computer time. We also would like to thank B. B. Anderson and K. J. Klabunde for a sample of **1** and J. Atwood and R. Davis for unpublished results and communications.

Appendix

The calculations were carried out with the extended Hückel method.[21] The metal orbital H_{ii}'s and exponents were taken from previous work.[7] The parameters are listed in Table VI. The modified Wolfsberg–Helmholz formula was used.[22] The following idealized bond lengths were used: C–H = 1.09, C–C = 1.41, Fe–C = 1.78, C–O = 1.14, Cr–P = 2.37, P–H = 1.42, Cr–C = 2.20, and Ni– 1.60 Å. Regular bond angles in the benzene ligand were utilized; the rest were taken from the average of the available structures.[3b,8b] The C–Fe–C, Fe–C–O, L–Ni–L, and P–Cr–P angles were set at 88, 180, 88, and 120°, respectively. The parameters used for the L ligand in **4** were identical with those of H.

Registry No. 1, 74153-73-4.

Supplementary Material Available: Listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

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Molecular Structure and Ligand-Exchange Reactions of Trichlorotris(*tert*-butyl isocyanide)vanadium(III). Synthesis of the Hexakis(*tert*-butyl isocyanide)vanadium(II) Cation

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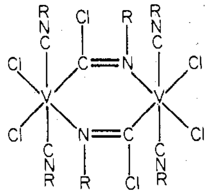
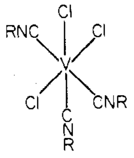
The reaction between vanadium(III) chloride and *tert*-butyl isocyanide is shown to produce *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$ rather than an insertion product as claimed by previous investigators. The compound crystallizes in the trigonal crystal system, space group $P3_121$, with $a = 11.765$ (1) Å, $c = 13.611$ (2) Å, and $Z = 3$. The structure was determined by single-crystal X-ray diffraction methods and refined to $R_1 = 0.048$. The molecule has crystallographically required twofold symmetry. The V–Cl bond lengths are 2.288 (4) Å (unique) and 2.317 (2) Å, and the V–C bond lengths are 2.186 (15) Å (unique) and 2.189 (9) Å. These values indicate a slightly greater structural trans effect for chloride compared with that for isocyanide in this molecule. The preference for the meridional form is attributed to steric factors since even in this isomer the Cl–V–Cl bond angles open to 97.2 (1)° with a concomitant reduction in Cl–V–C to 82.8 (1)°. Proton NMR spectroscopic studies of paramagnetic *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$ in deuterated chloroform revealed separate *tert*-butyl resonances of intensity ratio 2:1 that coalesce above 60 °C to a single peak. Addition of free isocyanide to $VCl_3(CN\text{-}t\text{-}Bu)_3$ at 33 °C produced selective exchange of the unique *tert*-butyl isocyanide ligand. This result shows that $Cl^- > CN\text{-}t\text{-}Bu$ in its kinetic trans effect. Trichlorotris(*tert*-butyl isocyanide)vanadium(III) reacts with 2,2′,2″-terpyridine to form VCl_3(terpy) and with excess *tert*-butyl isocyanide to yield the $[V(CN\text{-}t\text{-}Bu)_6]^{2+}$ cation. The latter is the first homoleptic isocyanide–vanadium complex and was also prepared directly from vanadium(III) chloride.

There are few literature reports of isocyanide complexes of vanadium. This situation is in marked contrast to the extensive and varied chemistry of the isocyanide complexes of Cr, Mo, and W[1] and presumably results from the lower thermal, hydrolytic, and oxidative stability of vanadium isocyanide complexes. The known vanadium isocyanide complexes include adducts with dicyclopentadienylvanadium[2] and reported insertion products of isocyanides with vanadium(III) chloride.[3] Structural data on these compounds have thus far been lacking.

In an extension of our synthetic, structural, and chemical studies of molybdenum and tungsten isocyanide complexes,[4] we have begun to explore vanadium isocyanide chemistry. Here we show that the previously reported "insertion" reaction,[3b] thought to yield **1**, in fact forms *mer*-$VCl_3(CNR)_3$, R = *tert*-butyl, **2**. We also describe the first homoleptic vanadium isocyanide complex, $[V(CNR)_6]^{2+}$, and the reaction of **2** with 2,2′,2″-terpyridine to produce VCl_3(terpy). Finally, proton NMR spectroscopic studies of paramagnetic *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$ are reported that, together with IR spectra, establish its structure in solution and demonstrate the greater trans effect of chloride vs. *tert*-butyl isocyanide in promoting exchange of bound and free isocyanides.



1



2

Experimental Procedure

Synthetic Work. All complexes were prepared and handled under an atmosphere of dry nitrogen with the use of Schlenk techniques or in a Vacuum Atmospheres drybox. *tert*-Butyl isocyanide was synthesized by a literature method.[5] All other starting materials were commercially available. Solvents were distilled from appropriate drying reagents, under nitrogen, immediately before use. Chemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

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Trichlorotris(*tert*-butyl isocyanide)vanadium(III), $VCl_3(CN\text{-}t\text{-}Bu)_3$ (2). This compound was prepared as described elsewhere.[3b] To a suspension of VCl_3 (3.8 g) in 90 mL of CH_2Cl_2 was added 7.2 mL of *t*-BuNC. After the mixture was stirred for 3 days, the resulting green solution was filtered and concentrated to about half the volume under reduced pressure. X-ray quality green crystals were obtained by layering 100 mL of diethyl ether onto the reaction mixture. After being filtered and washed twice with 20 mL of diethyl ether, the product was dried in vacuo. The yield was 5.2 g (58%). IR (Nujol mull): 2200 (s), 2160 (sh), 1240 (s), 1190 (s), 1040 (m), 930 (m), 700 (s), 520 (s), 430 (s), 370 (s), 360 (s), 350 (s), 310 (s) cm^{-1}.

Trichloro(2,2′,2″-terpyridine)vanadium(III), VCl_3(terpy). A 0.290-g portion (1.24 mmol) of freshly sublimed terpyridine in 150 mL of CH_2Cl_2 was mixed with 0.510 g (1.25 mmol) of **2** in 150 mL of CH_2Cl_2. The color of the solution changed from green to brown. After the solution was allowed to stand overnight, brown microcrystals precipitated and were collected by filtration. The yield was 0.25 g (52%). Anal. Calcd for $C_{15}H_{11}N_3VCl_3$: C, 46.13; H, 2.84; N, 10.76; V, 13.04; Cl, 27.23. Found: C, 45.97; H, 2.98; N, 10.67; V, 13.05; Cl, 27.29. This compound has also been prepared directly from VCl_3 and terpyridine as described elsewhere.[6]

Hexakis(*tert*-butyl isocyanide)vanadium(II) Hexafluorophosphate, $[V(CN\text{-}t\text{-}Bu)_6](PF_6)_2$. Method 1. To a suspension of VCl_3 (1.46 g, 9.30 mmol) in 30 mL of ethanol was added 8.0 mL (75 mmol) of *tert*-butyl isocyanide. A purple solution formed with the evolution of heat. Addition of 4.33 g (23.5 mmol) of KPF_6 produced a yellow precipitate which was collected and dissolved in methylene chloride; the mixture was filtered and the product was obtained as an air-sensitive yellow powder by removing the solvent under reduced pressure. The yield was 1.93 g (25%). Anal. Calcd for $C_{30}H_{54}N_6VP_2F_{12}$: C, 42.91; H, 6.48; N, 10.00; V, 6.07; P, 7.38; F, 27.15. Found: C, 43.74; H, 6.55; N, 9.88; V, 6.06; P, 6.64; F (by difference), 27.13. IR (Nujol mull): 2190 (s), 1240 (w), 1222 (m), 1180 (s), 1080 (w, br), 1010 (w, br), 920 (w), 870 (w), 830 (s), 540 (s), 505 (m) cm^{-1}.

Method 2. $[V(CN\text{-}t\text{-}Bu)_6](PF_6)_2$ was prepared in a manner analogous to method 1 using $VCl_3(CN\text{-}t\text{-}Bu)_3$ as the starting material in place of VCl_3.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer calibrated with polystyrene film. Solids were examined as Nujol mulls spread between KBr plates or in $CHCl_3$ solution. Proton NMR spectra were measured on a Perkin-Elmer R-32 spectrometer or on a Bruker WP-80 FT spectrometer equipped with a variable-temperature probe.

Collection and Reduction of X-ray Data for $VCl_3(CN\text{-}t\text{-}Bu)_3$ (2). The crystal used for data collection was a light green block of 0.20 mm edge length, bounded by the faces $(10\bar{1})$, $(\bar{1}01)$, $(\bar{1}1\bar{1})$, $(1\bar{1}1)$, $(0\bar{1}\bar{1})$, and (011), and was mounted in a capillary under nitrogen in an attempt to minimize decomposition. Weissenberg photographs and study on the diffractometer showed the crystal to belong to either of the trigonal space groups $P3_121$ (D_3^4, No. 152) or $P3_221$ (D_3^6, No. 154).[7] The quality of the data crystal was checked by taking ω scans of several strong, low-angle reflections and was found to be acceptable ($\Delta\bar{\omega}_{1/2} \sim 0.12°$).

The unit cell parameters and intensity data were obtained on a single-crystal diffractometer as reported in Table I. Reflections were prescanned at a rate of 6.71° min^{-1} in ω and were then rescanned in an attempt to make $I/\sigma(I) = 100$ within a maximum scan time of 60 s. Reflections for which $I/\sigma(I) < 1$, in the prescan, were considered weak and were not remeasured. After every 100 data, three orientation control reflections were centered, and if the measured position of any scattering vector deviated more than 0.15° from the calculated position, a new orientation matrix was calculated on the basis of the recentering of an additional 11 reflections. The formulas used to calculate the intensity for each reflection and its standard deviation are given in eq 1 and 2, respectively, where P is the total

$$I = S(P - 2B) \tag{1}$$

$$\sigma(I) = S(P + 4B)^{1/2} \tag{2}$$

number of integrated counts, B is the total background count, and S is the scan rate (see Table I for more details). The data were corrected for Lorentz–polarization (Lp) effects and the attenuator and were scaled[8] for a 17% anisotropic decay. Three other crystals, either mounted in a capillary tube or thickly coated with epoxy, all showed a similar decay. No absorption correction was applied since μ was 8.1 cm^{-1}, and a test calculation, using the Wehe–Busing–Levy ORABS program, revealed the transmission factors all to be ~0.86. The values of F_o and $\sigma(F_o)$ were then computed according to eq 3 and 4, respectively, where A is the attenuator constant (1.0 if no

$$F_o = (AI/LpTD)^{1/2} \tag{3}$$

$$\sigma(F_o) = (\sigma(I))A/2F_oLpTD \tag{4}$$

attenuator was used), T is the transmission factor (1.0 for this data set), and D is the decay correction factor. These F_o and $\sigma(F_o)$ values were read into the SHELX-76 system of programs,[9] which was used for all subsequent calculations, on a DEC VAX-11/780 computer.

Table I. Experimental Details of the X-ray Diffraction Study of $VCl_3(CN\text{-}t\text{-}Bu)_3$

(A) Crystal Parameters[a] at 26 °C

$a = 11.765$ (1) Å	space group = $P3_121$
$c = 13.611$ (2) Å	$Z = 3$
$V = 1631.6$ Å^3	ρ(calcd) = 1.242 g cm^{-3}
mol wt = 406.7	ρ(obsd)[b] = 1.26 (1) g cm^{-3}

(B) Measurement of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα ($\lambda_{\alpha_1} = 0.709\,30$ Å, $\lambda_{\bar{\alpha}} = 0.710\,73$ Å) graphite monochromatized
takeoff angle: 2.0°
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm
crystal–detector dist: 173 mm
scan technique: ω(crystal)–2θ(counter)
scan width: variable $\Delta\omega(0.9 + 0.35 \tan\theta)°$
scan rate: variable from 1.34 to 6.71° min^{-1} in ω
scan range: $3° \leqslant 2\theta \leqslant 45°$
bkgd measmt: moving crystal–moving detector, 25% added to scan width at both ends of each scan
stds: three reflections $(\bar{2}40)$, $(03\bar{4})$, and $(00\bar{6})$, measured every 3600 s of X-ray exposure time, used to scale the data for 17% anisotropic decay[c]

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 30°$. [b] By suspension in a mixture of cyclohexane and carbon tetrachloride. [c] Reference 8.

A total of 1637 reflections in the range ($h \leq 0$, $k \geq 0$, $l \geq 0$) were collected, 1296 of which were nonzero. Averaging of equivalent reflections gave 1162 unique data of which the 767 with $F_o > 4\sigma(F_o)$ were used in the structure solution and refinement. The R factor for averaging, eq 5, was 0.019, where the inner summations are over the

$$R_{av} = \{\sum[N\sum w(\bar{F} - F)^2]/\sum[(N - 1)\sum wF^2]\}^{1/2} \tag{5}$$

N equivalent reflections averaged to give $\bar{F}$ and the outer summations are over all unique reflections. Because of anomalous scatterng in point group 321, only $|F(hkil)|$, $|F(hik\bar{l})|$, and their (hki) cyclic permutations could be averaged.

Further details of the data collection and reduction are given in Table I.

Solution and Refinement of the Structure. The Patterson function was computed and solved for the position of the vanadium atom on the threefold axis, special position 3(a) of space group $P3_221$. Phasing on this atom gave an R_1 factor[10] of 0.40 and was sufficient to reveal the rest of the structure through successive difference Fourier maps and structure factor calculations.

The structure was then refined by least-squares methods. Toward the end of the refinement, a check was made on the validity of the $V\text{–}CNC(CH_3)_3$ linkage. With all nonhydrogen atoms except N(1), N(2), C(11), and C(21) assigned anisotropic thermal parameters, three cycles of refinement gave $R_1 = 0.052$ and $R_2 = 0.045$.[10] The isotropic temperature factors (U, Å^2) for the four above-mentioned

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(10) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

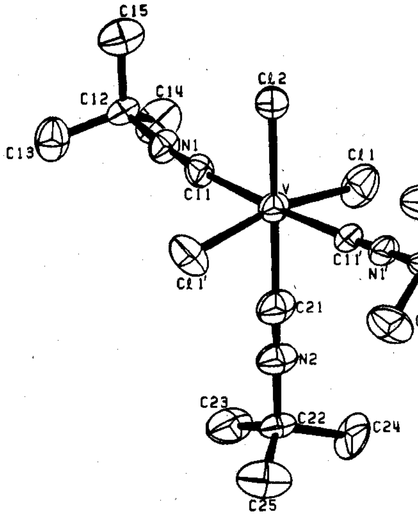

Figure 1. Geometry of $VCl_3(CN\text{-}t\text{-}Bu)_3$ showing the atom labeling scheme. Thermal ellipsoids are depicted at the 40% probability level. Hydrogen atoms are omitted for clarity. Atoms Cl(2), V, C(21), N(2), and C(22) lie on a crystallographically required twofold symmetry axis. *tert*-Butyl group 2 [C(23)–C(25)] is disordered over two sites, only one of which is shown.

atoms were 0.050 (2), 0.061 (4), 0.054 (3), and 0.065 (5), respectively. From the same initial parameters, but with N(1) and N(2) assigned carbon atom scattering factors and C(11) and C(21) assigned nitrogen atom scattering factors, three cycles of refinement gave $R_1 = 0.058$ and $R_2 = 0.050$ with the temperature factors (U, Å^2) for N(1), N(2), C(11), and C(21) being respectively 0.022 (2), 0.034 (4), 0.093 (3), and 0.102 (6). The original assumption that the linkage is $V–CN–C(CH_3)_3$, and not $V–NCC(CH_3)_3$, was therefore considered to be correct.

Full-matrix least-squares refinement of 117 variables in $P3_221$ converged at $R_1 = 0.051$ and $R_2 = 0.044$. Refinement of the enantiomorphic structure in $P3_121$ gave significantly better results ($R_1 = 0.048$; $R_2 = 0.041$) and was therefore used in all subsequent calculations. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1.1331/[\sigma^2(F_o) + 0.00037F_o^2]$. All nonhydrogen atoms were refined anisotropically. Methyl hydrogen atoms were located, placed in idealized positions (C–H = 0.95 Å; H–C–H = 109.5°), and included in the refinement as invariants with isotropic temperature factors fixed at $U = 0.10$ Å^2. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 11. The largest peak on a final difference Fourier map was 0.39 e Å^{-3}, and no parameter shifted by more than 0.02σ in the final cycle of refinement. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, $(\sin \theta)/\lambda$, $|h|$, $|k|$, or $|l|$, showed good consistency, and the weighting scheme was considered to be satisfactory.

Final atomic positional and thermal parameters, together with their estimated standard deviations, are reported in Tables II and III, respectively. The interatomic distances and angles, with estimated standard deviations, appear in Table IV. A listing of the final observed and calculated structure factor amplitudes is available as Table S1.[12] Figure 1 shows the molecular geometry and atom-labeling scheme.

Results and Discussion

The Chemical Formulation of $VCl_3(CN\text{-}t\text{-}Bu)_3$. The present work demonstrates that the compound originally formulated as **1**[3] in fact has structure **2**. The published synthesis was closely followed, gave the reported color change, and led to a product identical in elemental composition and C≡N infrared stretching band.

A medium-intensity absorption band at 1590–1700 cm^{-1}, the major basis for assigning structure **1** to the product,[3b] was occasionally observed in the $VCl_3(CN\text{-}t\text{-}Bu)_3$ infrared spectrum, taken as a Nujol mull. The band was quite small, however, and could be eliminated by recrystallization. Furthermore, if the Nujol mull was prepared by grinding the sample with exposure to the atmosphere, the peak at 1625 cm^{-1} significantly increased in intensity. It is possible that this absorption band, which had been attributed to the stretching mode of an iminomethyl (>C=NR) moiety,[3b] arises from coordinated *tert*-butylformamide, obtained through adventitious hydrolysis of the *tert*-butyl isocyanide ligand. This frequency lies ~40 cm^{-1} below that of free *tert*-butylformamide. A shift of this magnitude and direction is known to occur upon complexation of amides to titanium(III) chloride.[13]

Table II. Final Positional Parameters for $VCl_3(CN\text{-}t\text{-}Bu)_3$[a, b]

atom	x	y	z
V	−0.36726 (18)	0.0	−0.6667
Cl(1)	−0.4785 (2)	−0.1732 (3)	−0.77491 (18)
Cl(2)	−0.1728 (3)	0.0	−0.6667
N(1)	−0.2532 (7)	0.1954 (7)	−0.8614 (5)
N(2)	−0.6491 (10)	0.0	−0.6667
C(11)	−0.2949 (9)	0.1330 (8)	−0.7929 (7)
C(12)	−0.1983 (8)	0.2656 (8)	−0.9526 (7)
C(13)	−0.1710 (11)	0.4040 (10)	−0.9419 (7)
C(14)	−0.2994 (11)	0.1934 (11)	−1.0317 (6)
C(15)	−0.0720 (10)	0.2653 (10)	−0.9710 (7)
C(21)	−0.5530 (12)	0.0	−0.6667
C(22)	−0.7735 (12)	0.0	−0.6667
C(23)	−0.770 (3)	0.087 (3)	−0.748 (2)
C(24)	−0.884 (2)	−0.145 (2)	−0.691 (3)
C(25)	−0.801 (3)	0.035 (4)	−0.5677 (17)
H(131)	−0.1467	0.4422	−1.0055
H(132)	−0.1064	0.4597	−0.8956
H(133)	−0.2533	0.3953	−0.9243
H(141)	−0.2600	0.2356	−1.0921
H(142)	−0.3753	0.1998	−1.0202
H(143)	−0.3227	0.1037	−1.0353
H(151)	−0.0308	0.3150	−1.0285
H(152)	−0.0959	0.1763	−0.9817
H(153)	−0.0138	0.2996	−0.9172
H(231)	−0.8321	0.1123	−0.7658
H(232)	−0.7589	0.0403	−0.8002
H(233)	−0.6892	0.1614	−0.7316
H(241)	−0.9641	−0.1547	−0.7172
H(242)	−0.9046	−0.2120	−0.6441
H(243)	−0.8337	−0.1511	−0.7425
H(251)	−0.8864	0.0198	−0.5791
H(252)	−0.7436	0.1255	−0.5530
H(253)	−0.8012	−0.0168	−0.5141

[a] Atoms are labeled as indicated in Figure 1. Estimated standard deviations, in parentheses, occur in the last significant figure for each parameter. [b] Hydrogens are labeled such that H(*ij*) is the *j*th H on C(*i*). Atoms C(23), C(24), and C(25) are disordered over two sites and were included in the refinement at half-occupancy.

Two absorption bands, at 310 and 350 cm^{-1}, in the V–Cl stretching region of the infrared spectrum were previously reported.[3] The band at 350 cm^{-1} is slightly split in the mull spectrum of the unhydrolyzed sample. The presence of three absorptions in this region is consistent with the observed C_{2v} symmetry of *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$.

Structure of Trichlorotris(*tert*-butyl isocyanide)vanadium(III). The molecule has virtual C_{2v} symmetry and sits on a crystallographically required twofold symmetry axis that passes through atoms Cl(2), V, C(21), N(2), and C(22) (Figure 1). The methyl carbon atoms of the *tert*-butyl isocyanide ligand situated on the twofold axis are equally disordered between two orientations, only one of which is shown in Figure 1. The molecule is seen to adopt the meridional isomer. We ascribe this result to the greater steric crowding that would occur in the facial isomer if the three chloride ligands were to occupy

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(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(12) Supplementary material.

(13) Clark, R. J. H. "The Chemistry of Titanium and Vanadium"; Elsevier: Amsterdam, 1968; pp 106–114.

Table III. Final Anisotropic Thermal Parameters for $VCl_3(CN\text{-}t\text{-}Bu)_3$[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0.0478 (11)	0.0496 (16)	0.0486 (13)	0.0248 (8)	0.0060 (6)	0.0119 (12)
Cl(1)	0.0633 (19)	0.0755 (19)	0.0775 (19)	0.0106 (15)	−0.0093 (15)	−0.0104 (15)
Cl(2)	0.0505 (16)	0.054 (3)	0.075 (3)	0.0269 (13)	0.0003 (10)	0.0005 (20)
N(1)	0.050 (6)	0.050 (5)	0.046 (5)	0.024 (5)	0.001 (4)	0.017 (4)
N(2)	0.057 (7)	0.086 (10)	0.057 (8)	0.043 (5)	0.010 (4)	0.020 (7)
C(11)	0.049 (6)	0.042 (6)	0.064 (7)	0.026 (5)	−0.004 (5)	0.011 (5)
C(12)	0.032 (7)	0.053 (7)	0.036 (6)	0.018 (5)	0.001 (5)	0.007 (5)
C(13)	0.096 (9)	0.060 (7)	0.054 (7)	0.027 (6)	0.005 (6)	0.008 (5)
C(14)	0.078 (9)	0.106 (9)	0.051 (7)	0.030 (8)	−0.020 (7)	−0.005 (6)
C(15)	0.066 (8)	0.107 (10)	0.068 (7)	0.045 (7)	0.003 (7)	0.008 (7)
C(21)	0.064 (9)	0.077 (12)	0.066 (11)	0.039 (6)	0.014 (4)	0.028 (8)
C(22)	0.040 (7)	0.072 (11)	0.036 (9)	0.036 (5)	0.009 (4)	0.018 (8)
C(23)	0.08 (2)	0.11 (2)	0.10 (3)	0.06 (2)	0.023 (19)	0.05 (2)
C(24)	0.036 (15)	0.061 (16)	0.14 (3)	−0.004 (14)	−0.031 (17)	−0.010 (18)
C(25)	0.11 (2)	0.15 (3)	0.055 (17)	0.09 (3)	0.004 (17)	0.01 (2)

[a] See footnote *a*, Table II. Anisotropic temperature factors are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{12}hka^*b^* + ...)]$. For atoms V, Cl(2), N(2), C(21), and C(22) on the twofold axis, the following thermal parameter constraints were used: $U_{12} = {}^1/_2U_{22}$; $U_{13} = {}^1/_2U_{23}$. Isotropic temperature factors for all hydrogen atoms were fixed at $U = 0.10$ Å^2.

Table IV. Interatomic Distances (Å) and Angles (Deg) for $VCl_3(CN\text{-}t\text{-}Bu)_3$[a]

V-Cl(1)	2.317 (2)	C(12)-C(14)	1.512 (11)
V-Cl(2)	2.288 (4)	C(12)-C(15)	1.508 (12)
V-C(11)	2.189 (9)	N(2)-C(21)	1.130 (14)
V-C(21)	2.186 (15)	N(2)-C(22)	1.463 (15)
N(1)-C(11)	1.136 (9)	C(22)-C(23)	1.489 (24)
N(1)-C(12)	1.452 (10)	C(22)-C(24)	1.575 (20)
C(12)-C(13)	1.501 (12)	C(22)-C(25)	1.489 (25)

Cl(1)-V-Cl(1′)	165.6 (2)	N(1)-C(12)-C(14)	106.8 (7)
Cl(1)-V-Cl(2)	97.2 (1)	N(1)-C(12)-C(15)	107.4 (8)
Cl(1)-V-C(11)	88.6 (2)	C(13)-C(12)-C(14)	111.1 (9)
Cl(1)-V-C(11′)	91.8 (2)	C(13)-C(12)-C(15)	110.0 (8)
Cl(1)-V-C(21)	82.8 (1)	C(14)-C(12)-C(15)	112.4 (9)
Cl(2)-V-C(11)	88.2 (2)	C(21)-N(2)-C(22)	180.0
Cl(2)-V-C(21)	180.0	V-C(21)-N(2)	180.0
C(11)-V-C(11′)	176.4 (6)	N(2)-C(22)-C(23)	108.5 (11)
C(11)-V-C(21)	91.8 (2)	N(2)-C(22)-C(24)	106.4 (10)
C(11)-N(1)-C(12)	174.8 (9)	N(2)-C(22)-C(25)	110.8 (11)
V-C(11)-N(1)	174.0 (8)	C(23)-C(22)-C(24)	107.9 (14)
N(1)-C(12)-C(13)	109.1 (8)	C(23)-C(22)-C(25)	114.6 (13)
		C(24)-C(22)-C(25)	108.3 (13)

[a] See footnote *a*, Table II. Values reported have not been corrected for thermal motion.

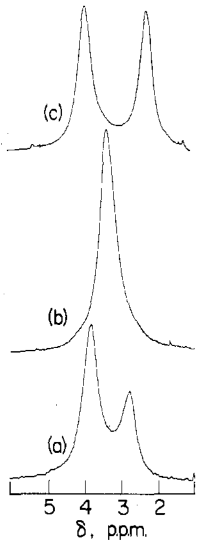

Figure 2. Proton NMR spectra of $VCl_3(CN\text{-}t\text{-}Bu)_3$ in deuterated chloroform (a) at 33 °C, (b) at 60 °C, and (c) at 33 °C in the presence of an equimolar concentration of added *tert*-butyl isocyanide.

the face of an octahedron. Isocyanide ligands, being linear, are sterically less encumbering than chloride ions. This difference is reflected in the intraligand bond angles of *mer*-$VCl_3(CN\text{-}t\text{-}Bu)_3$ (Table IV), with Cl(1)–V–Cl(2) opening up to 97.2 (1)° and a concomitant reduction in Cl(1)–V–C(21) to 82.8 (1)°.

Octahedral complexes of the type VX_3L_3, where L is a unidentate ligand, are well-known in vanadium chemistry.[13] The average V–Cl bond length in $VCl_3(CN\text{-}t\text{-}Bu)_3$ of 2.303 (14) Å is somewhat shorter than the average V–Cl distance of 2.361 (2) Å in the *trans*-$[VCl_2(H_2O)_4]^+$ cation,[14] again reflecting the low steric crowding of isocyanide ligands. The mutually trans V–Cl bonds are 0.030 (4) Å longer than the unique V–Cl bond (Table IV), illustrating the slightly greater structural trans effect (STE)[15] of chloride ion compared with that of *tert*-butyl isocyanide in this molecule. The two virtually identical V–C distances of 2.189 (9) and 2.186 (15) Å are slightly longer than those typically encountered for higher coordinate molybdenum and tungsten isocyanide complexes,[1,4] suggesting a weaker bonding interaction. In $K_4[V(CN)_6]$ and $K_4[V(CN)_7]\cdot 2H_2O$, the average V–C bond lengths are 2.161 (4) and 2.15 (1) Å, respectively.[16] The internal geometry of the *tert*-butyl isocyanide ligands is unexceptional.[4]

Ligand Exchange and Temperature-Dependent NMR Behavior of $VCl_3(CN\text{-}t\text{-}Bu)_3$. Synthesis of $[V(CN\text{-}t\text{-}Bu)_6]^{2+}$. The proton NMR spectrum of paramagnetic **2** in $CDCl_3$ at 33 °C exhibits two broad ($\Delta\nu_{1/2} \approx 25$ Hz) absorptions at δ 3.84 and 2.77 with an area ratio of 2:1, respectively (Figure 2a). The low-field absorption is assigned to the mutually trans *tert*-butyl isocyanide groups, and the high-field absorption is assigned to the isocyanide ligand trans to chloride. That the meridional conformation is maintained in solution is supported by the close similarity of the infrared spectrum of **2** taken in chloroform solution with that of the solid mulled in Nujol as well as by the number and area ratio of the NMR peaks. The NMR spectrum taken at 60 °C has only one peak (at δ 3.25, Figure 2b) due to rapid interchange of the ligands at the higher temperature, the mechanism of which is presently unknown. Addition of small increments of *tert*-butyl isocyanide to the NMR sample tube at 33 °C causes the δ 2.77 absorption to grow, sharpen, and move upfield toward the absorption position (δ 1.4) of free *tert*-butyl isocyanide. The spectrum taken after addition of 1 equiv of free ligand is shown in Figure 2c. Thus

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the free ligand exchanges rapidly on the NMR time scale with the isocyanide trans to chloride but not with the mutually trans isocyanide ligands. This phenomenon demonstrates that the kinetic trans effect of *tert*-butyl isocyanide is less than that of chloride ion. Such a result is not expected from the trans-effect series of the platinum metals, although it is in accord with the relative CO labilizing abilities of chloride ion and phenyl isocyanide in $M(CO)_5A$ complexes.[17]

The ligand-exchange properties of the isocyanide ligands were demonstrated chemically by the reaction of **2** with terpyridine to produce the known compound VCl_3(terpy).[6] The product was identified by its visible (mull) spectrum, its infrared spectrum, and elemental analysis.

A second derivative of **2** was isolated from its reaction with excess *tert*-butyl isocyanide in ethanol. The yellow compound, obtained as the hexafluorophosphate salt, was also prepared directly from vanadium(III) chloride. It is formulated as the homoleptic vanadium(II) isocyanide complex [V(CN-*t*-Bu)$_6$](PF$_6$)$_2$ on the basis of its elemental analysis and the presence of a C≡N absorption band at 2190 cm^{-1} in its infrared spectrum.[18]

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Registry No. 2, 74562-45-1; VCl_3(terpy), 64347-78-0; [V(CN-*t*-Bu)$_6$](PF$_6$)$_2$, 74552-65-1.

Supplementary Material Available: Table S1 listing observed and calculated structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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[18] The hexakis(*tert*-butyl isocyanide)vanadium(II) cation has now been crystallographically characterized in the compound [V(CN-*t*-Bu)$_6$][V(CO)$_6$]$_2$ (Silverman, L. D.; Corfield, P. W. R.; Lippard, S. J., to be submitted for publication).

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Entropy, Enthalpy, and Side-Arm Porphyrins. 2. Crystal and Molecular Structure of a 5-Coordinate Zinc Porphyrin with a Four-Atom Chain Attaching the Pyridyl Ligand to the Tetraphenylporphyrin

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The crystal and molecular structure of ZnTPP–NHC(O)$(CH_2)_2C_5H_4N\cdot C_6H_6\cdot {}^1/_2CH_3CH_2OH$, a 5-coordinate zinc porphyrin with a covalently attached axial pyridine ligand, has been determined. The compound crystallizes in the monoclinic system, space group $P2_1/c$ (C_{2h}^5), with $a = 13.970$ (4) Å, $b = 15.184$ (6) Å, $c = 26.110$ (8) Å, and $\beta = 121.54$ (2)° for a cell volume of 4720 (6) Å^3 and $Z = 4$. Refinement of 2372 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ led to $R = 0.069$ and $R_w = 0.086$. Each unit cell contains four discrete Zn porphyrin units, four benzene solvent molecules, and two ethanol solvent molecules well removed from the zinc. The plane of the axial pyridine ligand is found to be aligned over the metal and two diagonally opposed porphyrin nitrogens. The zinc out-of-plane displacement is 0.37 Å, the average Zn–N$_{por}$ distance is 2.059 Å, and the Zn–N$_{py}$ distance is 2.147(7) Å. Stability of the complex vs. bond strain and distortion, relations between solution NMR and electrochemical studies and the solid-state structure, and the orientation of the axial ligand for this and other related compounds are discussed.

Introduction

The synthesis and physicochemical investigation of a number of 5- and 6-coordinate metalloporphyrins and -chlorins in which the axial ligand(s) are covalently attached to the porphyrin ring have been reported over the past few years.[2–15] Covalent attachment of axial ligand(s) allows the coordination number and identity of axial ligand(s) to be controlled, eliminates the necessity of having excess free ligand in solution, and provides access to pure compounds of otherwise unstable coordination geometry such as 5-coordinate Fe(II) and Ni(II). Covalent attachment of axial ligands to the porphyrin ring thus allows inorganic chemists to mimic the coordination sphere of iron in the heme proteins, wherein the axial ligand(s) and coordination number are controlled by the protein residues which extend into the active site pocket. However, although covalent attachment controls coordination number and identity of axial ligands, a recent study[14] has shown that the stability

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