Inorganica Chimica Acta, *141* (1988) 91–98

Vanadium(II)– and Vanadium(III)–Formamidinato Compounds. Synthesis and Molecular Structure of $V(form)_2(NC_5H_5)_2$ and $V(\eta^5\text{-}C_5H_5)(form)_2$ [form = *N,N'*-di-*p*-tolylformamidine]

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(Received April 7, 1987)

Abstract

VCl_2py_4 and Li^+form^- in toluene afford $V(form)_2py_2$ (**1**) in 63% isolated yields. $VCp(form)_2$ (**2**) can be prepared in 60% yields from the thermal reaction between VCp_2 and Hform. *Crystal data.* Compound **1**: triclinic, space group $P\bar{1}$, $a = 9.549(3)$, $b = 12.366(3)$, $c = 16.194(3)$ Å, $\alpha = 108.77(2)$, $\beta = 90.94(2)$, $\gamma = 94.83(2)°$, $V = 1802(2)$ Å^3, $Z = 2$, $D_c = 1.208$ g cm^{-3}, $R = 0.050$ ($R_w = 0.062$) for 441 parameters and 3051 data with $F_o^2 > 3\sigma(F_o^2)$. Compound **2**: triclinic, space group $P\bar{1}$, $a = 13.135(1)$, $b = 15.452(3)$, $c = 8.064(1)$ Å, $\alpha = 103.41(1)$, $\beta = 102.92(1)$, $\gamma = 103.55(1)°$, $V = 1479(1)$ Å^3, $Z = 2$, $D_c = 1.263$ g cm^{-3}, $R = 0.058$ ($R_w = 0.078$) for 327 parameters and 2319 data having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We have been lately interested in the use of the *N,N'*-di-*p*-tolylformamidinato ion ($form^-$) as a bidentate ligand with the hope that this could stabilize metal–metal bonded cores that are difficult to assemble. As part of this agenda, we have succeeded in synthesizing the first quadruply bridged Ir(II) dimer, $Ir_2(form)_4$ [1], and we have also reported the synthesis and electrochemical oxidation of $M_2(form)_4$ (M = Ni, Pd) [2]. The ability of the formamidinato ligand to contribute to the stability of M_2^{n+} cores can be attributed to its high Lewis basicity. A strong electron donor is expected, in fact, to expand the metal orbitals, therefore increasing the overlap in the metal–metal interaction and ultimately strengthening the metal–metal bond. In addition, the small bite of the ligand and the presence of bulky substituents on the nitrogen donor atoms should favor, in principle, the bridging arrangement in a dinuclear structure with respect to chelation in mononuclear compounds or oligomerization.

We then decided to use the $form^-$ ligand to see whether it is possible to assemble a multiple bond between vanadium atoms. Metal–metal bonded dinuclear vanadium compounds are known [3], but none of them has the classical quadruply bridged structure which is common for other metals, e.g. in the carboxylates $M_2(OCOR)_4$ (M = Cr [4], Mo [5], W [6], Ru [7], Rh [8]). Another problem is that vanadium(II) appears to have a strong tendency to abstract oxygen atoms from oxygenated substrates, ultimately assembling V(III)-containing oxo-centered trimers [9]. We considered that the use of the nitrogen based formamidinato ligand and non-oxygenated solvents would eliminate this problem. A theoretical paper has appeared [10] in which calculations on the hypothetical $V_2(O_2CH)_4$ molecule have been reported, the conclusion being that such a species is anticipated to have a very strong metal–metal triple bond and a metal–metal distance between 2.0 and 2.1 Å.

We report here the results obtained by interacting the vanadium(II) starting materials VCl_2py_4 and VCp_2 (py = pyridine, Cp = $\eta^5\text{-}C_5H_5$) with the formamidinato ligand $form^-$, where, unfortunately, only mononuclear V(II) and V(III) compounds containing chelating formamidinato groups were obtained.

Experimental

All operations were carried out under an atmosphere of prepurified argon in standard Schlenkware. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. IR spectra were recorded on a Perkin-Elmer 783 grating spectrophotometer. VC_2py_4 [11], VCp_2 [12] and Hform [13] were prepared according to literature methods.

Preparation of $V(form)_2py_2$ *(1)*

VCl_2py_4 (1.94 g, 4.42 mmol) was added to a suspension of the equivalent amount of Li^+form^-, which was prepared *in situ* from Hform (2.06 g, 9.20 mmol) and 5.8 ml of a 1.6 M solution of n-BuLi in

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0020-1693/88/$3.50

TABLE I. Crystal Data for Compounds 1 and 2

	Compound 1	Compound 2
Formula	$C_{40}H_{40}N_6V$	$C_{35}H_{35}N_4V$
Formula weight	655.75	562.64
Space group	$P\bar{1}$	$P\bar{1}$
Systematic absences	none	none
a (Å)	9.549(3)	13.135(1)
b (Å)	12.366(3)	15.452(3)
c (Å)	16.194(3)	8.064(1)
α (°)	108.77(2)	103.43(1)
β (°)	90.94(2)	102.92(1)
γ (°)	94.83(2)	103.55(1)
V (Å^3)	1802(2)	1479(1)
Z	2	2
D_{calc} (g/cm^3)	1.208	1.263
Crystal size (mm)	0.25 × 0.45 × 0.85	0.2 × 0.3 × 0.7
μ(Mo Kα) (cm^{-1})	2.993	3.521
Data collection instrument	$P\bar{1}$	Rigaku-AFC5R
Radiation (monochromated in incident beam)	Mo Kα ($\lambda\bar{\alpha}$ = 0.71073 Å)	
Orientation reflections, number, range (2θ)	15, 20–25	25, 22–35
Temperature (°C)	20	20
Scan method	ω	ω–2θ
Data collection range, 2θ (°)	3–48.3	4–45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5748, 3051	5260, 2319
No. parameters refined	441	327
R^a	0.050	0.058
R_w^b	0.062	0.078
Quality-of-fit indicator^c	1.253	1.423
Largest shift/e.s.d., final cycle	0.30	0.07
Largest peak (e/Å^3)	0.235	0.356

${}^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ${}^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

n-hexane (9.28 mmol), in 100 ml of toluene. The mixture was stirred at room temperature overnight, then warmed to reflux, filtered hot, and cooled back to room temperature. A dark solid crystallized out of the very deep purple solution. The solvent was partially evaporated under reduced pressure (final volume *ca.* 20 ml) and the solid was recovered by filtration, washed with n-hexane and dried *in vacuo.* Yield 1.39 g (63%). Purification was accomplished by dissolution in toluene, followed by careful layering with n-hexane. This procedure also gave suitable crystals for the subsequent crystallographic study. IR (nujol mull): 1570m, 1535s, 1500s, 1310m, 1290s, 1220m, 1175w, 1150w, 1110w, 1070w, 1045w, 960w, 945w, 825s, 810m, 760m, 700s, 525m, 500m and 445w cm^{-1}.

Preparation of VCp(form)$_2$ (2)

VCp_2 (0.30 g, 1.67 mmol) was dissolved in 20 ml of toluene and treated with 0.75 g of Hform (3.35 mmol). No color change was noted upon stirring at room temperature for several hours. The mixture was then refluxed overnight. The color changed from dark purple to deep yellow–brown. After cooling, the volume was reduced to *ca.* 5 ml by evaporation under reduced pressure. This caused the precipitation of a microcrystalline material. The precipitation was completed by addition of 10 ml of n-hexane and the product was filtered off, washed with n-hexane and dried *in vacuo*. Yield 0.56 g (60%). Purification and crystal growth were accomplished as previously described for compound 1. IR (nujol mull): 1605w, 1540s, 1505s, 1310m, 1280s, 1265s, 1220s, 1110w, 1020w, 965m, 950m, 820s, 810s, 800s, 715w, 650w, 605w, 540m, 525m, 495m, 415w, 400w and 380w cm^{-1}.

X-ray Crystallography

The following procedure was followed for both compounds 1 and 2. A single crystal was glued to the inside of a thin-walled glass capillary, sealed under nitrogen, and mounted on the diffractometer. Data collection parameters along with crystal data are assembled in Table I. The data were corrected for

Lorentz and polarization factors. No correction for absorption and decay was necessary. Solution of the structures was accomplished by direct methods with the SHELXS-86 package [14], which revealed the entire structure for each compound. Refinement was performed, first isotropically, then anisotropically, by full-matrix least-squares cycles with the SHELX-76 software [15]. Hydrogen atoms were included at the calculated positions and used for structure factor calculations but not refined. For compound **2** the phenyl rings were constrained to be perfect hexagons with C–C = 1.395 Å. Fractional atomic coordinates are given in Table II for **1** and in Table III for **2**, and selected bond distances and angles are listed in Tables IV (compound **1**) and V (compound **2**).

Results and Discussion

(a) Syntheses

The interaction between VCl_2py_4 and 2 equivalents of Li^+form^- results in the formation of the mononuclear formamidinato derivative of vanadium(II), $V(form)_2py_2$ (**1**) in good yields, see eqn. (1).

$$VCl_2py_4 + 2Li^+form^- \xrightarrow[\text{room temp.}]{\text{toluene}} V(form)_2py_2 + 2LiCl + 2py \qquad (1)$$

As stated in the 'Introduction', our goal was the formation of a dinuclear compound containing a vanadium–vanadium triple bond. The use of the nitrogen based formamidinato ligand has avoided the problems encountered with acetate (the reaction between VCl_2py_4 and acetate afforded oxo-centered V(III) trimers) [9] and we obtain a V(II) derivative, but this is a mononuclear six-coordinate compound. We conclude that the elimination of the two residual pyridine molecules from compound **1** in the hypothetical reaction (2) is not a favorable process, at least at room temperature.

$$2V(form)_2py_2 \longrightarrow V_2(form)_4 + 4py \qquad (2)$$

TABLE II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for $V(form)_2py_2$ (**1**)[a]

Atom	*x*	*y*	*z*	*B* (Å^2)[b]
V1	0.5000	0.0000	0.0000	2.98(3)
V2	0.0000	0.0000	0.5000	3.46(3)
N1	0.4509(4)	−0.0839(3)	−0.1388(2)	3.4(1)
N2	0.6013(4)	0.0745(3)	−0.0929(2)	3.5(1)
N3	0.0435(4)	0.0822(4)	0.4008(3)	4.1(1)
N4	−0.1100(4)	−0.0748(4)	0.3715(2)	3.8(1)
N5	0.3245(4)	0.1041(3)	0.0060(2)	3.6(1)
N6	0.1709(4)	−0.1080(4)	0.4539(2)	4.0(1)
C1	0.5350(5)	−0.0066(4)	−0.1598(3)	3.7(1)
C2	−0.0436(5)	0.0036(4)	0.3430(3)	4.1(1)
C10	0.3643(5)	−0.1700(4)	−0.2028(3)	3.6(1)
C11	0.2700(6)	−0.2413(5)	−0.1740(3)	4.6(2)
C12	0.1833(6)	−0.3296(5)	−0.2323(4)	5.4(2)
C13	0.1847(6)	−0.3497(5)	−0.3204(4)	5.6(2)
C14	0.2760(7)	−0.2785(6)	−0.3491(4)	6.4(2)
C15	0.3654(6)	−0.1892(5)	−0.2923(3)	5.3(2)
C16	0.0881(8)	−0.4470(6)	−0.3854(5)	8.2(2)
C20	0.6952(5)	0.1594(4)	−0.1087(3)	3.2(1)
C21	0.7779(5)	0.1389(4)	−0.1816(3)	4.1(1)
C22	0.8636(5)	0.2273(5)	−0.1957(3)	4.9(2)
C23	0.8715(5)	0.3397(5)	−0.1378(4)	4.4(1)
C24	0.7910(5)	0.3591(4)	−0.0644(3)	4.1(1)
C25	0.7042(5)	0.2717(4)	−0.0495(3)	3.7(1)
C26	0.9647(7)	0.4350(5)	−0.1546(4)	6.8(2)
C30	0.1279(6)	0.1658(4)	0.3773(3)	4.1(1)
C31	0.2361(7)	0.2286(5)	0.4350(4)	5.8(2)
C32	0.3258(7)	0.3123(6)	0.4168(5)	6.9(2)
C33	0.3122(7)	0.3348(6)	0.3399(5)	6.3(2)
C34	0.2058(8)	0.2712(6)	0.2822(5)	7.6(3)
C35	0.1133(7)	0.1879(5)	0.2994(4)	6.2(2)
C36	0.4137(8)	0.4226(6)	0.3174(6)	9.2(3)
C40	−0.2018(5)	−0.1636(4)	0.3142(3)	3.5(1)
C41	−0.2799(5)	−0.1511(5)	0.2454(3)	4.6(1)
C42	−0.3625(6)	−0.2434(5)	0.1881(3)	5.2(2)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)[b]
C43	-0.3715(5)	-0.3519(5)	0.1988(3)	4.4(1)
C44	-0.2983(5)	-0.3631(5)	0.2698(3)	4.3(1)
C45	-0.2137(5)	-0.2702(5)	0.3258(3)	4.1(1)
C46	-0.4606(7)	-0.4535(6)	0.1358(4)	6.7(2)
C51	0.3389(6)	0.2173(5)	0.0474(4)	5.1(2)
C52	0.2336(8)	0.2870(6)	0.0476(5)	7.0(2)
C53	0.1074(8)	0.2397(7)	0.0051(5)	8.0(3)
C54	0.0896(7)	0.1245(8)	-0.0381(5)	8.4(3)
C55	0.2004(5)	0.0591(5)	-0.0366(4)	6.1(2)
C61	0.2940(6)	-0.0675(6)	0.4310(4)	6.7(2)
C62	0.4025(7)	-0.1377(8)	0.3979(5)	8.3(3)
C63	0.3799(8)	-0.2514(7)	0.3872(5)	8.0(3)
C64	0.2555(7)	-0.2960(6)	0.4091(4)	7.1(2)
C65	0.1545(6)	-0.2204(5)	0.4422(4)	5.4(2)
H1	0.5483(5)	-0.0097(4)	-0.2266(3)	7.8(3)*
H2	-0.0591(5)	0.0036(4)	0.2768(3)	7.8(3)*
H11	0.2645(6)	-0.2275(5)	-0.1049(3)	7.8(3)*
H12	0.1130(6)	-0.3837(5)	-0.2074(4)	7.8(3)*
H14	0.2786(7)	-0.2922(6)	-0.4184(4)	7.8(3)*
H15	0.4351(6)	-0.1355(5)	-0.3178(3)	7.8(3)*
H161	0.1039(8)	-0.4399(6)	-0.4494(5)	15.9(9)*
H162	-0.0221(8)	-0.4439(6)	-0.3717(5)	15.9(9)*
H163	0.1219(8)	-0.5273(6)	-0.3834(5)	15.9(9)*
H21	0.7753(5)	0.0531(4)	-0.2276(3)	7.8(3)*
H22	0.9257(5)	0.2087(5)	-0.2529(3)	7.8(3)*
H24	0.7961(5)	0.4445(4)	-0.0176(3)	7.8(3)*
H25	0.6431(5)	0.2903(4)	0.0082(3)	7.8(3)*
H261	1.0255(7)	0.4124(5)	-0.2123(4)	15.9(9)*
H262	1.0348(7)	0.4593(5)	-0.0972(4)	15.9(9)*
H263	0.9055(7)	0.5060(5)	-0.1535(4)	15.9(9)*
H31	0.2518(7)	0.2125(5)	0.4960(4)	7.8(3)*
H32	0.4077(7)	0.3604(6)	0.4644(5)	7.8(3)*
H34	0.1928(8)	0.2863(6)	0.2206(5)	7.8(3)*
H35	0.0307(7)	0.1411(5)	0.2519(4)	7.8(3)*
H361	0.4498(8)	0.4830(6)	0.3802(6)	15.9(9)*
H362	0.3552(8)	0.4654(6)	0.2816(6)	15.9(9)*
H363	0.5031(8)	0.3889(6)	0.2812(6)	15.9(9)*
H41	-0.2765(5)	-0.0681(5)	0.2363(3)	7.8(3)*
H42	-0.4207(6)	-0.2314(5)	0.1344(3)	7.8(3)*
H44	-0.3068(5)	-0.4443(5)	0.2819(3)	7.8(3)*
H45	-0.1558(5)	-0.2816(5)	0.3798(3)	7.8(3)*
H461	-0.4467(7)	-0.4578(6)	0.0688(4)	15.9(9)*
H462	-0.5696(7)	-0.4441(6)	0.1508(4)	15.9(9)*
H463	-0.4308(7)	-0.5313(6)	0.1450(4)	15.9(9)*
H51	0.4375(6)	0.2559(5)	0.0822(4)	7.8(3)*
H52	0.2507(8)	0.3783(6)	0.0812(5)	7.8(3)*
H53	0.0229(8)	0.2927(7)	0.0056(5)	7.8(3)*
H54	-0.0088(7)	0.0849(8)	-0.0729(5)	7.8(3)*
H55	0.1861(5)	-0.0319(5)	-0.0712(4)	7.8(3)*
H61	0.3104(6)	0.0226(6)	0.4381(4)	7.8(3)*
H62	0.5012(7)	-0.1020(8)	0.3816(5)	7.8(3)*
H63	0.4609(8)	-0.3072(7)	0.3610(5)	7.8(3)*
H64	0.2365(7)	-0.3862(6)	0.4011(4)	7.8(3)*
H65	0.0560(6)	-0.2551(5)	0.4596(4)	7.8(3)*

[a] e.s.d.s are given in parentheses. [b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for VCp(form)$_2$ (2)[a]

Atom	*x*	*y*	*z*	*B* (Å^2)[b]
V	0.41779(8)	0.72495(7)	0.1904(1)	3.46(3)
N1	0.4498(4)	0.8666(3)	0.1994(6)	3.6(1)
N2	0.2865(4)	0.7806(3)	0.1792(7)	3.6(1)
N3	0.5413(4)	0.7578(3)	0.4327(7)	4.0(2)
N4	0.3800(4)	0.6611(3)	0.3845(7)	3.9(2)
C1	0.3484(5)	0.8633(4)	0.1907(8)	3.9(2)
C2	0.4819(5)	0.6959(4)	0.4872(8)	3.8(2)
C3	0.5171(7)	0.6830(6)	0.002(1)	6.2(3)
C4	0.4268(7)	0.6961(6)	−0.100(1)	5.8(3)
C5	0.3351(7)	0.6302(6)	−0.101(1)	6.2(3)
C6	0.367(1)	0.5752(5)	0.000(1)	7.6(4)
C7	0.484(1)	0.6091(7)	0.070(1)	7.6(4)
C10	0.5290(3)	0.9495(3)	0.2111(5)	3.6(2)
C11	0.5367(3)	1.0359(3)	0.3234(5)	4.0(2)
C12	0.6215(3)	1.1148(3)	0.3431(5)	4.3(2)
C13	0.6985(3)	1.1073(3)	0.2505(5)	4.1(2)
C14	0.6908(3)	1.0209(3)	0.1382(5)	4.3(2)
C15	0.6060(3)	0.9420(3)	0.1186(5)	4.1(2)
C16	0.7933(6)	1.1920(5)	0.280(1)	5.9(2)
C20	0.1735(3)	0.7623(2)	0.1641(6)	3.7(2)
C21	0.1312(3)	0.8300(2)	0.2448(6)	5.2(2)
C22	0.0190(3)	0.8091(2)	0.2239(6)	6.5(3)
C23	−0.0510(3)	0.7204(2)	0.1222(6)	5.6(3)
C24	−0.0087(3)	0.6526(2)	0.0415(6)	6.1(3)
C25	0.1036(3)	0.6736(2)	0.0624(6)	5.3(2)
C26	−0.1750(6)	0.6964(8)	0.095(1)	8.3(4)
C30	0.6530(3)	0.8072(3)	0.5283(5)	3.9(2)
C31	0.7156(3)	0.8514(3)	0.4358(5)	5.7(2)
C32	0.8271(3)	0.8974(3)	0.5169(5)	5.7(3)
C33	0.8761(3)	0.8992(3)	0.6905(5)	5.2(2)
C34	0.8135(3)	0.8550(3)	0.7831(5)	7.7(3)
C35	0.7020(3)	0.8090(3)	0.7019(5)	6.4(3)
C36	1.0000(6)	0.9424(6)	0.773(1)	7.3(3)
C40	0.3082(3)	0.5821(3)	0.4044(6)	4.0(2)
C41	0.1991(3)	0.5792(3)	0.3843(6)	4.7(2)
C42	0.1257(3)	0.5030(3)	0.4023(6)	5.2(2)
C43	0.1615(3)	0.4297(3)	0.4404(6)	5.7(2)
C44	0.2707(3)	0.4325(3)	0.4605(6)	6.6(3)
C45	0.3440(3)	0.5087(3)	0.4425(6)	5.7(3)
C46	0.0797(8)	0.3456(6)	0.455(1)	8.4(3)
H1	0.3184(5)	0.9228(4)	0.1928(8)	8.0(4)*
H2	0.5131(5)	0.6756(4)	0.6033(8)	8.0(4)*
H3	0.6009(7)	0.7236(6)	0.027(1)	8.0(4)*
H4	0.4274(7)	0.7487(6)	−0.167(1)	8.0(4)*
H5	0.2515(7)	0.6230(6)	−0.169(1)	8.0(4)*
H6	0.314(1)	0.5169(5)	0.022(1)	8.0(4)*
H7	0.536(1)	0.5831(7)	0.158(1)	8.0(4)*
H11	0.4771(3)	1.0417(3)	0.3950(5)	8.0(4)*
H12	0.6275(3)	1.1817(3)	0.4300(5)	8.0(4)*
H14	0.7504(3)	1.0151(3)	0.0666(5)	8.0(4)*
H15	0.6000(3)	0.8751(3)	0.0317(5)	8.0(4)*
H21	0.1853(3)	0.8987(2)	0.3235(6)	8.0(4)*
H22	−0.0138(3)	0.8615(2)	0.2864(6)	8.0(4)*
H24	−0.0628(3)	0.5839(2)	−0.0372(6)	8.0(4)*
H25	0.1363(3)	0.6211(2)	−0.0001(6)	8.0(4)*
H31	0.6777(3)	0.8500(3)	0.3013(5)	8.0(4)*
H32	0.8756(3)	0.9316(3)	0.4453(5)	8.0(4)*
H34	0.8514(3)	0.8563(3)	0.9175(5)	8.0(4)*

(continued)

TABLE III. *(continued)*

Atom	x	y	z	B (Å^2)^b
H35	0.6535(3)	0.7748(3)	0.7735(5)	8.0(4)*
H41	0.1714(3)	0.6359(3)	0.3547(6)	8.0(4)*
H42	0.0412(3)	0.5008(3)	0.3867(6)	8.0(4)*
H44	0.2984(3)	0.3758(3)	0.4902(6)	8.0(4)*
H45	0.4285(3)	0.5110(3)	0.4581(6)	8.0(4)*
H161	0.8356(6)	1.1830(5)	0.179(1)	12.0(8)*
H162	0.8490(6)	1.2029(5)	0.409(1)	12.0(8)*
H163	0.7640(6)	1.2519(5)	0.282(1)	12.0(8)*
H261	−0.1994(6)	0.7530(8)	0.165(1)	12.0(8)*
H262	−0.1954(6)	0.6379(8)	0.146(1)	12.0(8)*
H263	−0.2176(6)	0.6756(8)	−0.046(1)	12.0(8)*
H361	1.0279(6)	0.9190(6)	0.886(1)	12.0(8)*
H362	1.0201(6)	1.0176(6)	0.815(1)	12.0(8)*
H363	1.0397(6)	0.9212(6)	0.674(1)	12.0(8)*
H461	0.1294(8)	0.3024(6)	0.491(1)	12.0(8)*
H462	0.0172(8)	0.3074(6)	0.330(1)	12.0(8)*
H463	0.0414(8)	0.3645(6)	0.558(1)	12.0(8)*

[a] e.s.d.s are given in parentheses. [b] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE IV. Selected Bond Distances (Å) and Angles (°) for $V(form)_2py_2$ (1)[a]

Atom 1	Atom 2	Distance
V1	N1	2.175(3)
V1	N2	2.200(4)
V1	N5	2.182(4)
V2	N3	2.189(5)
V2	N4	2.194(4)
V2	N6	2.184(4)
N1	C1	1.328(7)
N2	C1	1.323(5)
N3	C2	1.328(6)
N4	C2	1.322(7)

Atom 1	Atom 2	Atom 3	Angle
N1	V1	N1′	180.00(0)
N1	V1	N2	61.5(1)
N1	V1	N2′	118.5(1)
N1	V1	N5	89.5(1)
N1	V1	N5′	90.5(1)
N2	V1	N2′	180.00(0)
N2	V1	N5	90.0(2)
N2	V1	N5′	90.0(2)
N5	V1	N5′	180.00(0)
N3	V2	N3′	180.00(0)
N3	V2	N4	61.7(2)
N3	V2	N4′	118.3(2)
N3	V2	N6	89.7(2)
N3	V2	N6′	90.3(2)
N4	V2	N4′	180.00(0)
N4	V2	N6	89.9(1)
N4	V2	N6′	90.1(1)
N6	V2	N6′	180.00(0)
V1	N1	C1	92.1(2)
V1	N2	C1	91.2(3)
V2	N3	C2	91.2(3)
V2	N4	C2	91.2(3)
N1	C1	N2	115.2(4)
N3	C2	N4	115.9(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

We warmed a toluene solution of compound **1** to the reflux temperature, but this did not affect the nature of the product. We are therefore inclined to believe that the failure to obtain $V_2(form)_4$ by eqn. (2) is due to thermodynamic and not kinetic factors. This would imply that, roughly speaking, four V–py bonds are energetically more favorable than a V–V triple bond, even though one has to take into account the difference in energy caused by the rearrangement of the formamidinato ligands.

VCp_2 seemed to be an excellent alternative starting material. It was hoped that the interaction with the 'acid' Hform would displace the cyclopentadienyl groups according to eqn. (3).

$$VCp_2 + 2Hform \longrightarrow \tfrac{1}{2}V_2(form)_4 + 2CpH \qquad (3)$$

The strategy illustrated in eqn. (3) is successful in the synthesis of Cr_2^{4+} dimers from $CrCp_2$ [16]. The

TABLE V. Selected Bond Distnces (Å) and Angles (°) for VCp(form)$_2$ (2)^a

Atom 1	Atom 2	Distance
V	N1	2.110(5)
V	N2	2.094(5)
V	N3	2.107(5)
V	N4	2.122(6)
V	C3	2.290(10)
V	C4	2.312(8)
V	C5	2.314(7)
V	C6	2.308(8)
V	C7	2.279(12)
N1	C1	1.307(9)
N1	C10	1.417(6)
N2	C1	1.313(8)
N2	C20	1.416(7)
N3	C2	1.310(9)
N3	C30	1.424(5)
N4	C2	1.313(7)
N4	C40	1.424(7)

Atom 1	Atom 2	Atom 3	Angle
N1	V	N2	62.8(2)
N1	V	N3	92.0(2)
N1	V	N4	129.0(2)
N2	V	N3	120.7(2)
N2	V	N4	92.2(2)
N3	V	N4	62.0(2)
V	N1	C1	91.6(4)
V	N1	C10	146.5(4)
C1	N1	C10	121.9(5)
V	N2	C1	92.1(4)
V	N2	C20	145.9(4)
C1	N2	C20	122.0(5)
V	N3	C2	92.6(3)
V	N3	C30	144.8(4)
C2	N3	C30	121.9(5)
V	N4	C2	91.9(4)
V	N4	C40	142.4(3)
C2	N4	C40	120.2(6)
N1	C1	N2	113.5(6)
N3	C2	N4	112.3(6)

^{a}Numbers in parentheses are estimated standard deviations in the least significant digits.

reaction of VCp$_2$ with carboxylic acids has been studied [17], and dinuclear compounds of V(III) were obtained according to eqn. (4).

$$2VCp_2 + 4RCOOH \longrightarrow CpV(\mu\text{-}O_2CR)_4VCp + 2CpH + H_2 \qquad (4)$$

It was argued [17] that more steric bulk may help the residual cyclopentadienyl group to leave the vanadium center. Our formamidinato ligand, with its bulky *p*-tolyl groups attached to the nitrogen donor atoms, seemed to be well suited to test this hypothesis.

Interaction between VCp$_2$ and Hform does not afford the expected vanadium(II) dimer according to eqn. (3), nor a dimer of vanadium(III) analogous to the carboxylates of eqn. (4). It affords, instead, the mononuclear V(III) compound VCp(form)$_2$ (2) in good yields, see eqn. (5).

$$VCp_2 + 2Hform \xrightarrow[\text{reflux}]{\text{toluene}} VCp(form)_2 + CpH + \tfrac{1}{2}H_2 \qquad (5)$$

This reactivity is akin to that observed with carboxylic acids, but the nature of the product is obviously determined by the steric bulk of the ligand. The bulkiness does not therefore favor elimination of the residual cyclopentadienyl group, but it merely favors a mononuclear structure with respect to the dinuclear, bridged one.

(b) Molecular Structures

Compound **1** crystallizes in the triclinic $P\bar{1}$ space group, with two independent molecules sitting on two different inversion centers (at $\frac{1}{2}$, 0, 0 and 0, 0, $\frac{1}{2}$). The two molecules have the same geometry and structural parameters within the experimental errors. One of them is illustrated in Fig. 1. The arrangement of the ligands around the vanadium atom is that of a distorted octahedron. The main distortion is caused by the small bite angle of the chelating formamidinato ligand (average angle, 61.6(2)°). The axial pyridine ligands are practically perpendicular to the respective equatorial planes. The V–N bond lengths involving the pyridine and the formamidinato ligands are not significantly different from each other (average 2.187 Å). The V–N distance in the parent VCl$_2$py$_4$ compound is 2.189(2) Å [18].

Compound 2 crystallizes in the same space group as compound 1, with the molecule on a general posi-

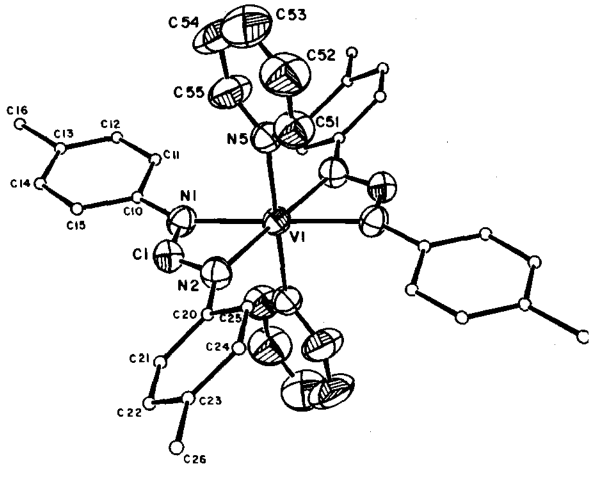

Fig. 1. An ORTEP view of one of the independent molecules of compound 1. For the sake of clarity, hydrogen atoms were omitted and the *p*-tolyl carbon atoms were drawn with arbitrary radii.

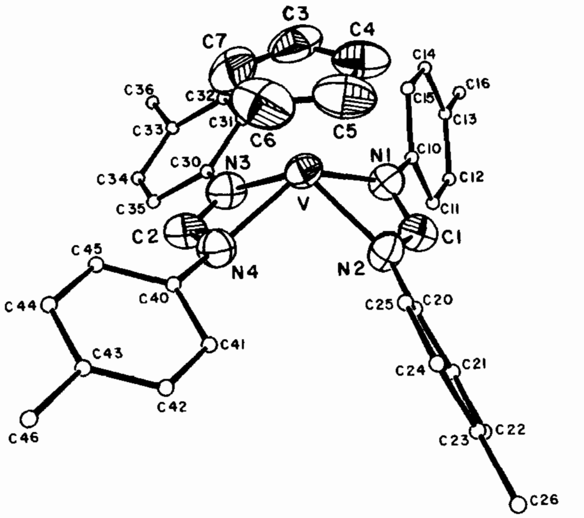

Fig. 2. An ORTEP view of compound **2**. For the sake of clarity, hydrogen atoms were omitted and the *p*-tolyl carbon atoms were drawn with arbitrary radii.

tion. The geometry, see Fig. 2, is that of a four-legged piano-stool, similar to those of cyclopentadienyl derivatives of d^4 ions (e.g. V(I), Nb(I), Ta(I), Cr(II), Mo(II), W(II), and Re(III)) the difference being, of course, that the latter are all 18-electron compounds, while compound **2** has 16 electrons in the valence shell for the d^2 V(III) ion. The bite angle of the formamidinato ligand (average 62.4(2)°) is similar to that found in compound **1**. The other angles between *cis* ligands (N1–V–N3 and N2–V–N4) average 92.1(2)°. The angles between *trans* ligands (N1–V–N4 and N2–V–N3) are substantially different from each other (129.0(2)° and 120.7(2)°, respectively) and can be compared, for example, with 122.4° in $VCp(CO)_4$*.

The vanadium–nitrogen bond lengths average 2.108 Å and are in the same range found for other V(III)–N single bonds [20]. This is *ca.* 0.08 Å shorter than the corresponding average value found for compound **1**. Such a difference can be attributed to a contraction of the metal ionic radius because of the increased oxidation state. The V–C(Cp) distances range between 2.28 and 2.31 Å, with a V–ring (center) distance of 1.973(1) Å. This compares quite well with the values found for $Cp_2V_2(\mu\text{-}O_2CPh)_4$ [17], while in $CpV(CO)_4$ the same distance is 1.93(0.7) Å [19]. This is opposite to the expected contraction because of the increase in oxidation state from I to III, and can be explained by a reduced π back-donation to the Cp ligand in the more oxidized species.

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*Value calculated from the fractional atomic coordinates given in ref. 19.

Supplementary Material

Full tables of bond distances and angles, and anisotropic displacement parameters for compound **1** (6 pages) and compound **2** (5 pages); a listing of observed and calculated structure factors for compound **1** (16 pages) and compound **2** (12 pages) may be obtained from author F.A.C.

Acknowledgements

We thank the National Science Foundation for financial support and Dr C. Day of Crystalytics, Lincoln, Nebraska, for collection of intensity data on compound **1**.

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