detectable species when the electrolysis of **3** was stopped at 50% completion, which rules out an appreciable concentration of V(IV) monomer, which should give an 9-line spectrum, or a mixed-valence dimer, which should have a multiline (≥17-line) spectrum. These data indicate that **3** and **4a** interconvert without the presence of detectable intermediates on the CV time scale.

Although the V(V) complexes prepared appear to be quite robust with respect to internal redox reactions, they are hydrolytically unstable. Dissolution of complexes in neutral aqueous solution leads to a series of UV spectral changes (Figure 7) that can be interpreted as hydrolysis of the Schiff base ligand. The alternative explanation (i.e. that water promotes the dissociation of the dimer) appears unlikely since the spectral changes seen are virtually the same as those when the ligand itself undergoes hydrolysis in aqueous solution.

In summary, the hydroxyl-rich Schiff base ligands described herein are unable to satisfy completely the coordination number of higher valent vanadium. Rather than obtaining discrete mononuclear pervanadyl compounds, one recovers stable dimers in the +4 and +5 oxidation states. The interconversion of these dimeric materials suggests that small quantities of mononuclear V(V) compounds may be accessible, especially in polar solvents. However, the instability of the imine linkage in water must be considered in future synthetic design. Fortunately we have been able to prepare stable, mononuclear peroxyvanadium(V)–SALA complexes as deep red solids. It is these compounds that we believe can be used to evaluate possible mechanistic proposals for the catalytic bromination of olefins by the vanadium bromoperoxidase.

Acknowledgment. We wish to thank Erlund Larson and Myoung Soo Lah for very useful technical assistance and discussions. V.L.P. thanks the G. D. Searle Family/Chicago Community Trust for a Biomedical Research Scholar's Award (1986–1989) and The Alfred P. Sloan Foundation for a Sloan Fellowship (1989–1991). C.J.C. acknowledges the support of the Robert A. Welch Foundation and thanks Professors Alan Cowley and Richard Jones, University of Texas at Austin, for the generous use of their X-ray diffractometer.

Supplementary Material Available: Table 9 (electrochemical potentials), Tables 10–12 (anisotropic thermal parameters), Table 13 (fractional atomic coordinates for hydrogen atoms in **3**), Tables 14–19 (complete bond angles and bond distances), and Table 23 (complete crystallographic data) (14 pages); Tables 20–22 (observed and calculated structure factors) (32 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Zirconium Tetrachloride. Crystal Structure of the 1:2 Adduct with Pinacolone

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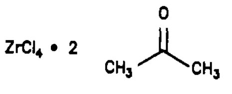
Studies of adducts **1**–**4** of zirconium tetrachloride with acetone, pinacolone, 3-pentanone, and tetrahydrofuran by infrared spectroscopy in solution and in the solid state, and by low-temperature ^{1}H NMR spectroscopy in solution, suggest that all four bases form octahedral 1:2 complexes. This conclusion is supported by the results of an X-ray crystallographic study of the 1:2 pinacolone adduct **2**, which crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.660$ (3) Å, $b = 11.935$ (4) Å, $c = 16.813$ (7) Å, $V = 1938.4$ Å^3, and $Z = 4$. Refinement of 3259 reflections yielded $R = 0.18$. The structure shows that the ketones are cis and σ-bound with an average C–O–Zr angle of 151°. In solution, bound and free acetone exchange by dissociation of complex **1** with $\Delta G^{\ddagger} = 12.4$ kcal/mol. Syn-anti isomerization is rapid in acetone adduct **1** and 3-pentanone adduct **3** even at −120 °C in CHF_2Cl, possibly because significant oxygen-p–zirconium-d π-bonding or an important electrostatic contribution to the energy of complexation facilitates inversion at oxygen.

Zirconium tetrachloride forms adducts with a wide variety of Lewis bases,[1] but no detailed structural information about these complexes is available.[2,3] In this paper, we characterize representative 1:2 adducts of zirconium tetrachloride with acetone (**1**),[4] pinacolone (**2**), 3-pentanone (**3**), and tetrahydrofuran (**4**)[5] by infrared spectroscopy in solution and in the solid state and by low-temperature ^{1}H NMR studies in solution. In addition, we describe the crystal structure of the pinacolone adduct **2**.



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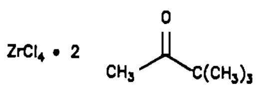

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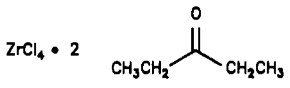

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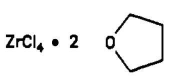

4

Treatment of a suspension of zirconium tetrachloride in dichloromethane at 0 °C with 2 equiv of acetone produced an adduct that crystallized in 79% yield after partial evaporation of the solvent. Earlier elemental analyses had already established the 1:2 stoichiometry of the product.[4a,b] The presence in its infrared spectrum of shifted carbonyl stretching bands at 1660 and 1635 cm^{-1} (Nujol) and at 1665 cm^{-1} ($CHCl_3$) confirmed that both

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Table I. Crystallographic Data for the 1:2 Adduct **2** of Zirconium Tetrachloride with Pinacolone

formula	$C_{12}H_{24}Cl_4O_2Zr$	Z	4
fw	433.4	d(calcd), g cm^{-3}	1.485
syst, space group	orthorhombic, $P2_12_12_1$	T, K	170
a, Å	9.660 (3)	μ, cm^{-1}	11.1
b, Å	11.935 (4)	radiation (λ, Å)	Mo Kα (0.71069)
c, Å	16.813 (7)		
V, Å^3	1938.4	R	0.18

carbonyl oxygens were bound to zirconium, presumably giving an octahedral complex. Splitting of the carbonyl band provided evidence for a cis orientation of the two bound molecules of acetone in the solid state. Examination of the zirconium–chlorine stretching region also indicated a preference for a cis orientation in the solid state, since two bands were present at 325 and 300 cm^{-1} instead of the single band expected for a trans 1:2 adduct of D_{4h} symmetry. In addition, the observation of a large dipole moment (7.67 D) for acetone adduct **1** in benzene provided evidence for a cis orientation in solution.[4c] Preference for a cis 1:2 adduct of zirconium tetrachloride with acetone is predictable, since both titanium tetrachloride[6] and tin tetrachloride[7] form similar complexes. In all three cases, a cis orientation of the ketones is favored because it places chlorines trans to the more weakly π-donating ketone ligands and thereby maximizes chlorine-p–metal-d π-bonding.[6a,8]

The ^{1}H NMR spectrum of acetone adduct **1** in $CDCl_3$ at 25 °C consisted of a singlet at δ 2.72 shifted 0.53 ppm downfield from free acetone. At −50 °C exchange with free acetone was slow, and the NMR spectra of solutions prepared by mixing equimolar amounts of 1:2 adduct **1** and acetone showed sharp singlets for bound and free acetone in a 2:1 ratio. The presence of a single peak for bound acetone indicated that only one adduct, presumably the cis 1:2 isomer, is present in solution under these conditions. The coalescence temperature for exchange in a 0.05 M solution of adduct **1** in $CDCl_3$ containing 0.05 M free acetone was −5 °C, so ΔG^* for exchange is approximately 12.4 kcal/mol.[9] This value suggests that the rate-limiting step is dissociation of acetone from the 1:2 adduct **1**.[6a,7b,10] As this mechanism requires, the rate of exchange remained constant when the concentration of free acetone was increased to 0.2 M.

Since we had expected zirconium tetrachloride to bind acetone to give a nonlinear σ-complex **5** with nonequivalent methyls, we were surprised to see only a sharp singlet in the ^{1}H NMR spectrum of adduct **1** even at −120 °C in CHF_2Cl containing 10% CD_2Cl_2. Since intermolecular exchange is extremely slow under these conditions, equivalence of the methyls requires either out-of-plane π-complexation,[11] a rigorously linear orientation of zirconium, the carbonyl oxygen, and the carbonyl carbon, or a bent planar arrangement with rapid inversion at oxygen or rapid rotation around the carbonyl carbon–oxygen bond.[12] We propose that the preferred structure is the nonlinear σ-complex **5** and that

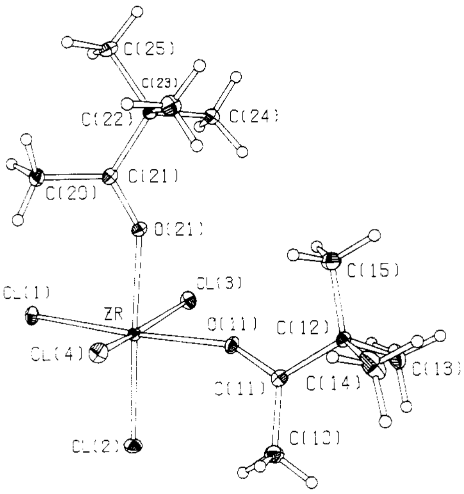

Figure 1. ORTEP drawing of the structure of the 1:2 adduct **2** of zirconium tetrachloride with pinacolone. The ellipsoids correspond to 50% probability. Hydrogen atoms are represented by spheres of arbitrary size.

Table II. Selected Interatomic Distances, Bond Angles, and Torsion Angles in the 1:2 Adduct **2** of Zirconium Tetrachloride with Pinacolone

Distances (Å)			
Zr–Cl(1)	2.2855 (7)	Zr–O(11)	2.1838 (19)
Zr–Cl(2)	2.3960 (8)	Zr–O(12)	2.1984 (19)
Zr–Cl(3)	2.4080 (6)	O(11)–C(11)	1.246 (3)
Zr–Cl(4)	2.4414 (6)	O(21)–C(21)	1.250 (3)
Bond Angles (deg)			
Cl(1)–Zr–Cl(2)	93.31 (3)	Cl(4)–Zr–O(11)	81.56 (5)
Cl(1)–Zr–Cl(3)	96.45 (3)	Cl(4)–Zr–O(21)	83.13 (5)
Cl(1)–Zr–Cl(4)	96.61 (2)	O(11)–Zr–O(21)	85.88 (7)
Cl(1)–Zr–O(11)	175.34 (5)	O(11)–C(11)–C(10)	120.0 (2)
Cl(1)–Zr–O(21)	89.66 (5)	O(11)–C(11)–C(12)	118.6 (2)
Cl(2)–Zr–Cl(3)	96.06 (3)	C(10)–C(11)–C(12)	121.4 (2)
Cl(2)–Zr–Cl(4)	95.30 (3)	O(21)–C(21)–C(20)	120.1 (2)
Cl(2)–Zr–O(11)	91.12 (6)	O(21)–C(21)–C(22)	118.6 (2)
Cl(2)–Zr–O(21)	176.79 (5)	C(20)–C(21)–C(22)	121.2 (2)
Cl(3)–Zr–Cl(4)	162.13 (3)	Zr–O(11)–C(11)	153.2 (2)
Cl(3)–Zr–O(11)	84.47 (5)	Zr–O(21)–C(21)	148.2 (2)
Cl(3)–Zr–O(21)	84.81 (5)		
Torsion Angles (deg)			
Zr–O(11)–C(11)–C(10)	12.6 (6)	Zr–O(21)–C(21)–C(20)	−1.4 (5)

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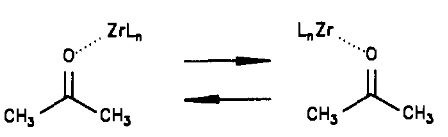

5 **6**

significant oxygen-p–zirconium-d π-bonding[13] or an important electrostatic contribution to the energy of complexation makes syn–anti isomerization particularly rapid by lowering the energy of the linear transition state. Equivalence of the methyls of each bound acetone also requires a symmetric average orientation with respect to the other ligands, not merely with respect to the atom of zirconium. This can presumably be achieved by rapid rotations around zirconium–oxygen bonds.

Further information about the binding of ketones by zirconium tetrachloride came from a study of the analogous 1:2 adduct **2** with pinacolone. Treatment of a suspension of zirconium tetrachloride in dichloromethane at 0 °C with 2 equiv of pinacolone produced an adduct that crystallized in 86% yield after partial evaporation of the solvent. An elemental analysis demonstrated that the product had a 1:2 stoichiometry, and its infrared spectrum showed shifted carbonyl bands at 1645 and 1625 cm^{-1} (Nujol) and 1650 cm^{-1} ($CHCl_3$) similar to those of the 1:2 adduct **1** with acetone. Splitting of the carbonyl band indicated that pinacolone adduct **2** favors a cis geometry in the solid state. Preference for a sterically disfavored cis 1:2 adduct of a bulky ketone emphasizes the importance of underlying electronic factors that favor a cis orientation of weak π-donors.[6a,8]

The ^{1}H NMR spectrum of adduct **2** in $CHCl_3$ at −55 °C consisted of two singlets at δ 1.32 (9 H) and δ 2.80 (3 H), which were shifted downfield by 0.16 and 0.70 ppm, respectively, from the corresponding signals of free pinacolone. Like acetone adduct **1**, pinacolone adduct **2** therefore shows a strong preference in $CHCl_3$ solutions for a single structure, presumably the cis isomer. Again, the coalescence temperature for exchange with free ketone was near 0 °C.

An X-ray crystallographic study revealed that 1:2 pinacolone adduct **2** has the structure shown in Figure 1. Crystallographic data are summarized in Table I, selected interatomic distances, bond angles, and torsion angles are listed in Table II, and atomic coordinates and isotropic temperature factors are provided in Table III. As expected, the coordination is nearly octahedral and the bound pinacolones are cis. The average Zr–O–C angle (151°) is noteworthy, since it is markedly larger than those of related ketone or aldehyde adducts of other Lewis acids.[3b,12] This may reflect significant oxygen-p zirconium-d π-bonding or an important electrostatic contribution to the energy of complexation, and it may explain why syn–anti isomerization of acetone adduct **1** is fast. In addition, the angle may open to reduce steric interactions of the metal and its ligands with the syn methyl. The large Zr–O–C angle may therefore indicate that distortion of the weak coordination bond has little electronic effect on the total energy.[12] The dihedral angles Zr–O–C–CH_3 are +12.6 and −1.4°, so the two ketones are almost purely σ-bonded. The observed angles suggest that out-of-plane π-complexation is disfavored but that small deviations of zirconium and the bound ketones from perfect coplanarity are acceptable. The average length of Zr–Cl bonds trans to a ketone ligand in adduct **2** is 2.341 Å, while the other Zr–Cl bonds are slightly longer (2.425 Å). The carbonyl C–O bonds average 1.248 Å in length, and the Zr–O bonds are approximately 2.191 Å. As expected, all are somewhat longer than the corresponding bonds in the 1:1 adduct of titanium tetrachloride with 3,3-dimethyl-2,4-pentanedione.[2b] In both adducts, the two chlorines cis to both pinacolones bend away from the other chlorines and thereby form Cl–Zr–Cl and Cl–Ti–Cl angles of 152.1 and 166.1°, respectively.

Table III. Atomic Coordinates (×10^4 for C, O; ×10^5 for Zr, Cl) and Equivalent Isotropic Temperature Factors (×10^3) for the Non-Hydrogen Atoms in the 1:2 Adduct **2** of Zirconium Tetrachloride with Pinacolone

atom	*x*	*y*	*z*	U_{eq}, Å^2
Zr	64591 (2)	61374 (2)	24369 (1)	18
Cl(1)	57460 (8)	47304 (6)	15162 (4)	30
Cl(2)	57708 (9)	76425 (6)	15808 (5)	34
Cl(3)	43805 (6)	61230 (7)	32274 (4)	31
Cl(4)	88925 (6)	61724 (7)	20455 (4)	31
O(11)	7212 (2)	7321 (2)	3328 (1)	27
O(21)	7170 (2)	4822 (2)	3256 (1)	23
C(10)	7865 (3)	9157 (2)	2965 (2)	33
C(11)	7735 (3)	8227 (2)	3540 (2)	22
C(12)	8212 (3)	8350 (2)	4391 (2)	21
C(13)	7165 (4)	9121 (3)	4813 (2)	47
C(14)	9638 (3)	8908 (4)	4417 (2)	53
C(15)	8255 (4)	7230 (3)	4812 (2)	45
C(20)	8126 (3)	3213 (2)	2648 (2)	31
C(21)	7716 (2)	3881 (2)	3347 (2)	21
C(22)	7997 (3)	3474 (2)	4180 (2)	22
C(23)	9508 (3)	3823 (3)	4352 (2)	35
C(24)	7012 (3)	4027 (3)	4773 (2)	29
C(25)	7884 (3)	2191 (2)	4239 (2)	31

The similar structures of acetone adduct **1** and pinacolone adduct **2** suggested that other 1:2 ketone adducts of zirconium tetrachloride would also prefer cis geometries. Treatment of a suspension of zirconium tetrachloride in dichloromethane at 0 °C with 2 equiv of 3-pentanone produced a 1:2 adduct **3** that crystallized in 86% yield after partial evaporation of the solvent. Its infrared spectrum showed shifted carbonyl bands at 1635 cm^{-1} (Nujol) and 1650 cm^{-1} ($CHCl_3$) similar to those of the 1:2 adducts **1** and **2** with acetone and pinacolone. Since the carbonyl band was not split in the solid state or in solution, and since only one band appeared at 320 cm^{-1} in the zirconium–chlorine stretching region (Nujol), we could not conclude that the cis isomer predominates. In CHF_2Cl at −120 °C, the ^{1}H NMR spectrum of 3-pentanone adduct **3** in the absence of added ketone showed a single triplet at δ 1.26 and a single quartet at δ 3.04. This indicates that only one structure, presumably a σ-bonded cis or trans 1:2 adduct, is present in solution under these conditions. Moreover, syn–anti isomerization must be rapid if the ligands are not bound linearly. Formation of a stable out-of-plane π-complex is unlikely, since the methylene hydrogens would be diastereotopic and potentially distinguishable at low temperature.

To complete our survey of the coordination chemistry of zirconium tetrachloride, we turned to a complex of a representative ether, the known 1:2 adduct **4** with tetrahydrofuran.[5] The presence of two bands for zirconium–chlorine stretching at 325 and 295 cm^{-1} in the infrared spectrum (Nujol) suggested that the ligands are cis in the crystalline solid,[15] but low-temperature ^{1}H NMR studies provided unambiguous evidence for the presence of both cis and trans isomers in solution.[18] A spectrum recorded in CD_2Cl_2 at −80 °C showed a signal at δ 4.41 shifted downfield by 0.66 ppm from the corresponding multiplet of free tetrahydrofuran. In addition, a much smaller peak could be detected at δ 4.70. We assign the major signal to the cis isomer (87%) and the minor downfield signal to the trans isomer (13%). The upfield multiplets had similar chemical shifts and could not be clearly distinguished. A spectrum recorded in $CDCl_3$ at −50 °C revealed similar features, but the signal at δ 4.50 corresponded to only 61% of the total, while the more deshielded signal at δ 4.81 corresponded to 39%. This confirmed our assignment of a cis structure to the major

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(15) The 1:2 adduct of titanium tetrachloride with tetrahydrofuran also appears to be cis in the solid state,[16] but evidence has been presented that the 1:2 adduct of hafnium tetrachloride with tetrahydrofuran is trans in the solid state.[17]

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(18) Similar observations have been made for the 1:2 adducts of titanium tetrachloride[6a] and tin tetrachloride[7b] with tetrahydrofuran.

isomer in solution, since it has a larger dipole moment than the trans isomer and its percentage should therefore decrease in solvents of lower dielectric constant. Interconversion of the cis and trans isomers took place at approximately the same rate as exchange of free and bound tetrahydrofuran, so isomerization presumably occurs by dissociation and recombination. At −50 °C, a ^{1}H NMR spectrum of a solution prepared in $CDCl_3$ by mixing tetrahydrofuran adduct **4** with 2 equiv of free acetone showed distinct signals characteristic of the cis and trans isomers of adduct **4** (80%), smaller amounts of a mixed adduct containing both tetrahydrofuran and acetone (20%), and appropriate amounts of free acetone and tetrahydrofuran. No significant amount of the 1:2 adduct **1** with acetone could be detected, so zirconium tetrachloride binds tetrahydrofuran more strongly than it binds acetone.[19] Preference for tetrahydrofuran and the observation of significant amounts of the trans isomer of tetrahydrofuran adduct **4** indicate that tetrahydrofuran is a stronger π-donor than typical ketones.[20]

This study of simple adducts of zirconium tetrachloride with typical Lewis bases has helped us understand the more complex behavior of a series of monodentate and bidentate zirconium chloride alkoxides described in the following article.[20]

Experimental Section

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 783 spectrometer using Nujol mulls held between CsI plates or solutions in sealed cells with NaCl windows. A Bruker WH-400 instrument was used to obtain ^{1}H nuclear magnetic resonance (NMR) spectra at low temperature. Routine ^{1}H NMR spectra were recorded on the same instrument or on a Varian VXR-300 spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Melting points were recorded on a Thomas-Hoover capillary apparatus and are not corrected. Tetrahydrofuran and pentane were dried by distillation from the sodium ketyl of benzophenone, dichloromethane was dried by distillation from CaH_2, and chloroform was dried by distillation from P_2O_5. Acetone, pinacolone, and 3-pentanone were dried over $CaCl_2$ and fractionally distilled. Tetrahydrofuran adduct **4** was prepared by a published procedure.[5a] All other reagents were commercial products of the highest purity available.

$ZrCl_4$(acetone)$_2$ (1).[4] A stirred suspension of zirconium tetrachloride (1.0 g, 4.3 mmol) in dichloromethane (10 mL) was treated dropwise at 0 °C under N_2 with acetone (0.50 g, 8.6 mmol). The mixture was stirred at 25 °C for 1 h and filtered. Partial evaporation of the supernatant produced a concentrate that was stored at −25 °C for 48 h. Crystals were then removed by filtration, the supernatant was further concentrated and treated with an equal volume of pentane, and the resulting solution was kept at −25 °C for 48 h. This produced a second crop of crystals. The two fractions were combined, washed with pentane, and dried in vacuo to provide a pure sample of 1:2 acetone adduct **1** (1.2 g, 3.4 mmol, 79%): mp 128 °C (lit. mp 113–115 °C,[4a] 125 °C[4c]); IR (Nujol) 1660, 1635, 325, 300 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.72 (s, 12 H).

$ZrCl_4$(pinacolone)$_2$ (2). A similar procedure provided a pure sample of 1:2 pinacolone adduct **2** (1.6 g, 3.7 mmol, 86%): mp 92 °C; IR (Nujol) 1645, 1625, 330 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 18 H), 2.80 (s, 6 H). Anal. Calcd for $C_{12}H_{24}Cl_4O_2Zr$: C, 33.26; H, 5.58. Found: C, 32.64; H, 5.65.

$ZrCl_4$(3-pentanone)$_2$ (3). A similar procedure that omitted the addition of pentane provided crystals of adduct **3** (2.4 g, 5.9 mmol, 86%): mp 155 °C; IR (Nujol) 1635, 320 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, 12 H), 2.99 (q, 8 H).

Crystallographic Data for the 1:2 Adduct 2 of Zirconium Tetrachloride with Pinacolone. Crystals suitable for an X-ray study were obtained by crystallization from dichloromethane/pentane. The sample selected for analysis had the following dimensions: 0.24 × 0.40 × 0.50 mm. Other crystallographic data are summarized in Table I.

Crystallographic Measurements and Structure Resolution. An Enraf-Nonius CAD-4 diffractometer was used to collect a set of intensity data according to a procedure described elsewhere.[21] Seven standard reflections checked every 1 h showed random fluctuations of less than ±1.5% about their respective means. A set of 7271 Mo K$\bar{\alpha}$ reflections ($2\theta \leq 50°$) was collected at 170 K. Of these, 3259 ($I > 3\sigma(I)$) were retained for structure resolution and refinement after averaging to the Laue 222 symmetry. These measurements were corrected for the Lorentz effect and polarization but not for absorption. The structure was solved by using direct methods (MULTAN) and difference-Fourier calculations (SHELX), and it was refined on $|F_o|$ by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Refinement converged to $R = 0.18$, and the goodness-of-fit ratio S was 0.90 for 269 parameters refined. The final ΔF map was essentially featureless, with a general background below ±0.30 e Å^{-3} and four peaks of 0.40–0.45 e Å^{-3} within 1.1 Å from Zr. The scattering curves for the non-hydrogen atoms[22] and the hydrogen atoms[23] were taken from standard sources. The contributions of Zr and Cl to anomalous dispersion were included.[24]

Selected interatomic distances, bond angles, and torsion angles are listed in Table II, and atomic coordinates and isotropic temperature factors are provided in Table III. Tables of anisotropic temperature factors and structure factors are included as supplementary material.

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Supplementary Material Available: For the 1:2 complex **2** of zirconium tetrachloride with pinacolone, Table SI, listing anisotropic temperature factors (1 page); Table SII, listing structure factors (13 pages). Ordering information is given on any current masthead page.

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