals or exceeds that of V(III) compounds, which tends to deny a previous suggestion that the halocarbon functions to keep vanadium in oxidation state +3. Moreover, the V(II) compounds fail to be oxidized to V(III) even by neat CH$_2$Cl$_2$.

Introduction

Recently groups at Indiana University, Phillips Petroleum, and Texas A&M have independently discovered that the zinc reduction of vanadium trichloride in tetrahydrofuran does not lead to a mixture of VCl$_2$(THF)$_2$ and ZnCl$_2$·xTHF as previously claimed,[1,2] but to a compound containing vanadium and zinc in a 2:1 ratio. This product has been characterized by X-ray crystallography as [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$.[3,4] Actually, the reaction of vanadium halides with zinc or dialkylzinc in ether solvents is even more complicated than this result indicates, as seen from the work of Thiele et al.[5] Thus, from reactions of vanadium tetrachloride and dimethylzinc, compounds formulated as 2VCl$_3$·ZnCl$_2$·8THF and 2VCl$_2$·ZnCl$_2$·6THF were reported. The latter material is identical with the dimer mentioned above.

In the area of high-activity Ziegler-Natta catalysts,[6] mixed chlorides of vanadium and zinc are relevant to two questions of current interest. One of these questions involves the oxidation state of vanadium in these catalysts, and the second is concerned with the role of electropositive metals, such as magnesium, in these catalysts. The compounds [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$ and [*trans*-VCl$_2$(THF)$_2$(H$_2$O)$_2$]ZnCl$_3$(THF) were characterized by earlier structural studies[3,4,7] while the product VCl$_3$·ZnCl$_2$·5THF was found to be isomorphous and presumably isostructural with [*trans*-TiCl$_2$(THF)$_4$]ZnCl$_3$(THF).[8] We continue here with a structural study of VCl$_2$·ZnCl$_2$·4THF and report on the use of these compounds as ethylene-polymerization catalysts.

Experimental Section

General Procedures and Materials. All manipulations were carried out under argon or nitrogen atmosphere with standard Schlenk or drybox

techniques. Tetrahydrofuran was dried by refluxing over potassium or Na/K/benzophenone. Anhydrous VCl$_3$ and VCl$_4$ were commercial materials while the dimer, [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$, and VCl$_3$·ZnCl$_2$·5THF were prepared as previously described.[3,7] Powder patterns were recorded with Cu Kα radiation on a Philips Norelco powder diffractometer equipped with a graphite monochromator.

Polymerizations. Polymerization of ethylene was carried out in a stirred 1-gal Autoclave Engineers reactor at 100 °C. The reactor was charged with 1.0 mmol of triethylaluminum, 2.0 mmol of 1,2-difluorotetrachloroethane, about 10 mg of vanadium compound, 2 L of isobutane, and a slight hydrogen pressure. After the mixture was heated to 100 °C, ethylene (the ethylene and isobutane were both Phillips polymerization grade passed over activated alumina) was added so as to increase the total pressure by 15.9 bar, and the pressure was held at this value for 1 h by supplying ethylene on demand. The reactor was finally vented and the polymer removed.

By an increase in the amount of hydrogen added to the reactor, the molecular weight of the polymer could be lowered to the desired value.

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(1) Kohler, F. H.; Prossdorf, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1977**, *32B*, 1026–1029.
(2) Hall, V. N.; Schmulbach, C. D.; Soby, W. N. *J. Organomet. Chem.* **1981**, *209*, 67–76.
(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.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377–1378.
(5) Thiele, K. H.; Jacob, von K.; Wagner, S.; Schumann, W. *Z. Anorg. Allg. Chem.* **1976**, *427*, 75–84.
(6) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In "Comprehensive Organometallic Chemistry"; Pergamon Press: New York, 1982; Vol. III, pp 475–547.
(7) Folting, K.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G.; Martin, J. L.; Smith, P. D. *Inorg. Chem.* **1984**, *23*, 4589.
(8) Folting, K.; Huffman, J. C.; Bansemer, R. L.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 3289.

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‡Indiana University.

While the molecular weight was not directly measured, the desired molecular weight was produced by preparing a polymer with a certain melt index (ASTM method D1238-65, condition E). For polymers with very high molecular weights, the high-load melt index was measured (ASTM method 1238-65, condition F).

Some duplicate runs have been included to indicate the degree of reproducibility of polymerizations and other difficulties that sometimes arise. Severe coating of the reactor walls, baffle, and stirrer by polymer was accompanied by low yields of polyethylene; such an occurrence has been indicated as a "fouled reactor".

VCl$_3$(THF)$_3$. This compound may be prepared by the usual THF extraction of anhydrous VCl$_3$ in the presence of a catalytic amount of sodium hydride or the method suggested by Thiele as follows:[5]

After a Lab Glass pressure reaction bottle containing 60 mL of THF in an ice bath was cooled, 15 mL of 3.7 M VCl$_4$ in CH$_2$Cl$_2$ was added slowly. A 1.1 M solution, 18 mL, of triethylboron was added next, and the bottle was cautiously placed in a well-shielded 90 °C oil bath for 1 h.[9] After cooling, the orange-red solid was filtered off, washed, and dried in a glovebox. Yield: 18.6 g (90%).

VCl$_3$·ZnCl$_2$·5THF from VCl$_4$. A pressure reduction bottle containing 50 mL of CH$_2$Cl$_2$ and 15 mL of 3.7 M VCl$_4$ in CH$_2$Cl$_2$ was cooled in an ice bath. Slowly, 13.5 mL of THF was added with stirring. The mixture was filtered in a glovebox to give 18.0 g of a dark brown solid, VCl$_4$(THF)$_2$.[10]

Another pressure bottle was loaded with 16.26 g (48.2 mmol) of the dark brown solid from above and 1.58 g (24.1 mmol) of zinc dust. After the pressure bottle was cooled in an ice bath, 50 mL of THF was added. A vigorous reaction ensued, leaving a dark red slurry. After warming to room temperature, the bottle was placed in an oil bath at 80 °C for 1 h.[9] The mixture was allowed to cool overnight and was then filtered in a glovebox. The product, 18.7 g, was an obvious mixture of red and green crystals.

The crude product was heated to reflux in 150 mL of THF and filtered hot to yield a green solid. Red crystals formed in the filtrate, 2.76 g, and were identified by an IR spectrum as VCl$_3$(THF)$_3$. The green solid from above was placed in a Soxhlet and extracted with THF. Light green crystals, 9.25 g (58% based on Zn), were filtered off in a glovebox. The solid begins to decompose at 85 °C and melts at 98–100 °C, in agreement with the corresponding values of an authentic sample of VCl$_3$·ZnCl$_2$·5THF.[7] IR (Nujol): ν_{COC}(THF) 830 (s, br), 880 (m), 997 (s), 1035 (m) cm^{-1}.

VCl$_2$·ZnCl$_2$·4THF from VCl$_4$. The dark brown VCl$_4$(THF)$_2$ was prepared as described above, and 16.5 g (49.0 mmol) was suspended in about 150 mL of THF in a three-neck flask fitted with a condenser. After the mixture was heated to reflux, 3.20 g (49.0 mmol) of zinc dust was added slowly. The mixture was refluxed for 1 h and filtered hot, yielding a light blue solid. This blue solid was extracted in a Soxhlet with about 125 mL of THF. The blue product was filtered off in a glovebox. Yield: 11.40 g (43%). Anal. Calcd for C$_{16}$H$_{32}$Cl$_4$O$_4$VZn: Cl, 25.95; V, 9.32; Zn, 11.96. Found: Cl, 25.93; V, 9.78; Zn, 12.42. IR (Nujol): ν_{COC}(THF) 845 (m, sh), 867 (s), 1023 (s) cm^{-1}.

VCl$_2$·ZnCl$_2$·4THF from [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$. Zinc chloride was dissolved in THF, and the excess THF was evaporated to give a thick slurry. Some of the white solid isolated, 2.0 g, and 5.79 g of [V$_2$(μ-Cl)$_3$(THF)$_3$]$_2$Zn$_2$Cl$_6$ were mixed in a glass pressure vessel, and 100 mL of dry THF was added. The mixture was heated to 90 °C for 3 h and then cooled; finally an aqua-colored solid was filtered off in a glovebox. The yield after drying was 7.79 g (90%). An X-ray powder diffraction pattern confirmed the product to be V(THF)$_4$(μ-Cl)$_2$ZnCl$_2$.

Stability of [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$ in Dichloromethane. Green crystals of the starting compound, 4.0 g, were dissolved in 30 mL of dry CH$_2$Cl$_2$, yielding a dark green solution. This solution was heated in a glass pressure bottle to 95 °C for ¹/₂ h, during which time a light green solid formed. After the mixture was cooled to room temperature, 15 mL of dry THF was added by syringe, and the resultant mixture was stirred for 4 h and allowed to stand for 72 h. All traces of the solid dissolved to give a dark green solution. The solvent was evaporated and replaced by 30 mL of THF, followed by heating to 60 °C for 2 h, cooling, and then filtration. The yield of green solid was 3.19 g (80% of the original), which decomposed at 205–208 °C in comparison to 206–208 °C for the starting material. An X-ray powder diffraction pattern of this product

(9) All operations that are carried out in borosilicate bottles and exceed the boiling point of the solvent should have proper precautions such as shielding. Bottles should be checked for faults and the temperature kept low enough that the pressure does not approach the bursting point of the crown seals, approximately 60 psig. Thermal shock should be avoided.

(10) Bridgeland, B. E.; Fowles, G. W. A.; Walton, R. A. *J. Inorg. Nucl. Chem.* **1965**, *27*, 385.

Table I. Crystal Data for VCl$_2$·ZnCl$_2$·4THF

empirical formula	C$_{16}$H$_{32}$O$_4$Cl$_4$VZn
color	blue-green
cryst dimens, mm	0.23 × 0.23 × 0.19
space group	$P2_1/c$
cell dimens (−158 °C; 30 reflcns)	
a, Å	14.732 (5)
b, Å	9.680 (3)
c, Å	16.207 (6)
β, deg	94.12 (2)
molecules/cell	4
vol, Å^3	2305.15
calcd density, g/cm^3	1.575
wavelength, Å	0.71069
mol wt	546.56
linear abs coeff, cm^{-1}	19.452
no. of unique intens	3020
no. of unique intens with $F > 3.00\sigma(F)$	2618
final residuals	
$R(F)$	0.0446
$R_w(F)$	0.0461
goodness of fit for the last cycle	1.229
max Δ/σ for last cycle	0.05
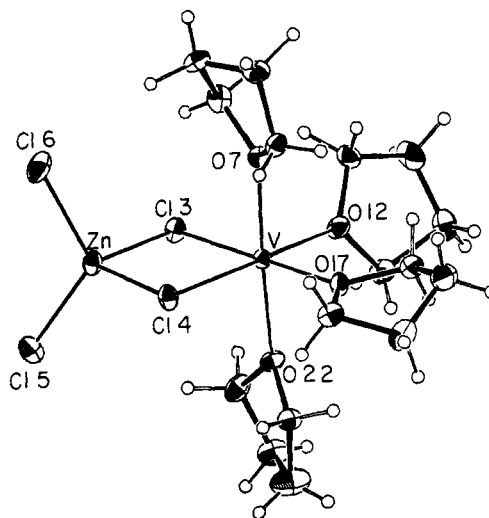
Figure 1. ORTEP drawing of V(THF)$_4$(μ-Cl)$_2$ZnCl$_2$, showing atom labeling.

compared well with that of [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$.

Redox Stability of VCl$_2$·ZnCl$_2$·4THF in Dichloromethane. In a pressure reaction bottle, 5.0 g of the light blue VCl$_2$·ZnCl$_2$·4THF was dissolved in 20 mL of CH$_2$Cl$_2$ to give a dark green solution. The solution was heated to 100 °C for 15 min and then cooled and filtered in a glovebox. A light green solid was obtained in a yield of 2.87 g and approximated the formula VCl$_2$·ZnCl$_2$·2THF. Anal. Calcd for C$_8$H$_{16}$Cl$_4$O$_2$VZn: Cl, 35.25; V, 12.66; Zn, 16.25. Found: Cl, 34.18; V, 12.81; Zn, 17.47. IR (Nujol): ν_{COC}(THF) 875 (s, br), 1025 (s) cm^{-1}.

VCl$_4$ Reduction with Diethylzinc. To a pressure reaction bottle were added 18.58 g (55.1 mmol) of VCl$_4$(THF)$_2$, prepared as above, and 50 mL of THF. After the mixture was cooled in an ice bath, 30.6 mL (27.6 mmol) of diethylzinc solution (0.90 M in heptane) was added slowly. The resultant mixture was stirred, allowed to warm to room temperature, and then filtered in a glovebox. The crude, violet solid, 25.52 g, was extracted with 250 mL of THF in a Soxhlet until the extract changed from violet to light blue. Fresh THF was then used to complete the extraction. From the second charge of THF, 8.67 g of light blue solid was isolated, melting at 216–218 °C. Anal. Calcd for VCl$_2$·ZnCl$_2$·4THF (C$_{16}$H$_{32}$Cl$_4$O$_4$VZn): Cl, 25.95; V, 9.32; Zn, 11.96. Found: Cl, 25.97; V, 10.2; Zn, 13.0. The yield corresponds to 58%, based on zinc.

Zinc Reduction of VCl$_3$·ZnCl$_2$·5THF. Zinc dust, 0.25 g (3.8 mmol), 5.0 g of VCl$_3$·ZnCl$_2$·5THF (7.6 mmol), and 100 mL of THF were refluxed for 24 h, and the mixture was filtered hot. The light blue product weighed 2.55 g (61% yield) and was identified as VCl$_2$·ZnCl$_2$·4THF by an X-ray powder diffraction pattern.

Crystallographic Study. Suitable crystals of VCl$_2$·ZnCl$_2$·4THF were grown by dissolving a sample in hot THF followed by slow cooling. A crystal of irregular habit was mounted and characterized by using techniques already reported.[11] Characteristics of the crystal, data collection
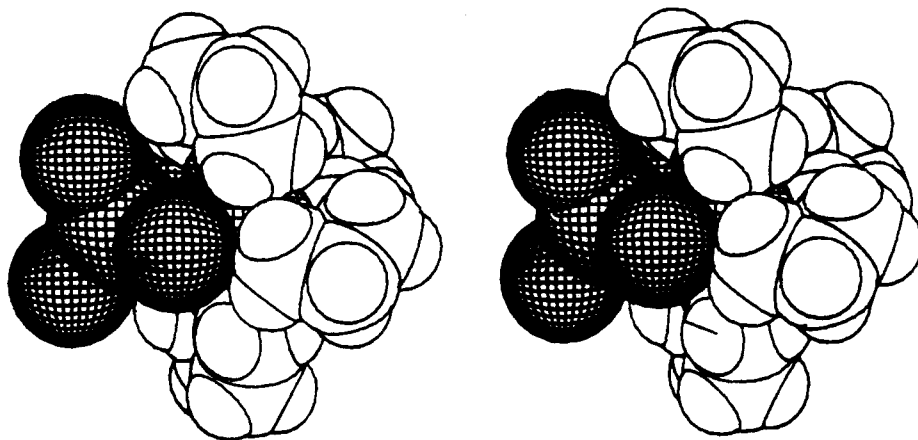
Figure 2. Stereo space-filling drawing of V(THF)$_4$(μ-Cl)$_2$ZnCl$_2$, viewed from the same perspective as Figure 1.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for (THF)$_4$V(μ-Cl)$_2$ZnCl$_2$

	10⁴x	10⁴y	10⁴z	10B_{iso}, Å²
Zn(1)	2430.3 (5)	908 (1)	8 396.6 (4)	15
V(2)	2561 (1)	−19 (1)	10 395 (1)	11
Cl(3)	3544 (1)	1306 (1)	9 477 (1)	15
Cl(4)	1482 (1)	−452 (2)	9 161 (1)	16
Cl(5)	3041 (1)	−266 (2)	7 393 (1)	21
Cl(6)	1753 (1)	2913 (2)	8 100 (1)	25
O(7)	1804 (2)	1795 (4)	10 698 (2)	13
C(8)	1965 (4)	3212 (7)	10 441 (4)	20
C(9)	1032 (4)	3859 (7)	10 307 (4)	19
C(10)	524 (5)	3164 (7)	10 971 (4)	19
C(11)	881 (4)	1690 (7)	10 942 (4)	17
O(12)	3552 (3)	361 (4)	11 387 (2)	17
C(13)	4239 (4)	−585 (7)	11 746 (4)	19
C(14)	4431 (5)	−20 (7)	12 629 (4)	22
C(15)	4429 (5)	1531 (8)	12 472 (4)	26
C(16)	3711 (4)	1713 (7)	11 748 (4)	18
O(17)	1762 (3)	−1180 (4)	11 202 (2)	15
C(18)	911 (4)	−1929 (7)	11 000 (4)	17
C(19)	771 (5)	−2789 (8)	11 760 (4)	24
C(20)	1126 (5)	−1820 (8)	12 438 (4)	25
C(21)	1964 (5)	−1223 (7)	12 100 (4)	20
O(22)	3287 (3)	−1901 (4)	10 159 (2)	15
C(23)	2865 (4)	−3255 (6)	10 157 (4)	18
C(24)	3585 (5)	−4302 (8)	9 957 (6)	33
C(25)	4430 (5)	−3426 (7)	9 862 (5)	23
C(26)	4064 (4)	−2024 (7)	9 661 (4)	21

[a] Isotropic B values for atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

(6° ≤ 2θ ≤ 45°, {$h,k,\pm l$}), and refinement are shown in Table I. The agreement factor for equivalent data was 0.04. No absorption correction was performed, as ψ scans for several reflections were essentially flat. The structure was readily solved by a combination of direct methods and Fourier techniques. Hydrogen atoms were refined, and a final difference Fourier was featureless, the largest peak being 0.45 e/Å³, located adjacent to the Zn position. The results of the structure determination appear in Tables II, III, and IV and Figures 1 and 2. Additional data have been deposited as supplementary material. The 32 refined C–H distances range from 0.81 (5) to 1.08 (6) Å and average 0.95 Å.

Results

The reduction of VCl$_3$ in THF by zinc has been shown[3,4] to produce the dimer [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$ rather than V-Cl$_2$·2THF as claimed.[1,2] Reduction of VCl$_4$ with zinc also leads to zinc-containing products with vanadium in the +2 or +3 oxidation state, depending upon the amount of zinc employed, rather than pure vanadium chlorides. Thus, refluxing VCl$_4$(THF)$_2$ with 1 equiv of zinc in THF yields light blue solid VCl$_2$·ZnCl$_2$·4THF. With less zinc or more mild conditions, the reaction can be stopped

(11) For general sample handling and data collection and processing methods, see: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table III. Selected Bond Distances (Å) and Angles (deg) for (THF)$_4$VCl$_2$ZnCl$_2$

Distances			
Zn–V	3.354 (1)	V–O(7)	2.155 (4)
Zn–Cl(3)	2.344 (2)	V–O(12)	2.125 (4)
Zn–Cl(4)	2.3381 (2)	V–O(17)	2.139 (4)
Zn–Cl(5)	2.227 (2)	V–O(22)	2.160 (4)
Zn–Cl(6)	2.220 (2)	mean C–O	1.455 (3)[a]
V–Cl(3)	2.504 (2)	mean C–C	1.516 (4)[a]
V–Cl(4)	2.499 (2)		

Angles			
Cl(3)–Zn–Cl(4)	96.29 (6)	Cl(4)–V–O(12)	175.97 (12)
Cl(3)–Zn–Cl(5)	109.38 (6)	Cl(4)–V–O(17)	93.15 (11)
Cl(3)–Zn–Cl(6)	107.33 (7)	Cl(4)–V–O(22)	90.64 (11)
Cl(4)–Zn–Cl(5)	112.81 (7)	O(7)–V–O(12)	91.44 (15)
Cl(4)–Zn–Cl(6)	109.33 (7)	O(7)–V–O(17)	88.45 (15)
Cl(5)–Zn–Cl(6)	119.14 (7)	O(7)–V–O(22)	176.40 (15)
Cl(3)–V–Cl(4)	88.39 (6)	O(12)–V–O(17)	90.41 (15)
Cl(3)–V–O(7)	92.77 (11)	O(12)–V–O(22)	87.60 (15)
Cl(3)–V–O(12)	88.01 (12)	O(17)–V–O(22)	88.09 (15)
Cl(3)–V–O(17)	178.03 (11)	Zn–Cl(3)–V(2)	87.48 (6)
Cl(3)–V–O(22)	90.66 (12)	Zn–Cl(4)–V(2)	87.71 (6)
Cl(4)–V–O(7)	90.54 (11)		

[a] Esd of mean value is calculated from the formula $\sigma(\text{mean}) = [\sum_i (d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i is one of n individual values and $\bar{d}$ is the mean value.

Table IV. Structural Features of THF Coordination

	V–O, Å	dist of V from COC plane, Å	dist of O from V C$_2$ plane, Å	angle between V–O line and COC plane, deg
O(7)	2.155 (4)	0.59	0.17	15.8
O(22)	2.160 (4)	0.71	0.21	19.3
O(12)	2.125 (4)	0.21	0.06	5.6
O(17)	2.139 (4)	0.16	0.05	4.4

at V^{3+}, isolated as a mixture of red and green crystalline solids, VCl$_3$(THF)$_3$ and VCl$_3$·ZnCl$_2$·5THF, respectively. VCl$_3$·ZnCl$_2$·5THF is isomorphous with TiCl$_3$·ZnCl$_2$·5THF,[7] which consists of octahedral TiCl$_2$(THF)$_4$$^+$ cations and the unusual ZnCl$_3$(THF)$^-$ anion.[8] Alternatively, VCl$_3$·ZnCl$_2$·5THF can be prepared by mixing VCl$_3$ and ZnCl$_2$ in THF.[7] VCl$_3$·ZnCl$_2$·5THF can be further reduced by zinc in refluxing THF to yield VCl$_2$·ZnCl$_2$·4THF.

The conversion of VCl$_3$ to VCl$_3$·ZnCl$_2$·5THF by added zinc chloride suggests the conversion of [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$ to VCl$_2$·ZnCl$_2$·4THF by added zinc chloride. This conversion has been effected without difficulty by heating the reactants to 90 °C in THF.

Attempts to replace zinc with diethylzinc as reducing agent brought smooth conversion of VCl$_3$(THF)$_3$ to the green [V$_2$(μ-Cl)$_3$(THF)$_6$]$_2$Zn$_2$Cl$_6$ in greater than 90% yield at 90 °C. However, reduction of VCl$_4$ by only $^1/_2$ mol of diethylzinc in THF at 0 °C proceeded all the way to V^{2+}, isolated as blue VCl$_2$·ZnCl$_2$·4THF

in 58% yield, based on zinc. Thiele et al. claim that alkyl compounds can be isolated when diethylzinc is reacted with VCl_4 in hydrocarbon solvents and that these compounds decompose in ethers with reduction of vanadium. In THF we have seen no evidence of alkyl formation. No attempt was made to isolate the 2:1 complex of V^{3+}, $2VCl_3 \cdot ZnCl_2 \cdot 8THF$, reported by Thiele et al.[5]

Molecular Structure. The X-ray study shows $VCl_2 \cdot ZnCl_2 \cdot 4THF$ to be composed of independent molecular units of composition $(THF)_4V(\mu\text{-}Cl)_2ZnCl_2$. The bimetallic molecular species has an approximate 2-fold rotational axis of symmetry passing through both metals, and the $VZnCl_4O_4$ unit has approximate C_{2v} molecular symmetry. Vanadium is six-coordinate and zinc four-coordinate, the octahedron and tetrahedron being linked by two chloride bridges. Because the Cl(3)–V–Cl(4) angle is not much compressed from 90°, the coordination geometry about vanadium approximates that of an octahedron: cis O–V–O angles are all within 2.4°, and cis Cl–V–O angles are within 3.2° of 90°. Bond lengths that should be equal by the idealized C_2 axis of symmetry are identical to within 4σ. The $V(\mu\text{-}Cl)_2Zn$ ring is particularly symmetric in this regard, and these atoms lie within 0.03 Å of their least-squares plane. Atoms O(12) and O(17) are also within 0.03 Å of this plane, while O(7) and O(22) are equidistant (2.15 Å) from the $V(\mu\text{-}Cl)_2Zn$ plane. Within the $V(\mu\text{-}Cl)_2Zn$ ring, the dihedral angle along the Cl(3)···Cl(4) line is 175.9°. The coordination geometry about zinc is approximately tetrahedral. The planes Zn–Cl(3)–Cl(4) and Zn–Cl(5)–Cl(6) intersect at an angle of 89.6°. The angle Cl(3)–Zn–Cl(4) is decreased from 109 to 96.2°, due to incorporation in the VCl_2Zn ring, and the opposite angle opens up to 119.14°; the other four angles average 109.7°. The angle between the plane V–Cl(3)–Cl(4) and the plane Zn–Cl(5)–Cl(6) is 89.9°.

Bond lengths in the $VZnCl_4$ unit show the typical pattern of shorter distances to terminal atoms: average values are Zn–Cl(terminal) = 2.223 Å and Zn–(μ-Cl) = 2.341 Å. The V–(μ-Cl) distances are longer still (2.502 Å). The V/Zn separation, at (3.354 Å) is long enough to exclude any direct V–Zn bonding. The four V–O distances are not identical but are pairwise equivalent: distances to the trans pair O(7) and O(22) average 2.158 Å, while those to O(12) and O(17) average 2.132; these average values differ by 7σ. Reinforcing this difference is a second structural distinction: two of the oxygen atoms are essentially coplanar with their attached atoms (V and two carbons), while the other two are distinctly pyramidal (Table IV). The pyramidal oxygens are consistently those more distant from vanadium.

The ring planes of the two THF ligands trans to chlorine do not both lie in the corresponding cis-Cl_2VO_2 plane. Space-filling diagrams (Figure 2) as well as molecular models show that this is impossible due to cis repulsion between the THF rings. If we define the orientation of the THF rings on vanadium by oxygen and the two attached carbons defining a plane, then the two THF rings trans to chlorine are rotated by 7° for O(17) and 73° for O(12) from the cis-Cl_2VO_2 plane. The two THF rings trans to each other both rotate out of the cis-$OClVO_2$ planes. Both rings rotate such that they remain coplanar (O(7)/O(22) plane dihedral angle is 2°).

Polymerization Studies. The results of ethylene polymerization tests on $VCl_2 \cdot ZnCl_2 \cdot 4THF$ and five related compounds are shown in Table V. Triethylaluminum was the cocatalyst, 1,2-difluorotetrachloroethane the activator, and hydrogen the molecular weight regulator. Also shown in Table V is the melt index of the resulting polyethylene, an empirical parameter inversely related to molecular weight. Discussion of these results will be deferred to the next section of this paper.

Discussion

Synthesis. The network of redox, chloride-transfer, and mixed-metal chloride condensation reactions observed to date for vanadium and zinc in THF solvent is summarized in Scheme I. Here, redox reactions are written vertically. The evident complexity arises because metallic zinc is a noncomplementary reductant toward V(III), combined with the fact that zinc and

Table V

compd	activator[a]/ hydrogen	productivity,[b] kg/g of V	melt index[c]	density, g/cm³
VCl_3	Y/N	19.5	(0)	0.9269
VCl_3	Y/Y	16.2	(17.2)	0.9630
VCl_3	N/Y	9.8	(10.6)	0.9611
VCl_3	N/N	22.0	(0)	0.9267
$VCl_3 \cdot 3THF$	Y/Y	176	1.3	
$VCl_3 \cdot 3THF$	Y/Y	fouled reactor		
$VCl_3 \cdot 3THF$	Y/N	fouled reactor		
$VCl_3 \cdot 3THF$	Y/N	24	(0)	
$VCl_3 \cdot 3THF$	N/N	7.3	(0)	
$VCl_3 \cdot ZnCl_2 \cdot 5THF$	Y/Y	59	1.6	
$VCl_3 \cdot ZnCl_2 \cdot 5THF$	Y/N	35	(0)	
$2VCl_2 \cdot ZnCl_2 \cdot 6THF$	Y/Y	254	2.1	
$2VCl_2 \cdot ZnCl_2 \cdot 6THF$	Y/Y	144	8.4	0.9865
$2VCl_2 \cdot ZnCl_2 \cdot 6THF$	Y/N	284	(0)	0.9287
$2VCl_2 \cdot ZnCl_2 \cdot 6THF$	Y/N	174	(0)	
$2VCl_2 \cdot ZnCl_2 \cdot 6THF$	N/N	17	(0)	0.9299
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	Y/Y	258	1.0	
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	Y/Y	120	6.6	0.9670
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	Y/Y	164	6.8	
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	Y/Y	152	28	0.9708
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	Y/N	279	(0)	0.9273
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	N/Y	7.5	14	0.9726
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	N/Y	7.5	2.2	
$VCl_2 \cdot ZnCl_2 \cdot 4THF$	N/N	34	(0)	0.9292
$VCl_2 \cdot ZnCl_2 \cdot 2THF$	Y/Y	247	1.1	
$VCl_2 \cdot ZnCl_2 \cdot 2THF$	N/Y	3.2	5.5	

[a] Y indicates the presence of $CFCl_2CFCl_2$ in the polymerization medium. [b] Productivity is the number of kilograms of polymer formed per gram of vanadium in 1 h. [c] A comparison of melt index (ASTM method D1238-65, condition E) and molecular weight is given in ref 22; values in parentheses indicate ASTM method D1238-65, condition F.

Scheme I
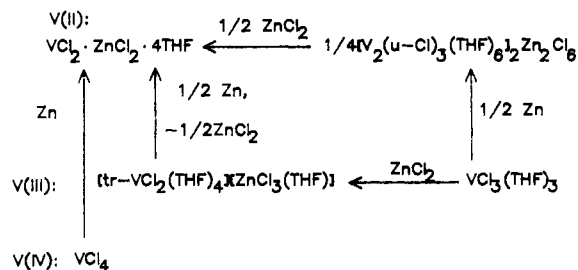
vanadium chloro complexes are reactive partners that can undergo condensation and halide transfer reactions; in Scheme I, these latter reactions are displayed horizontally. The reduction reaction from VCl_4 could be complementary, but it probably proceeds in 1-electron steps through V(III) and thus via a *mixture* of $VCl_3 \cdot ZnCl_2 \cdot 5THF$ and $VCl_3(THF)_3$. A possible exception is in the use of diethylzinc as reducing agent.

The reactions with $ZnCl_2$, shown horizontally, differ in character since that with V(III) involves chloride transfer from vanadium to zinc (to *generate* ions) while that with V(II) involves major structural reorganization (disruption of both divanadium and dizinc species) of ions, to generate the molecular species $(THF)_4V(\mu\text{-}Cl)_2ZnCl_2$. With our review of bimetallic transition metal/electropositive metal chloride compounds, we suggested that molecular species can be isolated from nonpolar solvents, while polar (coordinating) solvents promote ion formation.[8] Scheme I shows that this is an oversimplification, since addition of the Lewis acid $ZnCl_2$ to a THF solution of $VCl_3(THF)_3$ generates ions but addition to $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$ causes condensation to molecules.

The infrared C–O–C stretching modes are useful in structural assignments of THF complexes.[8] The infrared spectrum of $(THF)_4V(\mu\text{-}Cl)_2ZnCl_2$ shows two strong bands in the O–C single-bond stretching region. Both seem to have a slight shoulder,

which may indicate the presence of two overlapping sets of bands, consistent with two or more distinct THF environments. This has been noticed to a greater extent in *mer*-TiCl₃(THF)₃, *mer*-VCl₃(THF)₃, [*trans*-TiCl₂(THF)₄][ZnCl₃(THF)], and [*trans*-VCl₂(THF)₄][ZnCl₃(THF)].[7,8] On the other hand, [V₂(μ-Cl)₃-(THF)₆]₂Zn₂Cl₆, which has only one type of THF, shows only one set of bands. The small splitting observed for (THF)₄V(μ-Cl)₂ZnCl₂ is perhaps due to the relatively small difference in the two V–O bond lengths of 0.026 Å compared to 0.041 Å in *mer*-VCl₃(THF)₃[4] and 0.08 Å the Ti analogue.[12]

Molecular Structure. The coupling of octahedral vanadium and tetrahedral zinc in (THF)₄V(μ-Cl)₂ZnCl₂ yields V(μ-Cl) and (μ-Cl)₂ZnCl₂ bond lengths that differ negligibly from those in V₂(μ-Cl)₃(THF)₆⁺ (mean 2.477 Å) and Zn₂Cl₆²⁻ (2.217 and 2.357 Å). The difference in Zn–Cl(terminal) and Zn–(μ-Cl) distances (0.12 Å) is similar to that found for aluminum in LₙM(μ-Cl)₂AlCl₂ (M^II = transition metal) compounds,[13] indicating a similar bond weakening when chloride adopts a bridging function from Zn or Al. The corresponding difference to *iron* in (THF)₄Mg(μ-Cl)₂FeCl₂, where Mg²⁺ is six-coordinate and Fe²⁺ is four-coordinate, is 0.149 Å.[14]

The two V–O bond types in (THF)₄V(μ-Cl)₂ZnCl₂, trans to O (longer) and trans to μ-Cl (shorter), differ by 0.026 Å or 7σ. This difference may be compared to the V–O distances for *mer*-VCl₃(THF)₃ (2.103 (2) and 2.061 (8) Å), where the longer distance is to O trans to terminal Cl.[4] This inversion of relative V–O bond lengths from *mer*-VCl₃(THF)₃ to (THF)₄VCl₂ZnCl₂ may be due to a weak bond (to μ-Cl) lying trans. In addition to such a trans effect (or coupled to it) is the diminshed oxygen pyramidality for the shorter V–O bonds in (THF)₄VCl₂ZnCl₂, which we have suggested earlier may be indicative of bonding of the ether to the metal with more than one lone pair.[7] The arrangement of the two mutually cis THF rings seems to be consistent with this idea; one is essentially coplanar with the *cis*-Cl₂VO₂ plane and the other perpendicular. This suggests that the oxygen lone pairs not involved in direct M–O bonding may be interacting with two different d orbitals in a π-bonding manner. Molecular models also show that there are no unfavorable contacts associated with both THF rings being perpendicular to the *cis*-Cl₂VO₂, yet in this conformation the THF oxygens would have to share only one d orbital. However, since the more planar THF oxygens are also those that experience bulkier (THF) neighbors at 90°, the planarity may also be encouraged by steric effects.

There is a remarkable similarity in the molecular structures of (THF)₄Mg(μ-Cl)₂FeCl₂[14] and (THF)₄V(μ-Cl)₂ZnCl₂, although they do not form isomorphous crystals. Although the two compounds involve inverted roles for the transition metal and electropositive metal, the similarity even extends to very similar (±0.05 Å) metal–ligand bond lengths (i.e. Mg–X vs. V–X and Fe–Cl vs. Zn–Cl). The Mg/Fe compounds also shows shorter Mg–O bond lengths to THF molecules trans to μ-Cl, and the Mg–Fe distance is nonbonding at 3.45 Å. Recognizing the relationship of these two compounds leads to the question of the site (tetrahedral or octahedral) selected by each metal. In particular, why are I and II not adopted? Structure I is inferior perhaps not only because

I II
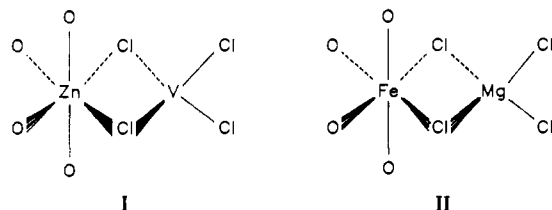
vanadium has too low a coordination number (or valence electron count) but also because zinc has too high a coordination number

in the presence of bulky THF and chloride ligands. The absence of structure II must be taken to indicate Mg²⁺ is less stable in four-coordination than is Fe²⁺.

Catalytic Applications. The discovery of high-activity, heterogeneous olefin polymerization catalysts based on chromium and titanium has greatly altered polyolefin production. Because of their high activity, it became possible to employ catalyst concentrations so low that postpolymerization catalyst removal by polymer washing is now unnecessary. At the same time, control of molecular weight with the high-activity Ziegler-Natta catalysts is achieved by using hydrogen as a chain terminator. These catalysts, while based on the same transition metal (titanium) as the original Ziegler-Natta catalysts, are produced by incorporation of magnesium compounds into the catalyst preparation as a common strategy for obtaining such high activity. The mechanism by which magnesium enhances catalyst activity is frequently attributed to the similar layer lattice structures of MgCl₂ and TiCl₃. Active-site measurements indicate that an unusually large fraction of the titanium atoms are active in these catalysts.[15-17] Six- and four-coordinate Zn²⁺ ions have radii of 0.75 and 0.60 Å, respectively, bracketing Ti³⁺ (0.67 Å) and differing little from the corresponding values for Mg²⁺.[18] However, the preference of zinc for four-coordination and magnesium for six-coordination is consistent with the suggestion that MgCl₂, by adopting layered structures with six-coordinate magnesium, provides the better support for stabilizing titanium active sites. However, some workers have indicated that the propagation constant for propylene polymerization on MgCl₂-supported catalysts is much larger than on unsupported TiCl₃ and that this factor, rather than the large number of active sites, is responsible for the high activity of the new generation of catalysts.[19,20] In addition, recent work has shown that the metal chloride is not required to have a layer lattice structure to enhance activity.[21] That is, even NdCl₃ and PrCl₃, which normally adopt the UCl₃ structure, can greatly enhance the polymerization activity of titanium. Zinc chloride evidently is not effective in boosting activity and receives little attention in the literature.

While high-activity catalysts based on chromium,[22] titanium,[23] and zirconium[24,25] have attracted considerable attention, high-activity vanadium catalysts have been largely neglected, although such catalysts have been known for some time.[26,27] High polymerization activities are often obtained with vanadium catalysts when these catalysts are used in conjunction with both an alkylaluminum cocatalyst and a special activator. A variety of activators have been effective with vanadium catalysts,[28,29] but the most common type is a chlorinated hydrocarbon such as benzyl chloride,[30] hexachlorocyclopentadiene, ethyl trichloroacetate,[31] or esters of chlorinated tetrahydrofuroic acid.[32] Although the

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exact role of the activators is not known; it was suggested that they are needed to oxidize purportedly inactive vanadium(II) to the active +3 oxidation state, which is in turn reduced to the inactive +2 state during chain termination.[33] Our interest in well-characterized mixed-metal chloride compounds of vanadium and zinc, with vanadium in the +2 or +3 oxidation state, therefore, also relates to the question of the role of activators in high-activity vanadium catalysts.

The data in Table V demonstrate the very high activities attainable with vanadium catalysts, which compare well with other high-activity catalysts. The highest activities are obtained when a chlorocarbon activator is present. For example, $VCl_2 \cdot ZnCl_2 \cdot 2THF$, $VCl_2 \cdot ZnCl_2 \cdot 4THF$, and $2VCl_2 \cdot ZnCl_2 \cdot 6THF$ increase in activity by more than a factor of 10 when the activator is present. The increase occurs either with or without hydrogen as a molecular weight modifier. The activator effects only small changes in the melt index and density of the polymer, and most of this can be attributed to normal variations between polymerizations. Hydrogen lowers the molecular weight of the polymer, as seen in an increase in melt index, and slightly depresses the activity in most cases. Exceptions to these rules arise with VCl_3 and $VCl_3 \cdot 3THF$. The latter compound usually fouled the reactor so badly that results were difficult to reproduce and conclusions dangerous. Reactor fouling of this type is often due to the formation of soluble catalyst species. VCl_3 was well-behaved, but responded only slightly to the activator and was considerably lower in activity than the other compounds. The molecular weights of the polymers produced by VCl_3 were also significantly higher and required a different set of conditions for measuring the melt index (see Table V). Of the compounds used in this study, those with vanadium in the +2 oxidation state were consistently more active than those containing V^{3+}. No significant change in activity was seen with an increase in the zinc content from $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$ [i.e. $2VCl_2 \cdot ZnCl_2 \cdot 6THF$] to $V(THF)_4(\mu\text{-}Cl)_2ZnCl_2$ [i.e. $VCl_2 \cdot ZnCl_2 \cdot 4THF$] or the addition of zinc chloride to $VCl_3(THF)_3$ to form $[V(THF)_4Cl_2]ZnCl_3(THF)$ [i.e. $VCl_3 \cdot ZnCl_2 \cdot 5THF$].

Christman has demonstrated that methyl trichloroacetate can oxidize V^{2+} to V^{3+}, even at 25 °C, and suggested that this activator operates through oxidation of inactive divalent vanadium to an active trivalent form. In our study, the possibility of oxidation of V^{2+} in $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$ by dichloromethane has been investigated. While not shown in Table V, dichloromethane is also very effective at activating the vanadium compounds toward ethylene polymerization. However, even after heating the V^{2+} dimer in dichloromethane at 95 °C for 0.5 h, 80% of the $[V_2(\mu\text{-}Cl)_3(THF)_6]_2Zn_2Cl_6$ could be recovered. The only reaction occurring under these conditions was the reversible formation of a solid, which probably involves loss of THF. From a similar reaction of $VCl_2 \cdot ZnCl_2 \cdot 4THF$, a solid with the approximate composition $VCl_2 \cdot ZnCl_2 \cdot 2THF$ was isolated. Extrapolating from the recrystallization of $[V_2Cl_3(THF)_5PPh_3]_2Zn_2Cl_6$ from CH_2Cl_2 reported by Cotton et al. to give $Ph_3P(Cl)Zn(\mu\text{-}Cl)_2V(THF)_2$-$(\mu\text{-}Cl)_2Zn(Cl)PPh_3$,[34] $VCl_2 \cdot ZnCl_2 \cdot 2THF$ is probably a polymer such as $\cdots[V(THF)_2(\mu\text{-}Cl)_2Zn(\mu\text{-}Cl)_2]_n\cdots$. Under actual polymerization conditions the ratio of activator to vanadium is in the range of 100 to 300, which is several times higher than in the above attempted oxidation of vanadium(II) with CH_2Cl_2. The most important factor, the *concentration* of activator, on the other hand, is more than 3 orders of magnitude lower. Thus, any reaction between the proposed inactive vanadium species, V^{2+}, and the activator, CH_2Cl_2, would easily be observed in the above attempted oxidation. That is, since V^{2+} was not oxidized in pure dichloro-

methane at 95 °C, it seems highly unlikely that dichloromethane oxidizes vanadium(II) under polymerization conditions. Rather, the oxidation of V^{2+} to V^{3+} observed by Christman with methyl trichloroacetate may actually be a competing reaction. It should be noted that activator was added only once during the course of polymerizations reported in Table V, while Christman added the activator throughout the polymerization. The methyl trichloroacetate used by Christman may have been consumed by the extraneous oxidation process and needed replenishing to undergo the activation mechanism, involving a different reaction. Little evidence exists upon which an alternate function for the activator can be proposed, but for chlorocarbon activators the formation of a carbene or carbenoid species is a possible step. Miller has proposed that the reaction of diiodomethane with triethylaluminum produces the species Et_2AlCH_2I, which is stable only at low temperatures and transfers a methylene group to cyclohexene to form bicyclo[4.1.0]heptane.[35] At polymerization temperatures near 100 °C the less reactive dichloromethane could react similarly, leading to Et_2AlCH_2Cl. Reaction of this carbenoid species with vanadium could ultimately lead to a metal carbene or a methylene species such as $\overline{VCH_2AlEt_2Cl}$, analogous to compounds known with titanium.[36] Even before the controversial carbene mechanism proposed by Green et al.,[37] Duck and Ridgewell studied the polymerization of ethylene over metal chlorides, including VCl_3, with diazomethane as initiator, and suggested that a carbene mechanism was likely.[38] Recently, Schrock et al. have shown that this idea cannot be excluded.[39] With the particular chlorocarbons that are effective as activators, this remains an appealing mechanism.

Conclusions

As a result of this series of studies, structures are now known for $mer\text{-}VCl_3(THF)_3$, $[VCl_2(THF)_4]ZnCl_3(THF)$, $[V_2(\mu\text{-}Cl)_3\text{-}(THF)_6]_2Zn_2Cl_6$, and $(THF)_4V(\mu\text{-}Cl)_2ZnCl_2$. Within this series, no clear correlations between structure and polymerization activity can be drawn. It is only in contrast to magnesium that any trends emerge. At present we see (1) a greater tendency for magnesium to form bridged structures than for zinc, (2) that magnesium tends to donate chloride ions[40] while zinc abstracts them, and (3) that magnesium shows a clear preference for six-coordination and zinc for four-coordination. Which of these trends will emerge as the primary reason for the high activities observed with magnesium can only be answered by further studies.

While efforts in the area of high-activity olefin polymerization catalysts have centered around chromium, titanium, and zirconium, high activities can also be obtained with vanadium catalysts in the presence of chlorocarbon activators. Although past thinking has leaned toward oxidation of vanadium by the activators as a mechanism to explain their role, such reactions seem doubtful and are in need of reinvestigation.

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