Table III. Buckingham Parameters for Nonbonded Interaction

interacn	$a/10^5$ kJ mol^{-1}	b/Å^{-1}	$c/10^2$ Å^6 kJ mol^{-1}
Rh···Lp	0.26	3.13	7.05
Rh···F	1.30	3.44	11.4
O···O	15.2	4.62	15.2
O···Lp,H	3.74	4.58	5.36
O···C	21.2	4.61	15.2
O···F	6.16	4.62	8.43
C···Lp,H	5.31	4.57	5.49
H,Lp···Lp,H	1.06	4.55	2.07
H,Lp···F	1.49	4.59	2.78
H,Lp···S	2.29	3.94	13.1
C···C	30.3	4.60	15.2
C···H	5.31	4.57	5.49
C···F	8.32	4.61	8.19
C···S	13.1	4.05	32.4
F···F	2.73	4.63	4.91
F···S	7.58	4.22	20.6
S···S	17.8	3.80	84.3

are summarized in Table I. All the structures were simulated satisfactorily by using values of r_0 within the range 2.41–2.45 Å, which is considered to be within experimental error.

The conclusion to be drawn is that the Rh–Rh bond order is unity in all cases and that observed variations in bond length are due entirely to steric factors. The previous discussion[1] of these effects still apply. The only difference is the revised values for (k, r_0) = (2.73 mdyn Å^{-1}, 2.43 Å). It is pointed out that any given molecular property can always be simulated in molecular mechanics by a matched pair of parameters $\{k, p_0\}$, consisting of a force constant and a characteristic value. In general, where neither is fixed by experimental evidence, a solution set can be chosen over an extensive range without affecting the simulation. The ultimate aim remains to have both parameters fixed experimentally for all bonds, but this objective is still to be achieved and easily frustrated by wrong assignments.

In the course of this study, we used the opportunity to improve on the previous force field for improved fit between observed and calculated structures. Modified parameters only are given in Tables II and III. We would like to thank Professor Robin Clark for drawing our attention to the new assignment of $\nu(Rh_2)$.

Registry No. $Rh_2(O_2CCH_3)_4(H_2O)_2$, 29998-99-0; $Rh_2(O_2CCH_3)_4(Me_2SO)_2$, 26023-60-9; $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, 65507-56-4; $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 72665-42-0; $Rh_2(O_2CC(CH_3)_3)_4(H_2O)_2$, 70084-27-4; Rh, 7440-16-6.

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Articles

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Novel Vanadium(II) Amine Complexes: A Facile Entry in the Chemistry of Divalent Vanadium. Synthesis and Characterization of Mononuclear L_4VCl_2 [L = Amine, Pyridine]: X-ray Structures of *trans*-$(TMEDA)_2VCl_2$ [TMEDA = *N,N,N',N'*-Tetramethylethylenediamine] and *trans*-$Mz_2V(py)_2$ [Mz = *o*-$C_6H_4CH_2N(CH_3)_2$, py = Pyridine]

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Reaction of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ with a slight excess of the nitrogen-containing ligand L [L = amine, pyridine] ruptured the bimetallic structure, allowing the large-scale preparation of the mononuclear high-spin V(II) derivatives *trans*-L_4VCl_2 [L = $^1/_2$ TMEDA (**1**), $^1/_2$ *N,N,N'*-trimethylethylenediamine (**2**), pyrrolidine (**3**), pyridine (**4**)] in crystalline form and good yield. Crystal data for **1** are as follows: monoclinic, $P2_1/n$, a = 7.900 (3) Å, b = 12.345 (5) Å, c = 9.142 (3) Å, β = 97.33 (3)°, V = 884.3 (7) Å^3, Z = 2. These complexes are versatile starting materials for the preparation of various V(II) complexes including the first dinitrogen derivative $[(py)(Mz)_2V]_2(\mu\text{-}N_2)$ (**5**) [Mz = *o*-$C_6H_4CH_2N(CH_3)_2$] and the monomeric aryl *trans*-$Mz_2V(py)_2$ (**6**). Crystal data for **6** are as follows: monoclinic, $P2_1/c$, a = 9.990 (1) Å, b = 15.536 (1) Å, c = 16.369 (1) Å, β = 95.17 (1)°, V = 2530.2 (3) Å^3, Z = 4.

Introduction

During the past 10 years interest in the chemistry of low-valent vanadium has been attracted by several interesting features. Dinitrogen fixation/activation,[1] V–V multiple-bond formation,[2] strong reducing power,[3] and the puzzling role of the high concentration of vanadium in several living organisms[4] are all areas of active research. In spite of this wide interest, however, the chemistry of low-valent vanadium remains rather unknown, especially for oxidation state II,[5] information being available on mainly cyclopentadienyl[6] and related systems.[7] Undoubtedly the retarding factor in the development of this chemistry has been the lack of suitable V(II) starting materials. In fact, although

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the redox and coordination chemistry of $[V(OH_2)_6]^{2+}$ in aqueous solutions has been examined extensively,[5a,8] much less is known about V(II) complexes.[5] Bimetallic V(II) halides, $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[M_2Cl_6]$ have been obtained in large scale by reduction of VCl_3 with a number of reducing agents (M = Zn,[9] Al,[10] Fe,[10] Co,[10]). The heterobimetallic nature of these compounds is quite robust and is preserved in the very diversified structures obtained by chloride or THF replacement reactions.[11,12] The only exception is provided by the chelating phosphine dmpe [dmpe = bis(dimethylphosphino)ethane], which, in sharp contrast to the aromatic analogues,[12] forms the monomeric $(dmpe)_2VCl_2$.[13] The isostructural $(py)_4VCl_2$ was prepared by electrochemical methods.[14]

We found that an unexpectedly high affinity of divalent vanadium for several nitrogen-containing ligands allows the easy rupture of the bimetallic structure of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$, providing a convenient preparation of monomeric, octahedral, high-spin V(II) complexes in crystalline form.

We wish to describe in this paper the convenient large-scale synthesis and characterization of a new class of V(II) amine complexes.

Table I. Crystal Data and Structural Analysis Results

complex	1	6
formula	$C_{12}H_{32}N_4Cl_2V$	$C_{28}H_{34}N_4V$
space group	$P2_1/n$	$P2_1/c$ (no. 14)
Z	2	4
a, Å	7.900 (3)	9.990 (1)
b, Å	12.345 (5)	15.536 (1)
c, Å	9.142 (3)	16.369 (1)
β, deg	97.33 (3)	95.17 (1)
V, Å^3	884.3 (5)	2530.2 (3)
D_{calcd}, g cm^{-3}	1.330	1.254
μ_{calcd}, cm^{-1}	8.43	4.0
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
T, K	130	294
R_F	0.033	0.039
R_{wF}	0.043	0.042

Experimental Section

All operations were performed under inert atmosphere (N_2 or Ar) with use of standard Schlenck techniques or in a nitrogen-filled drybox (BRAUN-MB 200). $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$,[9] MzLi,[15] and *N*,*N*,*N'*-trimethylethylenediamine[16] were prepared according to published procedures. Amines were dried by refluxing over melted potassium, and solvents were dried by following standard procedures. Infrared spectra were recorded on Unicam SP3-300 and on Bruker IFS88 FT-IR spectrophotometers. Nujol mulls were prepared in the drybox. Elemental analyses were carried out at the Microanalytical Department of the Rijksuniversiteit Groningen. Samples for magnetic measurements were weighed inside a drybox with a microanalytical balance and sealed into a calibrated Teflon capsule. Magnetic measurements were performed with a Faraday balance (Oxford Instruments) and corrected for the underlying diamagnetism.[17]

$VCl_2(TMEDA)_2$ (1) (TMEDA = *N,N,N',N'*-Tetramethylethylenediamine). A suspension of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ (36.4 g, 0.022 mol) in THF (350 mL) containing TMEDA (65.3 g, 0.56 mol) was refluxed for 1 h. The resulting light blue solution separated light blue crystals upon standing overnight at 10 °C. Analytically pure, large-size crystals of **1** (13.5 g, 0.38 mol; yield 42%) were obtained after recrystallization or extraction from THF (500 mL) containing a small amount of TMEDA (10 mL). Anal. Calcd (found) for $C_{12}H_{32}N_4Cl_2V$: C, 40.69 (40.64); H, 9.03 (9.17); N, 15.82 (15.57); Cl, 20.01 (19.98); V, 14.38 (14.89). IR (Nujol mull, KBr, cm^{-1}): 1380 (m), 1360 (s), 1290 (w), 1280 (s), 1235 (s), 1185 (s), 1150 (s), 1120 (s), 1105 (w), 1100 (w), 1070 (s), 1045 (m), 1015 (s), 955 (s), 920 (m), 775 (s), 720 (w), 595 (s), 490 (s), 470 (s), 460 (w). $\mu_{eff} = 3.68\mu_B$.

VCl_2(*N,N,N'*-trimethylethylenediamine)$_2$ (2). The addition of neat *N,N,N'*-trimethylethylenediamine (6 mL, 46 mmol) to a suspension of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ (5.95 g, 3.66 mmol) in THF (250 mL) caused the color to turn immediately to light purple. The mixture was refluxed for 30 min, and the solid, which precipitated at room temperature, was recrystallized from THF or CH_3CN (500 mL) (3.31 g, 10.1 mmol; yield 69%). Anal. Calcd (found) for $C_{10}H_{28}N_4Cl_2V$: C, 36.81 (36.96); H, 8.59 (8.62); N, 17.18 (17.00); Cl, 21.78 (21.64); V, 15.61 (15.60). IR (Nujol mull, KBr, cm^{-1}): 3575 (m), 1445 (s), 1435 (s), 1400 (w), 1370 (s), 1350 (m), 1275 (s), 1230 (w), 1210 (s), 1175 (s), 1145 (s), 1110 (s), 1080 (s), 1040 (s), 1030 (w), 1005 (m), 980 (m), 925 (s), 830 (s), 770 (s), 720 (w), 585 (m), 470 (s), 450 (w), 390 (s). $\mu_{eff} = 3.79\mu_B$.

$VCl_2(py)_4$. Method a (from VCl_3). A vigorous exothermic reaction took place upon addition of VCl_3 (20.4 g, 0.18 mol) to dry pyridine (500 mL). Zinc dust (7.5 g, 0.11 mol) was added to the violet suspension, and the resulting mixture was refluxed and stirred for 30 min. After being stirred for 20 h at room temperature, the burgundy red suspension was boiled and filtered when hot. Purple crystals of **4** separated upon cooling at 0 °C (54.2 g, 0.12 mol; yield 69%). Anal. Calcd (found) for $C_{20}H_{20}N_4Cl_2V$: C, 54.79 (54.74); H, 4.57 (4.56); N, 12.79 (12.01); Cl, 16.21 (16.10); V, 11.64 (11.73). IR (Nujol mull, KBr, cm^{-1}): 1585 (m), 1480 (s), 1435 (s), 1370 (m), 1200 (m), 1140 (s), 1070 (s), 1034 (s), 750 (s), 690 (s). $\mu_{eff} = 3.85\mu_B$.

Method b (from $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$). A suspension of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ (17.32 g, 0.11 mol) in THF (500 mL) was

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treated with pyridine (25 mL, 0.31 mol). The color turned immediately deep red, and the mixture was boiled for 30 min. Analytically pure deep red crystals of **4** were obtained when the mixture was allowed to stand overnight at room temperature (14.21 g, 0.032 mol; yield 76%).

VCl_2(pyrrolidine)$_4$ (3). The treatment of a suspension of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ (2.08 g, 1.28 mmol) in THF (75 mL) with dry pyrrolidine (5 mL, 60 mmol) afforded a light blue solid. After the mixture was boiled for 20 min, the microcrystalline solid was collected, and analyzed. Another crop of light blue microcrystalline solid precipitated upon cooling the mother liquor at room temperature (0.24 g, 0.61 mmol; yield 24%). Anal. Calcd (found) for $C_{16}H_{36}N_4Cl_2V$: C, 47.29 (46.93); H, 8.87 (8.63); N, 13.75 (13.49); Cl, 17.49 (18.01); V, 12.56 (12.21). IR (Nujol mull, KBr, cm^{-1}): 3160 (s), 1450 (m), 1420 (w), 1370 (w), 1310 (m), 1230 (m), 1080 (s), 1040 (s), 950 (w), 905 (s), 715 (w), 660 (m). $\mu_{eff} = 3.73\mu_B$.

$\{[o\text{-}C_6H_4CH_2N(CH_3)_2]_2V(py)\}_2(\mu\text{-}N_2)\cdot 2THF$ (5). A stirred suspension of $VCl_2(TMEDA)_2$ (1.32 g, 3.7 mmol) in THF (30 mL) was reacted with freshly sublimed (o-$Me_2NCH_2C_6H_4$)Li. The color turned immediately reddish brown, and the resulting mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo and the residual solid redissolved in Et_2O. After filtration and addition of pyridine (0.3 mL), the resulting reddish brown solution afforded deep red crystals of **5** upon standing at 0 °C overnight (0.93 g, 0.96 mmol, 52%). Anal. Calcd (found) for $C_{27}H_{37}N_4OV$: C, 66.87 (67.05); H, 7.64 (7.48); N, 11.56 (11.53); V, 10.52 (10.63). IR (Nujol mull, KBr, cm^{-1}): 1587 (s), 1500 (m), 1479 (s), 1467 (s), 1444 (s), 1424 (m), 1377 (m), 1360 (w), 1300 (m), 1250 (s), 1210 (m), 1190 (s), 1180 (w), 1200 (m), 1125 (w), 1110 (m), 1100 (m), 1036 (s), 1015 (m), 1000 (m), 991 (s), 940 (m), 850 (s), 825 (m), 797 (s), 759 (s), 744 (s), 720 (m), 705 (s), 630 (m), 520 (m). $\mu_{eff} = 3.47\mu_B$.

$[o\text{-}C_6H_4CH_2N(CH_3)_2]_2V[py]_2$ (6). A suspension of $VCl_2(TMEDA)_2$ (3.87 g, 10.7 mmol) in THF (50 mL) was reacted with (o-Me_2NCH_2)C_6H_4Li (3.18 g, 22.6 mmol). The color turned deep red, and the mixture was stirred for 4 h. After solvent evaporation in vacuo, the residual solid was redissolved in 150 mL of Et_2O. Addition of pyridine (10 mL) turned the color deep green, and deep green crystals of **6** separated when the solution was allowed to stand at 0 °C (3.13 g, 6.56 mmol; yield 61%). Anal. Calcd (found) for $C_{28}H_{34}N_4V$: C, 70.44 (70.68); H, 7.13 (7.23); N, 11.74 (11.42); V, 10.69 (10.82). IR (Nujol mull, KBr, cm^{-1}): 1583 (m), 1559 (m), 1475 (s), 1467 (s), 1436 (s), 1424 (m), 1358 (w), 1350 (w), 1238 (m), 1233 (w), 1206 (s), 1184 (m), 1107 (m), 1035 (s), 1102 (m), 1000 (m), 992 (s), 983 (m), 850 (s), 767 (s), 759 (s), 744 (s), 720 (s), 711 (s), 703 (s). $\mu_{eff} = 3.75\mu_B$.

Gas Volumetric Experiment. A round-bottomed flask containing a reddish brown solution of **5** (0.54 g, 0.56 mmol) in THF (15 mL) was connected to a vacuum line equipped with a Toepler pump. The solution was frozen (130 K), and pyridine (1 mL) was condensed into the flask. When the flask was warmed at 40 °C, the color of the mixture turned emerald green, and gas evolution was observed. The gas recovered was 0.53 mmol of nitrogen (94%), obtained after several evacuation cycles of the Toepler pump. The solution was evaporated to dryness, and the residual solid, redissolved in little amount of pyridine, was precipitated by addition of ether. The IR spectrum of the resulting solid identified the product as complex **6**.

X-ray Crystallography. The crystals used for this study were selected in a drybox equipped with a microscope. Suitable crystals were either sealed in thin-walled Lindemann glass capillaries (**6**) or glued on the top of a glass fiber covered with a thin layer of paraffin oil (**1**) and mounted on the diffractometer (CAD-4F), which was equipped with a locally modified cooling device. The net intensities of the data were corrected for the scale variation and Lorentz and polarization effects. Details on the structure determination and refinement are given in Table I. Tables of hydrogen atom positions, thermal parameters, extensive lists of bond distances and angles and tables of F_o, F_c, and $\sigma(F)$ are available as supplementary material. Scattering factors were obtained from Cromer and Mann[18] and anomalous dispersion factors from Cromer and Liberman.[19]

Compound 1. Final lattice parameters were determined by least-squares treatment, using the setting angles of 25 reflections in the range 8.2° $\leq \theta \leq$ 15.9°. Data were corrected for absorption (the linear absorption coefficient was 8.43 cm^{-1}). From a total of 2705 unique reflections in the range 1° $< \theta <$ 30°, 2114 satisfied the $I > 3\sigma(I)$ criterion of observability. The structure was solved by direct methods using the SDP/PDP (Enraf-Nonius) program system.[20] Block-diagonal least-squares of F with unit weights converged to a final value of $R_F = 0.033$ and $R_{wF} = 0.043$ with anisotropic temperature factors used for the non-hydrogen atoms and fixed isotropic temperature factors for the hydrogen atoms. The hydrogen atoms were located from difference Fourier maps and introduced in the refinement at their idealized positions. Conformational disorder was observed for the C2, C3, C4, and C5 atoms. The disorder

Table II. Final Coordinates and Equivalent Isotropic Thermal Parameters for **1** (Esds in Parentheses)

atom	x	y	z	B, Å^2
V	0.500	0.000	0.500	1.215 (9)
Cl1	0.28062 (7)	0.13093 (5)	0.56178 (7)	1.85 (1)
N1	0.6300 (2)	0.1367 (2)	0.3809 (2)	1.77 (4)
N2	0.3523 (2)	−0.0217 (2)	0.2658 (2)	1.71 (4)
C1	0.6108 (5)	0.2466 (2)	0.4319 (4)	4.09 (9)
C2	0.7991 (6)	0.1188 (4)	0.3277 (6)	2.00 (9)
C2′	0.8245 (6)	0.1299 (4)	0.4197 (6)	2.3 (1)
C3	0.5042 (6)	0.1552 (4)	0.2337 (5)	1.61 (8)
C3′	0.5839 (7)	0.1036 (4)	0.2337 (5)	1.97 (9)
C4	0.4566 (6)	0.0461 (4)	0.1632 (5)	1.67 (8)
C4′	0.3967 (7)	0.0778 (4)	0.2037 (5)	1.93 (9)
C5	0.1619 (6)	−0.0266 (5)	0.2758 (6)	2.4 (1)
C5′	0.1747 (6)	0.0187 (4)	0.2326 (6)	1.98 (9)
C6	0.3749 (5)	−0.1255 (3)	0.1948 (3)	3.28 (7)

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters for **6** (Esds in Parentheses)

atom	x	y	z	U(eq),[a] Å^2
		Molecule 1		
V1	1	1/2	1/2	0.0350 (3)
N11	0.9126 (3)	0.4139 (2)	0.3910 (2)	0.045 (1)
N21	0.9650 (3)	0.6212 (2)	0.4269 (2)	0.041 (1)
C11	1.1804 (4)	0.4667 (3)	0.4352 (2)	0.040 (2)
C21	1.3112 (4)	0.5000 (3)	0.4355 (3)	0.046 (2)
C31	1.4092 (5)	0.4671 (3)	0.3892 (3)	0.057 (2)
C41	1.3810 (5)	0.3978 (3)	0.3395 (3)	0.060 (2)
C51	1.2540 (5)	0.3610 (3)	0.3360 (3)	0.055 (2)
C61	1.1574 (4)	0.3951 (3)	0.3831 (2)	0.041 (2)
C71	1.0218 (4)	0.3511 (3)	0.3808 (3)	0.049 (2)
C81	0.8899 (5)	0.4644 (3)	0.3152 (3)	0.063 (2)
C91	0.7876 (5)	0.3663 (3)	0.4017 (3)	0.071 (2)
C101	0.8438 (4)	0.6598 (3)	0.4158 (2)	0.045 (2)
C111	0.8253 (5)	0.7388 (3)	0.3793 (3)	0.054 (2)
C121	0.9330 (5)	0.7831 (3)	0.3540 (3)	0.058 (2)
C131	1.0568 (5)	0.7434 (3)	0.3629 (3)	0.057 (2)
C141	1.0690 (4)	0.6639 (3)	0.3983 (3)	0.047 (2)
		Molecule 2		
V2	1/2	0	1/2	0.0350 (3)
N12	0.3879 (3)	0.1036 (2)	0.4182 (2)	0.046 (1)
N22	0.3159 (3)	−0.0329 (2)	0.5622 (2)	0.041 (1)
C12	0.5330 (4)	0.1216 (3)	0.5738 (3)	0.039 (2)
C22	0.5728 (4)	0.1416 (3)	0.6562 (2)	0.041 (2)
C32	0.5843 (4)	0.2247 (3)	0.6870 (3)	0.048 (2)
C42	0.5561 (5)	0.2939 (3)	0.6362 (3)	0.054 (2)
C52	0.5176 (4)	0.2787 (3)	0.5542 (3)	0.049 (2)
C62	0.5075 (4)	0.1953 (3)	0.5248 (2)	0.039 (2)
C72	0.4695 (4)	0.1835 (3)	0.4335 (3)	0.050 (2)
C82	0.2539 (4)	0.1198 (3)	0.4446 (3)	0.062 (2)
C92	0.3731 (6)	0.0884 (3)	0.3292 (3)	0.068 (2)
C102	0.2196 (4)	−0.0853 (3)	0.5274 (3)	0.052 (2)
C112	0.1141 (4)	−0.1143 (3)	0.5675 (3)	0.063 (2)
C122	0.1050 (5)	−0.0908 (3)	0.6476 (3)	0.073 (2)
C132	0.2013 (5)	−0.0360 (3)	0.6842 (3)	0.063 (2)
C142	0.3029 (4)	−0.0078 (3)	0.6395 (3)	0.049 (2)

[a] U(eq) = one-third of the trace of the orthogonalized **U** matrix.

Table IV. Selected Bond Distances (Å) and Angles (deg)

1		**6**	
dist	angle	dist	angle
V-Cl1 = 2.487 (1)	N1-V-N2 = 81.44 (7)	V-C11 = 2.233 (4)	C11-V-N11 = 76.5 (1)
V-N1 = 2.318 (2)	Cl1-V-N1 = 89.82 (5)	V-N11 = 2.335 (3)	N11-V-N21 = 92.5 (1)
V-N2 = 2.320 (2)	Cl1-V-N2 = 90.10 (5)	V-N21 = 2.241 (3)	C11-V-N21 = 92.0 (1)

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(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(20) Computer software: SDP/PDP, Enraf-Nonius & B. A. Frenz & Associates, Inc.

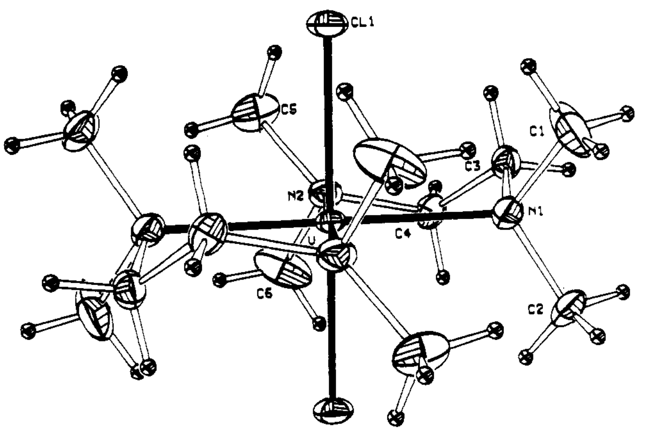
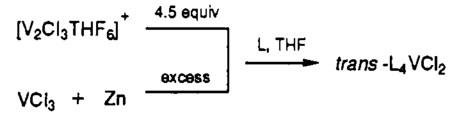


Figure 1. ORTEP drawing of **1** showing the labeling scheme. Thermal ellipsoids drawn at the 50% probability level.

Scheme I[a]



[a] L = $^1/_2$ *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (**1**), $^1/_2$ *N,N,N'*-trimethylethylenediamine (**2**), pyrrolidine (**3**), pyridine (**4**).

was resolved by splitting the positions of the atoms in the two conformations with an equal occupancy of 50%. Final atomic coordinates are listed in Table II. Relevant bond distances and angles are reported in Table IV.

Compound 6. Unit cell parameters were determined for a dark green plate-shaped crystal from a least-squares treatment of the SET4 setting angles of 25 reflections with $8.5° < \theta < 14.0°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[21] Data were corrected for *Lp* and for linear decay (8.6%) of the intensities during the 52 h of X-ray exposure time, but not for absorption. The structure was solved by direct methods (SHELXS86).[22] Refinement on *F* was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All the non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were refined with one common isotropic thermal parameter (U = 0.061 (2) Å^2). Final atomic coordinates and equivalent isotropic thermal parameters are given in Table III. Data on geometry are reported in Table IV. All the calculations were performed with SHELX76[23] and the EUCLID package[24] (geometrical calculations and illustrations) on a MicroVAX cluster computer.

Results and Discussion

According to Scheme I, the reactions proceeded exothermically in THF and analytically pure Zn-free complexes were isolated in the case of **1**, **2**, and **3**, as light-blue air-sensitive crystals after recrystallization or extraction from boiling THF.

The utilization of a slight excess of amine (at least 4.5 equiv/vanadium) is necessary to avoid the contamination of the product by unreacted starting material. Conversely, the utilization of larger amounts of amine led to the precipitation of L_2ZnCl_2 as a poorly soluble contaminant that could not be properly removed by simple recrystallization. While no appreciable reaction was observed with $(i\text{-Pr})_2NH$ even in neat refluxing amine, the formation of the deep red $VCl_2(py)_4$ (**4**) occurs instantaneously at room temperature and can be more conveniently carried out in a one-pot reduction of VCl_3 with an excess of Zn in boiling pyridine.

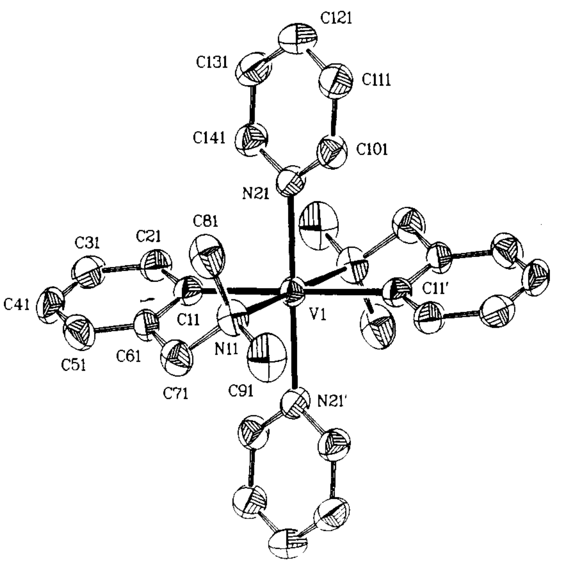
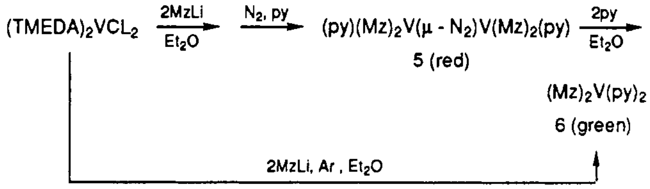


Figure 2. Thermal ellipsoid plot at 50% probability level of one of the two nearly identical molecules of **6** showing the labeling scheme.

Scheme II



All the complexes showed values of the magnetic moment as would be expected for a V(II) d^3 high-spin electronic configuration [$\mu_{eff}(\mu_B)$ = 3.68 (**1**), 3.79 (**2**), 3.73 (**3**), and 3.85 (**4**) μ_B].

The monomeric nature of **1** was demonstrated by an X-ray analysis. The molecule (Figure 1) has the *trans*-dihalide geometry previously observed for *trans*-L_4VCl_2 [L = $^1/_2$dmpe, py][13,14] with similar values of the V–Cl distance [V–Cl = 2.487 (1) Å]. Conversely, the V–N distances [V–N1 = 2.318 (2) Å] are considerably longer than those observed in **4**, reflecting the absence of V→N back-bonding and suggesting a higher lability of the amine ligands.

In agreement with this hypothesis, preliminary reactivity results showed that complex **1** readily dissociates the chelating amine molecules from the molecular equatorial plane during the chlorine substitution reactions, forming highly reactive V(II) species. This behavior is in sharp contrast with that of the V(II) phosphine derivatives, which retain the coordinated phosphine during the substitution with alkyls and hydride,[12,25] and the reactivity of **4**, whose versatility as starting material is hampered by easy deprotonation of the para positions of the coordinated pyridine. Conversely, complex **1** is a versatile starting material for the preparation of a number of monomeric and dimeric V(II) complexes, including the first dinuclear V(II) complex of dinitrogen $[(py)(Mz)_2V(\mu\text{-}N_2)V(Mz)_2(py)]$ [Mz = $o\text{-}C_6H_4CH_2N(CH_3)_2$] (**5**) in crystalline form and good yield (Scheme II). The synthesis and characterization of **5** have been the subject of a previous paper.[26] The coordination of dinitrogen in complex **5** appears to be quite robust.[26] However, further reaction of **5** with 2 equiv of pyridine allows the evolution of stoichiometric amounts of dinitrogen with formation of the monomeric, octahedral, emerald green V(II) aryl *trans*-$(Mz)_2V(py)_2$ (**6**) (Scheme II).

The reaction is probably achieved via preliminary dissociation of dinitrogen. The presence of association/dissociation equilibrium

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in solution is in fact suggested by the reversible color change from the reddish brown to the emerald green and vice versa, observed when a toluene solution of **5** is warmed (60 °C) and cooled (room temperature) during several cycles. We believe that the dissociation of dinitrogen leads to a quite reversible molecular reorganization where the monomeric **6** is formed as the main component of the product distribution. However the formation of unknown byproducts should necessarily be admitted. In agreement with the supposed high thermodynamic stability of complex **6**, attempts to prepare coordinatively unsaturated, N_2-free, highly reactive species, carried out by repeating the preparation of **5** under argon atmosphere, led only to variable amounts of **6** in spite of the careful stoichiometry control.

The crystal structure of **6** showed the compound as composed of two crystallographically independent and chemically equivalent monomeric molecules. The overall molecular geometry is shown in Figure 2. Even in this case, the vanadium atom is positioned on an inversion center of a highly symmetrical octahedron with the two pyridine molecules in trans positions. The values of the V–N distances are significantly different for the two unequivalent nitrogen atoms of the pyridine and Mz ligands [V–N21 = 2.241 (3) Å; V–N11 = 2.335 (3) a] as a result of the different nature of the bonding to vanadium. The V–C distance [V–C11 = 2.233 (4) Å] compares well with those found in the homoleptic $Li_4(Et_2O)_4VPh_6$.[5f]

Further work to investigate this point and to define the chemical reactivity of these V(II) complexes as well as synthetic efforts to prepare isostructural Ti derivatives is in progress at the moment.

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Supplementary Material Available: Tables with numerical details of the structure determination, hydrogen atom positions, thermal parameters, bond distances, and bond angles for **1** and **6** and a table of torsion angles for **6** (13 pages); listings of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and X-ray Crystal Structure of $[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$

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The complex *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$ (where trpy = 2,2′:6′,2″-terpyridine and PMe_3 = trimethylphosphine), has been prepared by using a five-step synthesis, starting from $RuCl_3{\cdot}3H_2O$, with a total overall yield of 27%. In addition, a three-step synthesis for the formation of *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$ was developed, where an increase in the total overall yield from 27% to 71% was observed. Characterization of *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$ was accomplished through UV–visible, IR, and ^1H and ^{13}C NMR spectroscopies, cyclic voltammetry, coulometry, and elemental analysis. An X-ray crystallographic structural determination was also performed, where *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)$ crystallized in the monoclinic space group $P2_1/c$ with cell parameters of a = 16.102 (11) Å, b = 10.365 (7) Å, c = 16.788 (12) Å, β = 108.23 (5)°, and Z = 4. Final discrepancy indices were R_F = 7.1% and R_{wF} = 6.4% for all 3169 nonzero data and R_F = 4.2% and R_{wF} = 5.1% for those 2186 reflections with $|F_o| > 6\sigma(|F_o|)$. The ruthenium to nitrogen bond distances were Ru–N(nitro) = 2.074 (6) Å and Ru–N(trpy) = 2.088 (6), 1.985 (5), and 2.093 (7) Å. The ruthenium to phosphorus bond distances were Ru–P = 2.361 (3) and 2.368 (3) Å.

Introduction

There has been considerable interest in ruthenium complexes that contain tertiary phosphine ligands, due to the well-documented use of low-valent ruthenium complexes in the area of homogeneous catalysis.[1-11] The chemistry of high-valent ruthenium complexes has also received much attention, in light of the potent oxidizing ability of these species.[12-17] Our research has been directed toward the utilization of tertiary phosphine ligands with high-oxidation-state ruthenium centers, where we have synthesized and characterized high-oxidation-state ruthenium complexes containing tertiary phosphine ligands. The phosphine ligands confer interesting properties on (oxo)ruthenium(IV) complexes[18-20] and on *trans*-$[Ru(NO_2)(PMe_3)_2(trpy)](ClO_4)_2$,[21] where both the stability and reactivity of these complexes are strongly affected by the phosphine ligands. For example, both the rates of substrate oxidation by (oxo)(phosphine)ruthenium(IV) complexes[22] and the resulting product distributions[23] depend on the ligand environment of the ruthenium complexes. Furthermore, linear rate enhancements were observed, based on the hydrophobicity of the substrate, for the oxidation of primary alcohols in water with these (oxo)(tertiary phosphine)ruthenium(IV) complexes.[22,24] Recently, we reported the synthesis and characterization of the first stable (nitro)ruthenium(III) complex, *trans*-$[Ru(NO_2)(PMe_3)_2$-

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