Chemistry of the Vanadium–Carbon σ Bond. 3. Reactivity of a Homoleptic Tris(η^2-iminoacyl) Complex of Vanadium(III)

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Received October 8, 1992

The chemistry of the homoleptic tris(iminoacyl)vanadium(III) compound [V{(η^2-C(Mes)=NBu^t}$_3$] (1) has been explored in the following ways. (i) Reactions with CO_2 analogues: the reaction with CO_2 led to a double insertion of CO_2 into the V—C bond with the formation of [V{η^2-C(Mes)=NBu^t}{Bu^{t}N=C(Mes)—C(=O)—O}$_2$] (2), containing an α-imino acid anion as ligand. An α-imino amide complex was obtained from the reaction of 1 with CyNCO (Cy ≡ C_6H_{11}), leading to [V{η^2-C(Mes)=NBu^t}$_2${Bu^{t}N=C(Mes)—C(=O)—NC$_6$H$_{11}$}] (3). (ii) Reactions with carbon monoxide and isocyanides: the reaction with CO leads to the isolation of the unusual monocarbonyl adduct [V{η^2-C(Mes)=NBu^t}$_3$(CO)] (4), which is diamagnetic and has a CO band at 1867 cm^{-1}. The reaction with Ph_2CN_2 was facilitated by the electron richness of 1 and gave the diamagnetic adduct [V{η^2-C(Mes)=NBu^t}$_3$(η^2-Ph$_2$C=N=N)] (5). The reaction of 1 with Bu^{t}NC is more complex and led to a V(IV) metallacycle, [V{η^2-C(Mes)=NBu^t}$_2$-{Bu^{t}N=C(Mes)—C(CN)—NBu^t}] (6), via a one-electron oxidation of vanadium. (iii) Reaction with hydrogen: complex 1 reacts with H_2 at −30 °C in the absence of catalyst to give, by hydrogenation of iminoacyl groups, [V{η^2-C(Mes)=NBu^t}$_2$(Bu^{t}N-CH$_2$Ph)] (9) and [V{η^2-C-(Mes)=NBu^t}(Bu^{t}N—CH$_2$Ph)$_2$] (10). Complex 10 decomposes at room temperature, leading to a dimeric diamagnetic V(IV) complex containing a single metal—metal bond, 17. (iv) Oxidation of 1 by C–Cl, P–Cl, and S–S bonds: reaction of 1 with PhCH$_2$Cl, PhCOCl, and Ph$_2$PCl led to the formation of the corresponding V(IV) derivative [V{η^2-C(Mes)=NBu^t}$_3$(Cl)] (18), while the reaction with PhSSPh gave [V{η^2-C(Mes)=NBu^t}$_3$(SPh)] (19). Crystallographic details: 2 is triclinic, space group $P\bar{1}$, with a = 11.253(1) Å, b = 22.818(2) Å, c = 8.538(1) Å, α = 93.85(1)°, β = 94.58(1)°, γ = 100.95(1)°, Z = 2, and R = 0.056; 3 is monoclinic, space group $P2_1/n$, with a = 24.420(2) Å, b = 15.902(1) Å, c = 12.089(1) Å, $\alpha = \gamma$ = 90°, β = 104.00(1)°, Z = 4, and R = 0.056; 6 is monoclinic, space group $P2_1/n$, with a = 20.440(2) Å, b = 21.143(2) Å, c = 11.647(1) Å, $\alpha = \gamma$ = 90°, β = 97.15(1)°, Z = 4, and R = 0.060; 17 is monoclinic, space group $P2_1/c$, with a = 10.049(1) Å, b = 20.675(2) Å, c = 18.107(2) Å, $\alpha = \gamma$ = 90°, β = 102.30(1)°, Z = 4, and R = 0.043; 18 is monoclinic, space group $P2_1/n$, with a = 14.656(1) Å, b = 24.710(1) Å, c = 11.112(1) Å, $\alpha = \gamma$ = 90°, β = 90.39(1)°, Z = 4, and R = 0.051; 19 is orthorhombic, space group $Pbca$, with a = 36.456(3) Å, b = 12.411(1) Å, c = 19.943(1) Å, $\alpha = \beta = \gamma$ = 90°, Z = 4, and R = 0.058.

Introduction

Metal acyls and metal iminoacyls are fundamental organometallic functionalities.[1,2] While much attention has been devoted to their formation by the migratory insertion of carbon monoxide and isocyanides into the metal–carbon bond,[1–3] their chemistry has been little explored, except for early-transition-metal η^2-acyl complexes. They undergo reductive-elimination reactions,[4] show generally carbenoid behavior,[5,6] and are transformable to metal enolates or metal ketenes.[7] The apparently low reactivity contrasts with the usual assumption that metal acyls or metal iminoacyls are intermediates in metal-mediated catalytic processes. There are therefore some questions to be addressed for understanding the intermediacy of such species in catalytic processes. Among

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0276-7333/93/2312-1811$04.00/0

Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 2, 3, 6, 17, 18, and 19

	2	3	6	17	18	19
cryst habit	prisms	prisms	prisms	unshaped fragments	unshaped fragments	prisms
formula	$C_{44}H_{60}O_4N_3V$	$C_{49}H_{71}ON_4V$	$C_{48}H_{69}N_5V\cdot 0.5C_6H_{14}$	$C_{36}H_{60}N_4V_2$	$C_{42}H_{60}ClN_3V$	$C_{48}H_{65}SN_3V$
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthothrombic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$	*Pbca*
cell params at 295 K[a]						
a, Å	11.253(1)	24.420(2)	20.440(2)	10.049(1)	14.656(1)	36.456(3)
b, Å	22.818(2)	15.902(1)	21.143(2)	20.675(2)	24.710(2)	12.411(1)
c, Å	8.538(1)	12.089(1)	11.647(1)	18.107(2)	11.112(1)	19.943(1)
α, deg	93.85(1)	90	90	90	90	90
β, deg	94.58(1)	104.00(1)	97.15(1)	102.30(1)	90.39(1)	90
γ, deg	100.95(1)	90	90	90	90	90
V, Å^3	2137.9(4)	4555.0(6)	4994.3(8)	3675.6(7)	4024.1(6)	9023.3(11)
Z	2	4	4	4	4	8
D_{calcd}, g cm^{-3}	1.159	1.142	1.077	1.176	1.144	1.129
mol wt	745.9	783.1	810.1	650.8	693.4	767.1
cryst dimens, mm	0.23 × 0.31 × 0.58	0.28 × 0.30 × 0.60	0.18 × 0.28 × 0.55	0.31 × 0.40 × 0.45	0.48 × 0.50 × 0.61	0.32 × 0.48 × 0.60
linear abs coeff, cm^{-1}	22.68	2.46	19.22	5.19	3.34	25.12
transmissn factor range	0.550–1.000	0.951–1.000	0.452–1.000	0.713–1.000	0.940–1.000	0.579–1.000
diffractometer	Siemens AED	Siemens AED	Siemens AED	Siemens AED	Philips PW1100	Siemans AED
diffraction geometry	equatorial	equatorial	equatorial	equatorial	equatorial	equatorial
radiation	*b*	*c*	*b*	*c*	*d*	*b*
2θ range, deg	6–120	6–46	6–120	6–46	6–46	6–140
scan type	θ–2θ	θ–2θ	θ–2θ	θ–2θ	ω–2θ	θ–2θ
scan speed, deg min^{-1}	3–12	3–12	3–12	3–12	3–12	4–12
scan width, deg	1.20 + 0.015 tan θ	1.20 + 0.35 tan θ	1.20 + 0.015 tan θ	1.20 + 0.35 tan θ	1.20 + 0.35 tan θ	1.20 + 0.015 tan θ
rflns measd	$\pm h,\pm k,l$	$\pm h,k,l$	$\pm h,k,l$	$\pm h,k,l$	$\pm h,k,l$	*hkl*
unique total data	6373	6351	7441	5128	5615	8574
criterion for observn	2	2	2	2	2	2
unique obsd data	4002	2599	4077	2870	3111	5444
no. of variables	433	460	463	355	388	430
overdetermn ratio	9.2	5.7	8.8	8.1	8.0	12.7
max Δ/σ on last cycle	0.03	0.001	0.1	0.1	0.1	0.1
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.056	0.056	0.060	0.043	0.051	0.058
$R_w = \sum w^{1/2}\lvert\Delta F\rvert/\sum w^{1/2}\lvert F_o\rvert$	0.063	0.057	0.065	0.044	0.056	0.065
GOF = $[\sum w\lvert\Delta F\rvert^2/(N_o - N_v)]^{1/2}$	0.36	0.49	0.82	0.53	0.58	1.48

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centered reflections from diverse regions of reciprocal space. [b] Ni-filtered cu Kα (λ = 1.541 78 Å). [c] Nb-filtered Mo Kα (λ = 0.710 688 Å). [d] Graphite-monochromated Mo Kα (λ = 0.710 688 Å).

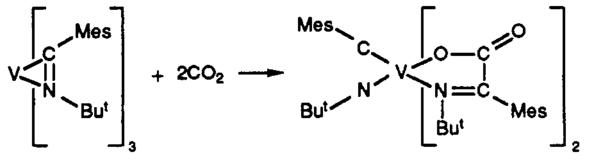
them are the following: can the metal acyl (or iminoacyl) insert other functionalities,[8] and can it be reduced under mild conditions by molecular hydrogen?[9]

This paper deals with the chemistry of the rare homoleptic complex [V{η^2-C(Mes)=NBu^t}$_3$] (Mes ≡ 2,4,6-$Me_3C_6H_2$; 1). Three aspects of its chemistry have been explored: (i) insertion into the V—C bond leading to a doubly functionalized organic fragment, (ii) reduction of the η^2-iminoacyl functionality by molecular hydrogen at −30 °C without any catalyst, and (iii) the redox behavior of the metal center. Some of the present results have been briefly communicated.[10]

Results and Discussion

The η^2-iminoacyl functionality in 1 has a remarkably reactive V–C bond in insertion reactions and with molecules containing even weakly acidic protons.

(1) Reaction of 1 with CO_2 and Isocyanates. The reaction of 1 with carbon dioxide (eq 1) occurs at room temperature in THF with the insertion of two molecules of CO_2 into two η^2-iminoacyl groups to give 2.



1 2 (1)

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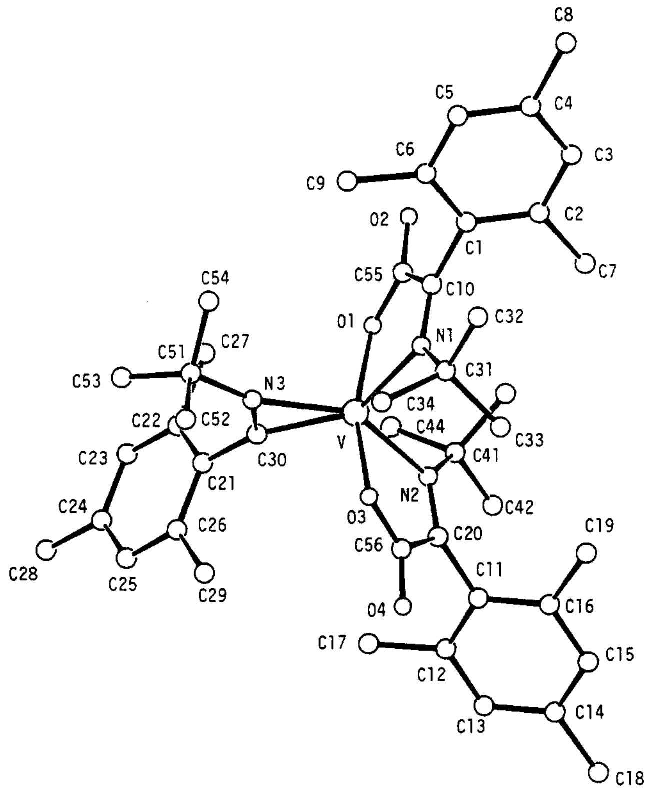

Figure 1. SCHAKAL[29] view of complex **2**.

Reaction 1 is irreversible, and **2** has been isolated in crystalline form. The organic moiety formed by the insertion of CO_2 corresponds to the metal-controlled synthesis of an α-imino acid. This is a rare case in which we observe migatory aptitude of an iminoacyl.[1,6] If the migratory ability is due to the carbanionic properties of the acyl carbon, it seems plausible that migration occurs when **1** is reacted with a strong electrophile such as CO_2. The insertion of CO_2 into a metal–α-functionalized carbon bond is rare,[11d] since normally CO_2 inserts into metal–alkyl or metal–aryl bonds.[11] The structure of **2** is reported in Figure 1, with selected bond distances and angles listed in Table VIII. Vanadium binds a η^2-iminoacyl group with structural parameters very close to those found for **1**. Each of the two α-imino carboxylates forms a five-membered N,O metallacycle with an envelope conformation; vanadium is displaced by 0.142(1) and 0.183(1) Å from the mean plane through the N1,O1,C10,C55 and N2,O3,C20,-C56 groups of atoms, respectively. The values listed in Table VIII support the bonding scheme shown for complex **2**. The substituents at the N1···O1 chelation ring lie nearly in the plane defined by the N1,C10,C55,O1 atoms, O2, C1, and C3 being displaced by 0.024(5), −0.009(2), and −0.023-(5) Å, respectively. The other ring shows more distortion, O4, C11, and C41 being displaced by −0.100(4), 0.074(3), and −0.066(5) Å, respectively, from the plane defined by N2,C10,C56,O3. The dihedral angle between the mean planes running through the chelation rings is 67.9(1)°. Such planes are nearly perpendicular to the plane through the η^2-bonded atoms (V, N3, C30), the dihedral angles they form being 84.3(1) and 84.6(2)° for N···O1 and N2···O3, respectively.

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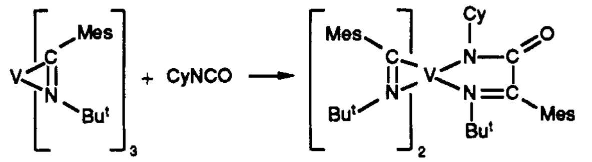
Carbon dioxide can be replaced by cyclohexyl isocyanate in reaction 1. The major difference is that single rather than double insertion is observed, which may be due to steric reasons:



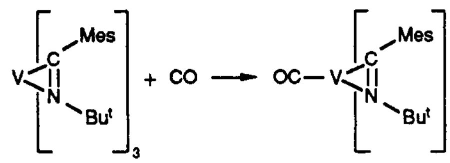
(2)

1 3

Cy = C_6H_{11}

That an N,N rather than a N,O metallacycle is observed is probably due to steric effects rather than to a preference for N vs O by the vanadium(III). The metal in **3** is bonded to two η^2-iminoacyls and to the deprotonated form of an α-imino amide, as shown in Figure 2. The two η^2-iminoacyl fragments are almost unaffected by the new environment in comparison with complex **1**. The structural parameters listed in Table IX support the bonding scheme shown for the metallacycle, though some delocalization may be envisaged, as supported by the planarity of the ring. Vanadium is displaced by 0.057(1) Å from the mean plane through the N1,C10,C55,N4 group of atoms, and the O1 oxygen atom lies in this plane. The substituents at N1···N4 do not lie exactly in the plane defined by the N1,C10,-C55,N4 atoms, O1, C1, and C31 being displaced by −0.057-(6), 0.192(6), and 0.080(7) Å, respectively. The dihedral angle between the V,N2,C20 and V,N3,C30 is 52.9(3)°. These planes form angles of 66.3(3) and 65.2(4)°, respectively, with the plane through the chelation ring. The stability of metallacycles in complexes **2** and **3** may be the driving force for these insertion reactions.

(2) Reaction of 1 with CO and Bu^{t}NC. The electron richness of complex **1** is highlighted by the strong irreversible coordination of carbon monoxide:



(3)

1 4

Complex **4** was isolated as a red crystalline solid. The rather low C=O stretching vibration at 1867 cm^{-1} (Nujol) is in agreement with a very high electron density at vanadium(III). Thus, complex **1** is unique in that, although it does not contain cyclopentadienyl ligands, it is able to bind carbon monoxide. The 16-valence-electron (16-ve) configuration, unlike in bis(cyclopentadienyl) series,[12] is low-spin in complex **4**. The ^{1}H NMR spectrum down to 0 °C does not show anything unusual (see the Experimental Section), while at −40 °C there is no longer free rotation of the Mes groups, as evidenced by the inequivalency of the two ortho methyls and the two meta protons of all mesityls at this temperature.

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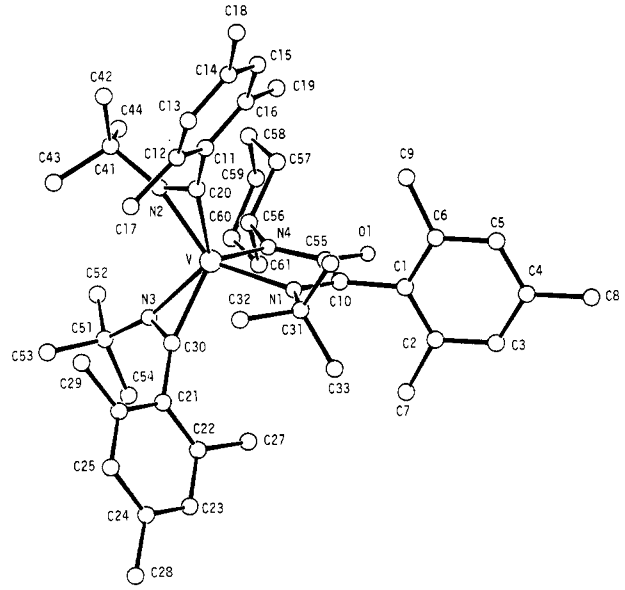
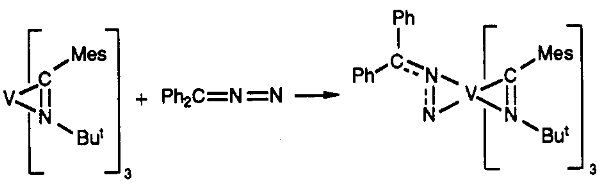


Figure 2. SCHAKAL[29] view of complex 3.

The coordination of CO and the strong back-donation to it show that vanadium(III) not only binds π-acids but also should be prone to oxidative-addition reactions. Complex 1 was thus reacted with diphenyldiazomethane, Ph_2CN_2. Similar reactions have been reported with vanadocene and titanocene derivatives.[13] The reaction proceeds smoothly and forms a 1:1 adduct:

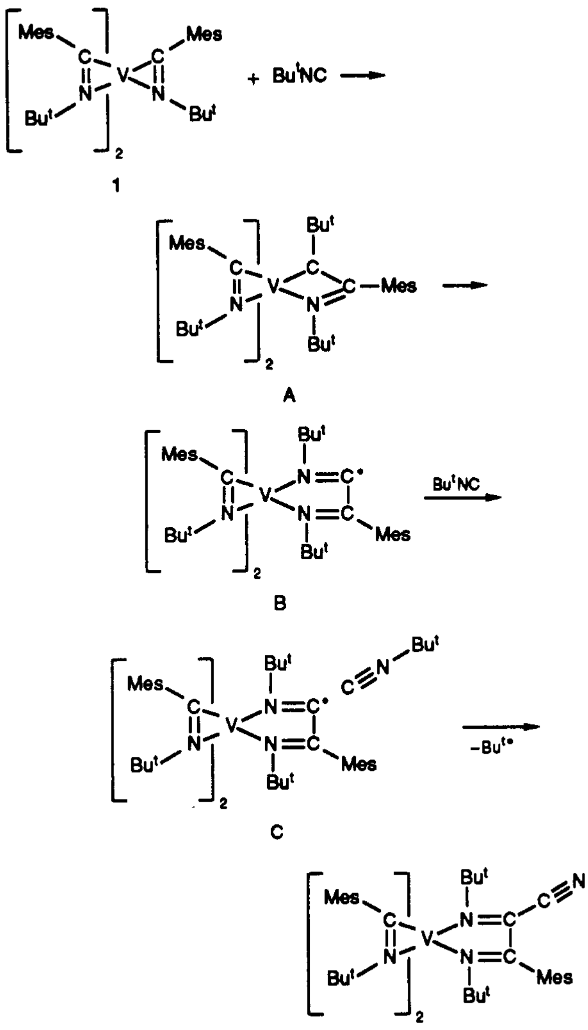


(4)

1 5

Complex **5** is diamagnetic. The metal should be formally considered as vanadium(V) or 16-e$^-$ low-spin vanadium(III). The cumulene structure of diphenyldiazomethane disappears upon coordination, as shown by the highest band in the IR spectrum at 1675 cm^{-1}. We propose the side-on bonding mode we found in the case of vanadocene,[13] rather than the end-on bonding mode observed in the case of decamethylvanadocene.[14] This corresponds to a π-acidic behavior of diphenyldiazomethane and is consistent with the ^{1}H and ^{13}C NMR spectra of **5**. The three η^2-iminoacyls are equivalent at +40 °C in the ^{1}H and ^{13}C NMR spectra. The three become inequivalent at −40 °C in toluene, with two of them quite close, so that the inequivalence is really between one vs the other two. The structures of **4** and **5** should be very similar. Considering the imino group as a monodentate ligand, both complexes have a pseudo-tetrahedral geometry. Because of the cylindrical symmetry of M—CO, the three mesityls should be equivalent in **4**, while they are not in **5**, because of the noncylindrical geometry of the diphenyldiazomethane residue.

Complex **1**, which is an electron-rich vanadium(III) d^2 complex, seems to be particularly appropriate for binding a π-acidic functionality, and in that sense it should be described as having a carbene-type reactivity. Reaction of **1** with a large excess of isocyanide led to the unexpected result summarized in reaction 5.



(5)

The isocyanide inserts into one of the M—C bonds, yielding the strained metallacycle A, which rearranges via the homolytic cleavage of a V—C bond to a more stable five-membered metallacycle, B. The free radical B reacts with excess Bu^{t}NC to give **6** and Bu^t radical. Dealkylation by free-radical-type metals of isocyanides has precedents in the literature.[15] The nature of **6** was proved by an X-ray analysis. The structure is shown in Figure 3 with the essential structural parameters in Table X. Complex **4** contains an unpaired electron (μ = 1.72 μ_B at 288 K), and it has a very strong band in the IR spectrum at 2176 cm^{-1} (C≡N) and bands at 1628 and 1605 cm^{-1} (C═N and C═C, respectively).

The bond connectivity shown for the metallacycle is only partially supported by the structural data, since (Table X) C10–N1, C10–C55, and C55–N4 have almost the same character of double bond: 1.352(7), 1.384(9) and 1.376(7) Å, respectively. We have to admit a high degree of electronic delocalization in the metallacycle and to give the two limiting formulas D and E, which correspond to two different formal oxidation states of the metal. D should be preferred on the basis of the magnetic results.

(13) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 1918; **1983**, *105*, 7295.
(14) Floriani, C.; Chiesi-Villa, A.; Guastini, C. Unpublished results.

(15) (a) References to dealkylation of isocyanide ligands are listed in: Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142. Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739.

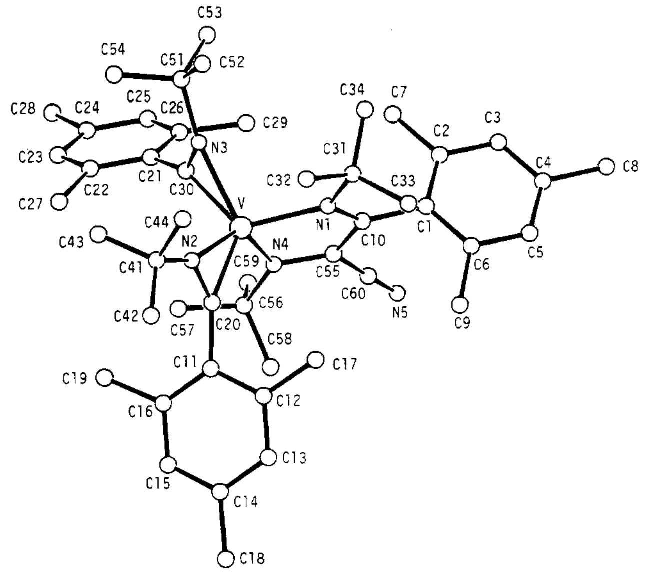
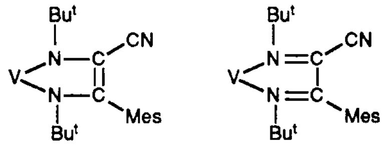


Figure 3. SCHAKAL[29] view of complex **6**.



D E

The five-membered chelation ring has an envelope conformation with vanadium lying at 0.101(1) Å from the plane through N1,C10,C55,N4. The C1 atom line is tilted with respect to this plane by 4.1(3)°, corresponding to out-of-plane displacements of 0.116(7) and 0.199(8) Å for C60 and N5, respectively. The geometry of the two η^2-(N,C)-bonded ligands is very close to that observed in **1**, while their mutual orientation is slightly different as a consequence of different intraligand steric interaction. The dihedral angle between the set of atoms V,N2,C30 and V,N3,C30 is 66.4(3)°. They form dihedral angles of 63.9(2) and 66.3(2)° with the mean plane through the five-membered chelation ring.

(3) Reaction of 1 with H_2. Uncatalyzed reduction of metal acyls or metal iminoacyls with dihydrogen to the corresponding alkoxo and amido species by H_2 does not have precedent.[1] Such a reaction has been invoked as a key step in the chain growth of the Fischer–Tropsch synthesis.[16]

Complex **1** reacts under very mild conditions with dihydrogen at −30 °C. When the temperature was maintained at −30 °C, the isolation of **10** as a crystalline solid was achieved. The proposed Scheme I can be justified by a number of experimental data and considerations.

Complex **1** absorbs ca. 1 mol of H_2 per vanadium. The proposed oxidative addition of H_2 to vanadium(III) is largely supported by the electron richness of the metal, as shown in the reaction with carbon monoxide discussed above. The reductive elimination[7] of a hydride with an η^2-iminoacyl should lead to the imine complex **8**. On the other hand, it has been reported that C—N multiple bonds insert into, for example, the Zr—H bond.[17] Like **1**, complex

Table II. Fractional Atomic Coordinates (×10⁴) for Complex 2

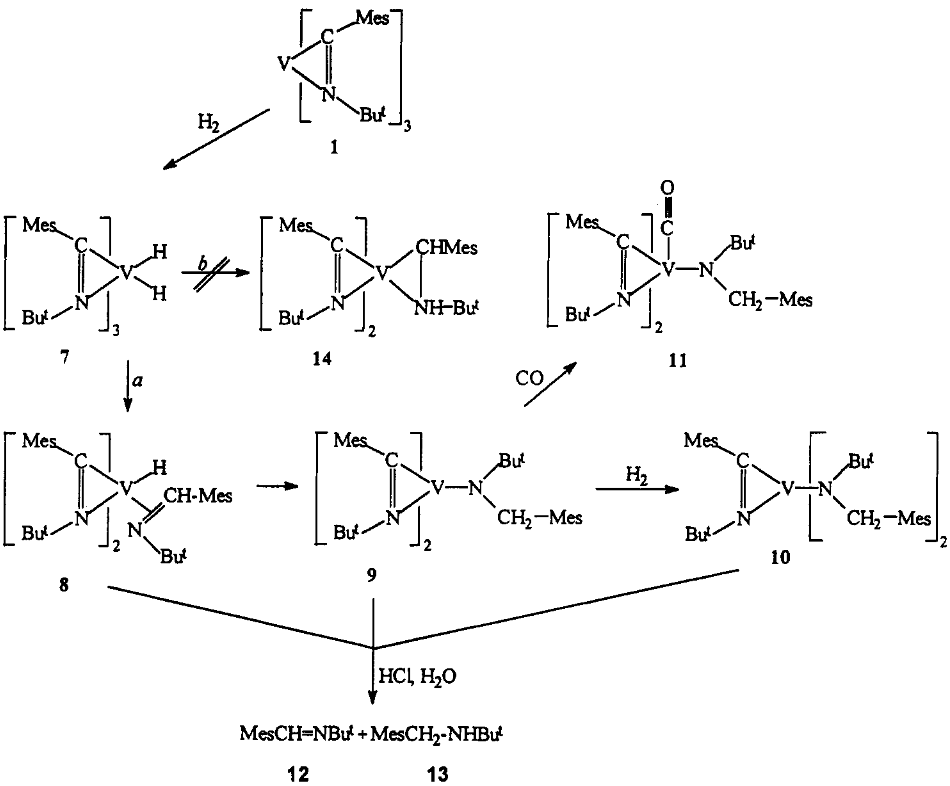
atom	x/a	y/b	z/c	U_{eq},[a] Å²
V	7092.3(6)	2238.8(3)	3025.1(9)	419(3)
O1	7453(3)	1789(1)	4805(3)	492(11)
O2	7782(4)	945(2)	5758(4)	885(18)
O3	7196(3)	2620(1)	1065(3)	489(11)
O4	7991(4)	3400(2)	−180(4)	783(16)
N1	7544(3)	1347(2)	1911(4)	421(13)
N2	8815(3)	2950(2)	3476(4)	450(13)
N3	5292(3)	2135(2)	3094(4)	452(12)
C1	7964(2)	371(1)	2899(4)	443(16)
C2	9150(2)	272(1)	2889(4)	535(18)
C3	9362(2)	−312(1)	2808(4)	624(18)
C4	8389(2)	−796(1)	2738(4)	621(21)
C5	7204(2)	−697(1)	2748(4)	565(18)
C6	6991(2)	−114(1)	2829(4)	480(16)
C7	10227(4)	784(2)	2994(7)	735(23)
C8	8618(6)	−1429(3)	2634(8)	830(26)
C9	5708(4)	−14(2)	2917(7)	679(21)
C10	7720(3)	995(2)	2986(5)	427(15)
C11	9901(2)	3807(1)	2052(4)	529(16)
C12	9728(2)	4386(1)	2456(4)	664(19)
C13	10614(2)	4879(1)	2207(4)	809(24)
C14	11672(2)	4794(1)	1555(4)	847(26)
C15	11845(2)	4216(1)	1151(4)	740(23)
C16	10960(2)	3722(1)	1400(4)	591(17)
C17	8569(6)	4485(2)	3131(9)	904(26)
C18	12670(7)	5334(3)	1363(11)	1269(41)
C19	11150(5)	3106(2)	857(8)	787(25)
C20	8963(4)	3277(2)	2320(5)	447(14)
C21	5255(3)	3102(1)	4696(3)	480(17)
C22	5101(3)	3090(1)	6299(3)	545(17)
C23	4615(3)	3536(1)	7069(3)	705(21)
C24	4284(3)	3994(1)	6236(3)	786(26)
C25	4438(3)	4007(1)	4633(3)	747(22)
C26	4924(3)	3561(1)	3863(3)	599(20)
C27	5459(5)	2599(3)	7229(6)	711(20)
C28	3765(6)	4479(3)	7125(10)	1143(34)
C29	5116(5)	3602(2)	2145(7)	740(23)
C30	5779(4)	2633(2)	3865(5)	445(15)
C31	7580(4)	1205(2)	160(5)	495(16)
C32	7689(5)	564(2)	−400(6)	703(23)
C33	8682(5)	1640(2)	−308(6)	636(20)
C34	6407(4)	1332(2)	−639(6)	598(17)
C41	9609(4)	3060(2)	5036(6)	558(17)
C42	10606(6)	3618(3)	5273(7)	871(26)
C43	10201(5)	2514(3)	5161(7)	751(21)
C44	8739(5)	3092(3)	6306(6)	777(21)
C51	4006(4)	1810(2)	2748(6)	608(19)
C52	3646(6)	1871(4)	1003(9)	1293(42)
C53	3119(5)	2059(3)	3681(9)	990(30)
C54	4006(6)	1171(3)	2994(13)	1387(46)
C55	7648(4)	1248(2)	4669(5)	503(17)
C56	7988(4)	3092(2)	930(5)	480(17)

[a] U_{eq} is in the form $^1/_3\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

9 has an electron-rich metal center and should react with H_2 to give the hydrogenation of a second η^2-iminoacyl. As expected, **9** reacts with CO to form the adduct **11**, which has a CO stretching frequency at 1839 cm^{-1}. Complex **11** is diamagnetic and thermally labile. It is another remarkable example of a monocarbonyl derivative of vanadium(III) without cyclopentadienyls. The hydrolysis of the hydrogenated solution gave a variable ratio of **12**:**13** from 2:1 to 1:2, while the hydrolysis of the isolated **10** gave **12**:**13** in the expected 1:2 molar ratio. We carried out the reaction on **1** with D_2 to find out whether the hydrogenation was occurring through pathway a or b. Pathway b implies the formation of an imino complex, though the hydrolysis should give the same compounds **12** and **13**. The reaction with D_2 followed by hydrolysis showed that the only deuterated form is $MesCD_2$—NH—Bu^t, supporting pathway a. Hydrogenation at room temperature (Scheme II) yielded a crystalline solid derived from the thermal

(16) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (b) Geoffroy, G. L. *J. Am. Chem. Soc.* **1986**, *108*, 1315.
(17) Froemberg, W.; Erker, G. *J. Organomet. Chem.* **1985**, *280*, 343, 355. Erker, G.; Froemberg, W.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1984**, *96*, 72.

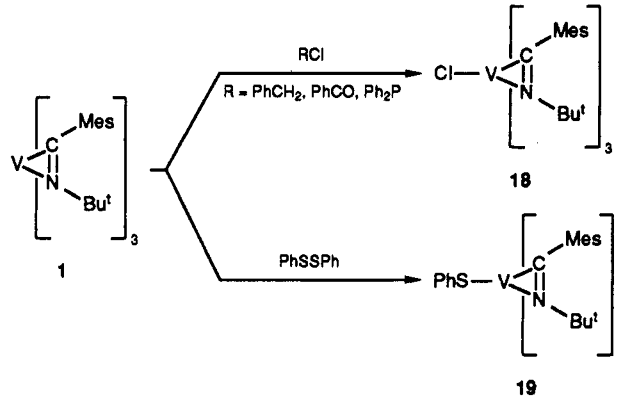
Scheme I



decomposition of either **9** or **10**. In an independent experiment we proved that the thermal decomposition of **10** at room temperature leads to the same complex **17**.

The elimination of **12** and the ortho metalation of the methyl from the mesitylene is a known process in other early transition metals.[18] It has been observed that, in other reactions, vanadium(III) is able to promote homolytic cleavage of bonds in organic fragments attached to it.[12] The nitrene **16** may form by that route, but because of its unsaturation, it dimerizes to form **17**. The structure of this diamagnetic vanadium(IV) organometallic derivative was clarified by an X-ray analysis (Table XI), and the picture of the dimer is reported in Figure 4. The two pseudotetrahedral vanadium atoms are joined by two bridging amido groups. The two metallacycles are puckered. The V_2N_2 core is nearly planar, N3 and N4 deviating from the mean plane by only 0.039(4) Å. The V—N bond distances within the V_2N_2 fragment are very short compared to other V—N bridging distances. This is in favor of a sort of metallaazacyclobutadiene, which is further supported by the trigonal-planar geometry around N3 and N4. The very short V—V distance of 2.460(1) Å seems to be in strong agreement with an unprecedented V(IV)—V(IV) single bond.[19]

(4) Reaction of 1 with C–Cl and P–Cl Bonds. The tris(η^2-iminoacyl) compound **1** reacts in a surprising way with typical compounds used in oxidative-addition reactions. These reactions preserve the integrity of the V–η^2-iminoacyl moiety, to form unusually stable vanadium(IV) organometallic derivatives containing three V—C bonds:



(6)

18 and **19** have closely related properties, including the structures shown in Figures 5 and 6, respectively. In both complexes the vanadium atom has a pseudotrigonal coordination and is displaced from the mean best plane running through the six η^2-bonded atoms (basal plane N1,C10,N2,C20,N3,C30) toward the apical atom by 0.481(1) and 0.483(1) Å for complexes **18** and **19**, respectively. The V—Cl and V—S bonds form dihedral angles of 12.1(1) and 13.2(1)° with the normal to the basal planes. Bond distances and angles within the [V{η^2-C(Mes)=NBu^t}$_3$] moieties are in good agreement with those found in **1**[20] (Tables XII and XIII). The mutual orientations of the η^2-bonded groups are very similar in the two complexes. The presence of the phenyl group on the sulfur atom in complex **19** does not seem to affect significantly the orientation of the mesityl groups with respect to the V,N,C planes. In both compounds the mesityl groups are nearly perpendicular to their respective V,N,C planes. Complexes **18** and **19** are examples of rare organometallic derivatives of vanadium(IV).[12]

(18) Berno, P.; Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 2669.

(19) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886. Cotton, F. A.; Diebold, M. P.; Shim, I. *Inorg. Chem.* **1985**, *24*, 1510. Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1983**, *22*, 378, 560. Cotton, F. A. *Polyhedron* **1987**, *6*, 667. Gambarotta, M.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1116.

(20) Part 1 of this series: *Organometallics*, preceding paper in this issue.

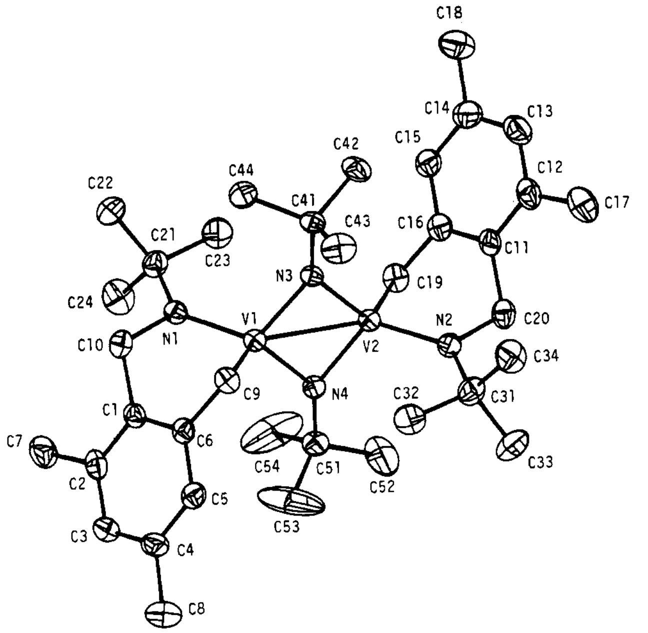
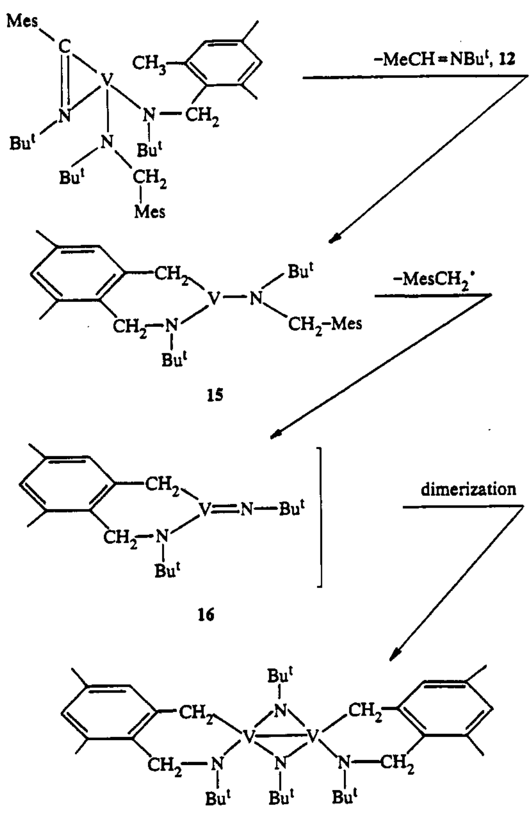


Figure 4. ORTEP[30] view of complex 17 (30% probability ellipsoids).

Scheme II



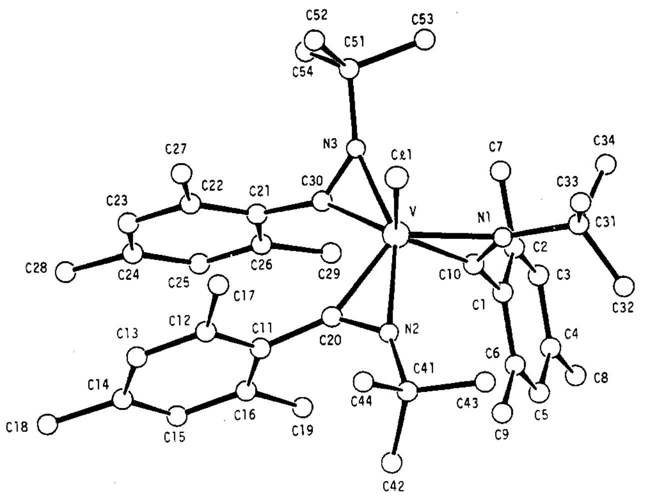


Figure 5. SCHAKAL[29] view of complex 18.

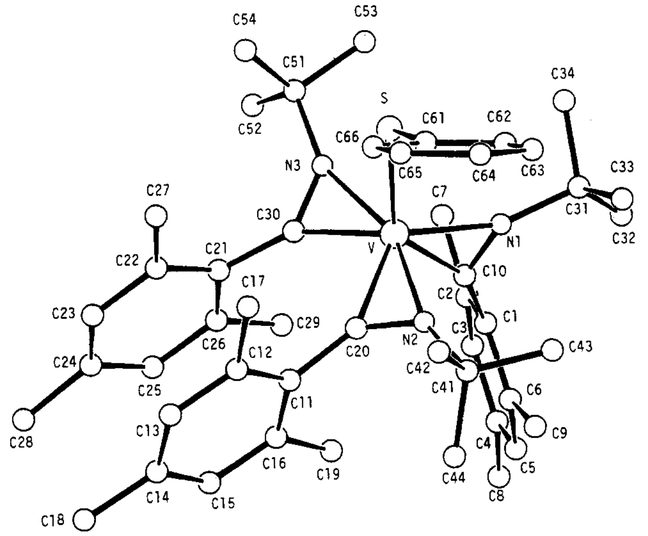


Figure 6. SCHAKAL[29] view of complex 19.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. [V{η^2-C(Mes)=NBu^t}$_3$] (1) was prepared as reported.[10] Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer; NMR spectra were measured on a Bruker 200-AC instrument. Magnetic measurements were made with a Faraday balance.

Reaction of 1 with Carbon Dioxide: Synthesis of 2. A THF (80 mL) solution of 1 (3.33 g, 5.06 mmol) was reacted with CO_2 at room temperature. The color suddenly changed to dark red. The solution was stirred for 30 min, and solvents were evaporated to dryness. A dark solid was obtained, which, after extraction with diethyl ether, gave dark red crystals (1.5 g, 40%). Anal. Calcd for $C_{44}H_{60}N_3O_4V$: C, 70.85; H, 8.11; N, 5.63. Found: C, 70.61; H, 7.97; N, 5.54. μ_{eff}: 2.68 μ_B at 288 K. ν(C=O) (Nujol): 1673 cm^{-1} (s). The CO_2 derivative did not show any loss of CO_2 under vacuum either in the solid state or in solution.

Reaction of 1 with CyNCO: Synthesis of 3. A THF (100 mL) solution of 1 (3.0 g, 4.56 mmol) was reacted with CyNCO (1.74 mL, 13.7 mmol). The mixture was stirred at room temperature and the original green color became lighter. The solvent was evaporated to dryness; then *n*-hexane (100 mL) was added. At first the solid seemed to dissolve completely, but then a blue crystalline solid precipitated, which was filtered and dried (1.80 g, 50%). Suitable crystals for X-ray analysis were obtained by extracting the blue solid with diethyl ether. Anal. Calcd for $C_{49}H_{71}N_4OV$: C, 75.16; H, 9.14; N, 7.15. Found: C, 74.91; H, 9.07; N, 6.89. μ_{eff}: 2.74 μ_B at 293 K.

Reaction of 1 with CO: Synthesis of 4. A THF (100 mL) solution of 1 (1.81 g, 2.75 mmol) was reacted with an excess of CO. The color turned suddenly to red. The solution was stirred for 15 min and then concentrated to dryness under vacuum; the residue was extracted with *n*-hexane (50 mL) and the extract filtered. Upon concentration and cooling, a red crystalline product was obtained (1.00 g, 53%). Anal. Calcd for $C_{43}N_{60}N_3$-OV: C, 75.30; H, 8.82; N, 6.13. Found: C, 75.03; H, 8.56; N, 6.00. Complex 4 is diamagnetic. ν(C=O) (Nujol): 1867 cm^{-1}. ν(C=N) (Nujol): 1662 and 1571 cm^{-1}. The gas-volumetric measurement showed that 1 mol of CO was absorbed per mole of 1. ^{1}H NMR

Table III. Atomic Coordinates (×10⁴) for Complex 3

atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
V1	1152(1)	2646(1)	2484(1)	321(4)
O1	−140(2)	1050(4)	2726(5)	662(27)
N1	1312(2)	1396(4)	3173(4)	314(21)
N2	1197(3)	3176(4)	973(5)	409(27)
N3	1111(3)	3763(4)	3463(5)	416(27)
N4	376(2)	2209(4)	2376(5)	357(25)
C1	775(2)	44(2)	3367(5)	386(31)
C2	738(2)	−234(2)	4441(5)	456(32)
C3	649(2)	−1084(2)	4622(5)	501(35)
C4	597(2)	−1657(2)	3728(5)	591(40)
C5	633(2)	−1379(2)	2654(5)	576(34)
C6	722(2)	−529(2)	2473(5)	515(36)
C7	735(4)	361(5)	5402(7)	550(37)
C8	511(4)	−2578(5)	3922(9)	839(47)
C9	689(4)	−244(6)	1264(7)	664(42)
C10	851(3)	961(4)	3134(6)	321(29)
C11	1741(2)	2048(3)	247(4)	402(31)
C12	2316(2)	2167(3)	339(4)	456(34)
C13	2586(2)	1727(3)	−376(4)	432(31)
C14	2281(2)	1168(3)	−1182(4)	502(34)
C15	1706(2)	1048(3)	−1274(4)	496(34)
C16	1436(2)	1488(3)	−559(4)	438(33)
C17	2665(3)	2793(6)	1169(7)	603(36)
C18	2572(4)	751(6)	−2010(7)	727(40)
C19	813(3)	1354(6)	−715(7)	633(37)
C20	1452(3)	2470(5)	1049(6)	400(31)
C21	1913(2)	3335(3)	5072(3)	397(31)
C22	1791(2)	3019(3)	6062(3)	421(29)
C23	2193(2)	3073(3)	7100(3)	473(36)
C24	2716(2)	3442(3)	7147(3)	485(35)
C25	2838(2)	3759(3)	6158(3)	485(32)
C26	2437(2)	3705(3)	5120(3)	372(31)
C27	1257(3)	2560(5)	6031(7)	614(33)
C28	3145(4)	3530(6)	8276(7)	739(42)
C29	2613(4)	4017(6)	4103(7)	634(36)
C30	1498(3)	3266(5)	3971(6)	358(30)
C31	1896(3)	1009(5)	3530(6)	347(29)
C32	2330(3)	1684(5)	3580(8)	631(37)
C33	2000(3)	616(6)	4724(7)	660(38)
C34	1990(4)	374(5)	2682(8)	668(40)
C41	1099(4)	3847(6)	93(8)	617(39)
C42	1322(6)	3671(8)	−903(10)	1449(70)
C43	1402(6)	4622(7)	679(12)	1227(68)
C44	487(4)	4040(8)	−184(9)	1082(57)
C51	937(4)	4594(5)	3819(8)	586(37)
C52	416(4)	4877(6)	2978(8)	750(40)
C53	1402(5)	5211(6)	3938(10)	1086(56)
C54	780(5)	4494(7)	4960(10)	1030(58)
C55	316(3)	1423(5)	2735(6)	406(33)
C56	−125(3)	2719(5)	1912(6)	387(27)
C57	−505(3)	2347(5)	819(7)	591(35)
C58	−971(4)	2970(6)	307(8)	729(44)
C59	−1322(4)	3193(6)	1165(11)	864(50)
C60	−953(4)	3514(6)	2246(9)	764(50)
C61	−481(3)	2905(5)	2762(7)	581(35)

(C_7D_8, 0 °C): δ 6.90 (s, 2 H, Mes), 2.34 (s, 3 H, *p*-Me Mes), 2.15 (s, 6 H, *o*-Me Mes), 1.58 (s, 9 H, Bu^t). ^{1}H NMR (C_7D_8, −40 °C): δ 6.91 (s, 1 H, Mes), 6.88 (s, 1 H, Mes), 2.36 (s, 6 H, *o*- + *p*-Me Mes), 2.02 (s, 3 H, *o*-Me Mes), 1.55 (s, 9 H, Bu^t).

Reaction of 1 with Diphenyldiazomethane: Synthesis of 5. To a THF (50 mL) solution of 1 (1.462 g, 2.22 mmol) was added diphenyldiazomethane (0.431 g, 2.22 mmol). The color turned suddenly to red. The solution was stirred for 1 h and then concentrated to dryness, and the residue was dissolved in *n*-hexane (50 mL) and the solution filtered. Upon cooling of the solution, dark red crystals were obtained (1.00 g, 53%). Anal. Calcd for $C_{53}H_{70}N_5V$: C, 76.87; H, 8.52; N, 8.46. Found: C, 77.42; H, 9.13; N, 8.39. Complex 5 is diamagnetic. ^{1}H NMR (C_7D_8, +40 °C): δ 7.40–7.20 (m, 6 H, Ph), 7.78–7.73 (m, 4 H, Ph), 6.69 (s, 2 H, Mes), 2.36 (s, 3 H, *p*-Me Mes), 2.20 (s, 6 H, *o*-Me Mes), 1.44 (s, 9 H, Bu^t). ^{1}H NMR (C_7D_8, −40 °C): δ 8.00–7.20 (m, 10 H, Ph), 6.85 (s, 2 H, Mes), 6.62 (s, 2 H, Mes), 6.52 (s, 2 H, Mes), 2.50 (s, 6 H, *o*-Me Mes), 2.38 (s, 9 H, *p*-Me Mes), 2.01 (s, 6 H, *o*-Me Mes), 1.93 (s, 6 H, *o*-Me Mes), 1.51 (s, 18 H, Bu^t), 1.43 (s, 9 H, Bu^t). ^{13}C NMR (C_7D_8, +40 °C): δ 223 (Mes—C═NBu^t). ^{13}C NMR (C_7D_8, −40 °C): δ 232.6 (1C, Mes—C═NBu^t), 219.12 (2C, Mes—C═NBu^t). ν(C═N) (Nujol): 1675 cm^{-1}.

Table IV. Fractional Atomic Coordinates (×10⁴) for Complex 6

atom	*x/a*	*y/b*	*z/c*	U_{eq}, Å^2
V1	4322.6(4)	7392.7(4)	774.9(8)	381(3)
N1	4800(2)	8186(2)	365(4)	437(16)
N2	3830(2)	7347(2)	2255(4)	467(14)
N3	3436(2)	7442(2)	−449(4)	466(16)
N4	5162(2)	7026(2)	368(3)	399(15)
N5	6737(3)	7246(3)	−584(7)	1142(36)
C1	5833(2)	8561(2)	−556(3)	531(22)
C2	5727(2)	8694(2)	−1737(3)	580(22)
C3	6158(2)	9094(2)	−2231(3)	672(25)
C4	6695(2)	9360(2)	−1544(3)	723(29)
C5	6802(2)	9226(2)	−362(3)	712(25)
C6	6371(2)	8827(2)	132(3)	631(24)
C7	5214(4)	8351(4)	−2557(6)	947(34)
C8	7165(3)	9800(3)	−2104(7)	935(33)
C9	6561(3)	8653(4)	1360(6)	1033(38)
C10	5384(2)	8092(3)	−40(5)	468(20)
C11	4813(2)	6886(2)	3556(3)	472(20)
C12	5302(2)	7287(2)	4089(3)	500(21)
C13	5744(2)	7068(2)	5013(3)	570(22)
C14	5697(2)	6448(2)	5404(3)	619(23)
C15	5208(2)	6047(2)	4872(3)	579(23)
C16	4766(2)	6266(2)	3948(3)	574(23)
C17	5362(3)	7957(3)	3689(6)	684(25)
C18	6199(3)	6194(4)	6387(6)	846(28)
C19	4242(3)	5805(3)	3443(6)	752(26)
C20	4413(3)	7130(2)	2474(5)	440(20)
C21	3643(2)	6383(1)	−1352(3)	464(19)
C22	3274(2)	5859(1)	−1085(3)	547(20)
C23	3183(2)	5352(1)	−1854(3)	593(24)
C24	3460(2)	5367(1)	−2889(3)	633(24)
C25	3829(2)	5891(1)	−3156(3)	613(22)
C26	3920(2)	6398(1)	−2387(3)	517(22)
C27	3028(3)	5803(3)	100(6)	767(25)
C28	3345(4)	4832(3)	−3763(6)	839(29)
C29	4368(3)	6936(3)	−2668(5)	653(22)
C30	3745(2)	6932(3)	−546(5)	473(20)
C31	4528(3)	8846(2)	467(5)	561(22)
C32	3978(3)	8787(3)	1236(6)	678(24)
C33	5035(3)	9305(3)	1119(7)	807(29)
C34	4260(3)	9111(3)	−730(6)	716(27)
C41	3292(3)	7441(3)	3020(5)	588(22)
C42	3488(4)	7344(7)	4212(8)	2031(73)
C43	2746(4)	7015(5)	2566(10)	1615(56)
C44	3014(5)	8081(5)	2869(10)	1627(59)
C51	2811(3)	7663(3)	−1172(5)	624(20)
C52	2582(3)	8275(3)	−691(7)	887(29)
C53	2932(3)	7754(4)	−2433(6)	892(30)
C54	2269(3)	7172(3)	−1104(6)	758(28)
C55	5583(2)	7466(3)	−9(5)	468(20)
C56	5418(3)	6358(2)	518(5)	485(20)
C57	4870(3)	5946(3)	892(6)	670(26)
C58	6001(3)	6341(3)	1480(6)	679(26)
C59	5600(3)	6075(3)	−618(6)	705(26)
C60	6223(3)	7337(3)	−327(6)	692(27)
C1S	6394(11)	440(11)	4167(19)	
C2S	5881(15)	331(13)	4692(24)	
C3S	5295(9)	86(10)	4794(17)	

Reaction of 1 with Bu^{t}NC: Synthesis of 6. To a THF (100 mL) solution of 1 (2.07 g, 3.15 mmol) was added Bu^{t}NC (1.07 mL, 9.44 mmol). The color turned suddenly to dark red. The solution was stirred for 12 h and concentrated to dryness; the residue was extracted with *n*-hexane (100 mL) and the extract filtered. Upon concentration of the solution, dark red crystals were obtained (1.23 g, 51%). Anal. Calcd for $C_{48}H_{69}N_5V \cdot n\text{-}C_6H_{14}$: C, 77.11; H, 8.51; N, 8.33. Found: C, 76.00; H, 9.10; N, 8.48. μ_{eff}: 1.72 μ_B at 288 K. ν(C≡N) (Nujol): 2175 cm^{-1}. ν(C═N) (Nujol): 1628 and 1605 cm^{-1}.

Reaction of 1 with Hydrogen: Synthesis of 10. A *n*-hexane (100 mL) suspension of 1 (0.787 g, 1.2 mmol) was treated with an excess of H_2 at −30 °C. The mixture was stirred for 2 h at

Table V. Fractional Atomic Coordinates (×10^4) for Complex 17

atom	x/a	y/b	z/c	U_{eq}, Å^2
V1	2776.4(8)	3844.6(4)	2851.7(4)	332(3)
V2	5067.0(8)	3670.9(4)	2609.5(4)	342(3)
N1	2138(4)	4068(2)	3718(2)	382(14)
N2	5742(4)	3430(2)	1771(2)	427(17)
N3	3845(4)	3112(2)	2924(2)	343(15)
N4	3975(4)	4394(2)	2492(2)	369(16)
C1	167(3)	4499(2)	2753(1)	424(20)
C2	–475(3)	5100(2)	2722(1)	536(22)
C3	–984(3)	5393(2)	2025(1)	559(23)
C4	–851(3)	5085(2)	1359(1)	565(25)
C5	–209(3)	4484(2)	1390(1)	473(19)
C6	300(3)	4191(2)	2088(1)	412(20)
C7	–641(7)	5463(3)	3416(3)	695(27)
C8	–1465(7)	5395(3)	607(4)	876(32)
C9	1041(5)	3572(2)	2105(3)	426(20)
C10	641(5)	4152(3)	3512(3)	466(21)
C11	7734(3)	3013(2)	2746(2)	445(21)
C12	8401(3)	2419(2)	2781(2)	602(26)
C13	8887(3)	2123(2)	3479(2)	686(26)
C14	8706(3)	2421(2)	4141(2)	721(28)
C15	8039(3)	3015(2)	4106(2)	559(23)
C16	7553(3)	3311(2)	3409(2)	471(21)
C17	8637(7)	2054(3)	2105(4)	793(29)
C18	9281(7)	2119(4)	4909(4)	1004(32)
C19	6801(5)	3928(2)	3382(3)	487(20)
C20	7249(5)	3357(3)	1983(3)	505(24)
C21	2735(5)	4117(3)	4534(3)	488(21)
C22	2059(6)	3638(3)	4998(3)	657(24)
C23	4257(6)	3973(3)	4647(3)	647(27)
C24	2569(7)	4810(3)	4814(3)	732(27)
C31	5159(6)	3339(3)	948(3)	563(23)
C32	3627(6)	3444(3)	831(3)	659(26)
C33	5773(7)	3832(3)	484(3)	802(27)
C41	3688(5)	2417(2)	3058(3)	384(20)
C42	5067(6)	2136(2)	3430(3)	585(22)
C43	3169(6)	2095(3)	2295(3)	656(25)
C44	2686(6)	2313(2)	3582(3)	595(24)
C34	5423(7)	2659(3)	695(3)	721(26)
C51	4099(5)	5080(2)	2303(3)	467(21)
C52	5352(8)	5197(3)	2017(6)	1353(52)
C53	2934(9)	5299(4)	1750(6)	1722(52)
C54	4114(14)	5469(3)	2964(5)	1796(68)

room temperature. The resulting red solution was then concentrated and maintained under H_2 at –30 °C for 1 day. A red crystalline solid formed (0.51 g, 64%). Anal. Calcd for $C_{42}H_{64}N_3V$: C, 76.21; H, 9.75; N, 6.35. Calcd for $C_{42}H_{62}N_3V$: C, 76.44; H, 9.47; N, 6.37. Found: C, 75.52; H, 9.24; N, 5.96. μ_{eff}: 2.77 μ_B. A solution of the hydrogenated product in *n*-hexane was treated with an excess of aqueous HCl concentrated at –30 °C. The solution suddenly became light yellow. The solvent was evaporated to dryness. ^{1}H NMR analysis ($CDCl_3$) revealed two organic cations, $[MesCH{=}NHBu^t]^+$ and $[MesCH_2{-}NH_2Bu^t]^+$, in a 1:2 molar ratio. If the hydrogenation is not complete, the hydrolysis leads to variable ratios of the two cations, from 2:1 to 1:2. This is indicative of the presence of variable amounts of **9**.

Synthesis of 17. When the reaction of **1** with H_2 was carried out in THF at room temperature, the solution turned red in 20 min. The mixture was stirred for 1 day and evaporated to dryness and *n*-hexane added to the residue. After the mixture stood for 1 day at room temperature, black crystals were obtained in a rather low yield. Compound **17** was also obtained by keeping **10** in THF at room temperature for 1 day. Anal. Calcd for $C_{36}H_{60}N_4V_2$: C, 66.44; H, 9.29; N, 8.61. Found: C, 66.31; H, 9.10; N, 8.43. Complex **17** is diamagnetic. ^{1}H NMR (C_7D_8, +20 °C): δ 6.84 (s, 1 H, Mes), 6.47 (s, 1 H, Mes), 4.92 (s, 2 H, $CH_2{-}N$), 2.61 (s, 2 H, $CH_2{-}V$), 2.25 (s, 6 H), 1.83 (s, 9 H, Bu^t), 1.57 (s, 9 H, Bu^t).

Reaction of 1 with Deuterium: Synthesis of $[V\{\eta^2\text{-}C(Mes){=}NBu^t\}\{CD_2(Mes){-}NBu^t\}_2]$. A suspension of **1** (1.4 g, 2.13 mmol) in *n*-hexane (100 mL) was treated with an excess of D_2 at –30 °C. After 3 h of stirring at that temperature, the red solution obtained was concentrated and cooled, resulting in a red crystalline precipitate (0.7 g, 50%). Anal. Calcd for $C_{42}H_{60}D_4N_3V$: C, 75.76; H, 9.08; N, 6.31. Found: C, 75.75; H, 9.48; N, 6.61. A solution of the deuterated product in hexane was treated with an excess of aqueous concentrated HCl at –30 °C. The solution suddenly became light yellow. The solvent was evaporated to dryness and the residue redissolved in $CDCl_3$ for ^{1}H NMR measurements. Only two organic cations were detected, $[MesCH{=}NHBu^t]^+$ and $[MesCD_2{-}NH_2Bu^t]^+$.

Table VI. Fractional Atomic Coordinates (×10^4) for Complex 18

atom	x/a	y/b	z/c	U_{eq}, Å^2
V	–2766.8(5)	1471(0)	2201.4(7)	510(3)
Cl1	–3517.4(11)	2313.6(6)	1851.9(14)	820(6)
N1	–3711(3)	1097(2)	3238(4)	571(15)
N2	–3292(3)	1222(2)	478(4)	585(16)
N3	–1849(3)	1825(2)	3295(4)	604(16)
C1	–2899(2)	224(1)	3691(4)	613(22)
C2	–2509(2)	167(1)	4833(4)	739(24)
C3	–2325(2)	–348(1)	5290(4)	975(29)
C4	–2532(2)	–805(1)	4606(4)	1106(37)
C5	–2922(2)	–749(1)	3464(4)	991(34)
C6	–3106(2)	–234(1)	3007(4)	777(24)
C7	–2257(4)	639(3)	5574(5)	889(28)
C8	–2293(5)	–1359(3)	5146(9)	1412(43)
C9	–3497(4)	–187(3)	1810(7)	997(30)
C10	–3056(3)	769(2)	3168(4)	545(20)
C11	–1731(2)	1289(1)	–459(3)	524(18)
C12	–1498(2)	1740(1)	–1147(3)	648(21)
C13	–748(2)	1718(1)	–1912(3)	744(23)
C14	–231(2)	1245(1)	–1989(3)	759(23)
C15	–465(2)	794(1)	–1301(3)	680(21)
C16	–1215(2)	816(1)	–536(3)	589(19)
C17	–2018(4)	2265(2)	–1066(5)	818(24)
C18	607(5)	1226(3)	–2779(6)	1071(31)
C19	–1431(4)	335(2)	216(5)	753(21)
C20	–2453(3)	1310(2)	459(4)	535(18)
C21	–458(2)	1403(1)	2281(3)	593(20)
C22	8(2)	1774(1)	1566(3)	725(23)
C23	880(2)	1651(1)	1148(3)	972(28)
C24	1284(2)	1157(1)	1445(3)	981(31)
C25	818(2)	786(1)	2160(3)	845(26)
C26	–53(2)	909(1)	2578(3)	659(21)
C27	–388(5)	2302(3)	1196(6)	977(31)
C28	2255(5)	1022(3)	1040(9)	1425(40)
C29	–514(4)	516(2)	3388(6)	848(26)
C30	–1424(3)	1509(2)	2603(4)	539(17)
C31	–4617(4)	1068(2)	3851(6)	758(25)
C32	–5092(5)	556(3)	3619(9)	1357(40)
C33	–5174(5)	1543(3)	3426(9)	1428(41)
C34	–4481(5)	1135(6)	5148(8)	1890(62)
C41	–3958(4)	1092(3)	–502(6)	804(26)
C42	–3676(4)	586(3)	–1164(6)	1003(29)
C43	–4875(4)	1041(4)	87(7)	1320(36)
C44	–3986(5)	1569(3)	–1360(7)	1280(37)
C51	–1572(4)	2231(2)	4235(5)	762(24)
C52	–1660(5)	2785(3)	3678(6)	1117(32)
C53	–2245(5)	2171(3)	5260(6)	984(27)
C54	–608(5)	2130(3)	4662(6)	997(29)

Reaction of 1 with Hydrogen and Then CO: Synthesis of 11. A *n*-hexane (150 mL) solution of **1** (0.98 g, 1.49 mmol) was reacted with H_2 at –20 °C and then stirred for 3 h. The excess H_2 was pumped off in vacuo. The resulting red solution was kept at –20 °C and reacted with CO with stirring for 1 h. The solution was concentrated and cooled to –40 °C. A red crystalline solid was obtained (0.40 g, 38%). Anal. Calcd for $C_{43}H_{62}N_3OV$: C, 75.10; H, 9.02; N, 6.11. Found: C, 74.87; H, 9.02; N, 5.76. ν(CO) (Nujol): 1839 cm^{-1}. Complex **11** is diamagnetic and is not stable in solution at temperatures higher than –20 °C for more than 1 h. ^{1}H NMR (C_7D_8): δ 7.05 (s, *m*-H), 6.98 (s, *m*-H), 6.10 (s, *m*-H), 6.08 (s, $-CH_2-$), 2.91 (s, *o*-Me), 2.46 (s, *o*- + *p*-Me), 2.43 (s, *o*- + *p*-Me), 2.37 (s, *p*-Me), 2.05 (s, *o*-Me), 1.66 (s, $C{=}NBu^t$), 1.23 (s, $C{=}NBu^t$). The hydrogenation of the iminoacyl species was not observed upon reacting **4** with H_2.

Table VII. Fractional Atomic Coordinates (×10⁴) for Complex 19

atom	x/a	y/b	z/c	U_{eq}, Å^2
V	6242.7(2)	8095.7(1)	1556.1(1)	463(2)
S1	6165.0(3)	7639.0(12)	406.6(5)	782(4)
N1	6233(1)	9761(2)	1580(2)	562(9)
N2	5677(1)	7786(2)	1857(1)	532(10)
N3	6793(1)	7738(2)	1383(2)	545(10)
C1	6431(1)	10096(2)	2778(1)	580(14)
C2	6797(1)	10373(2)	2887(1)	652(15)
C3	6907(1)	10770(2)	3510(1)	794(18)
C4	6651(1)	10891(2)	4024(1)	856(21)
C5	6285(1)	10614(2)	3915(1)	774(18)
C6	6175(1)	10217(2)	3292(1)	631(13)
C7	7077(1)	10278(4)	2346(3)	842(19)
C8	6773(2)	11264(5)	4711(3)	1239(30)
C9	5779(1)	9988(4)	3162(2)	806(18)
C10	6327(1)	9470(3)	2157(2)	525(12)
C11	5885(1)	6117(2)	2506(1)	520(12)
C12	5804(1)	5104(2)	2242(1)	610(14)
C13	5828(1)	4190(2)	2646(1)	701(16)
C14	5934(1)	4289(2)	3316(1)	704(15)
C15	6015(1)	5302(2)	3581(1)	627(14)
C16	5990(1)	6216(2)	3176(1)	540(12)
C17	5699(1)	4953(4)	1512(2)	836(18)
C18	5969(2)	3291(4)	3748(3)	1074(25)
C19	6078(1)	7296(3)	3480(2)	648(13)
C20	5899(1)	7102(3)	2078(2)	496(11)
C21	6837(1)	6394(2)	2357(1)	533(13)
C22	6789(1)	5307(2)	2203(1)	586(13)
C23	6865(1)	4521(2)	2684(1)	686(14)
C24	6989(1)	4822(2)	3318(1)	713(17)
C25	7038(1)	5909(2)	3472(1)	668(15)
C26	6962(1)	6695(2)	2992(1)	581(12)
C27	6654(1)	4941(4)	1533(2)	812(19)
C28	7055(2)	3980(4)	3858(3)	1036(21)
C29	7019(1)	7847(4)	3184(2)	784(18)
C30	6690(1)	7245(3)	1893(2)	496(10)
C31	6179(1)	10838(3)	1245(2)	695(16)
C32	6273(2)	11753(4)	1681(4)	1585(43)
C33	5803(2)	10908(5)	1006(4)	1662(39)
C34	6435(2)	10846(5)	641(4)	1449(35)
C41	5268(1)	7872(4)	1959(2)	651(15)
C42	5075(1)	7035(4)	1517(3)	877(19)
C43	5161(1)	9004(4)	1735(3)	817(16)
C44	5168(1)	7693(4)	2693(2)	831(18)
C51	7142(1)	7720(4)	980(2)	730(16)
C52	7469(1)	7654(6)	1434(3)	1172(24)
C53	7151(1)	8753(5)	583(3)	1016(22)
C54	7130(2)	6812(6)	499(4)	1434(32)
C61	5711(1)	7450(3)	91(1)	702(16)
C62	5487(1)	8335(3)	−42(1)	925(22)
C63	5141(1)	8182(3)	−327(1)	1127(27)
C64	5020(1)	7144(3)	−478(1)	1157(30)
C65	5245(1)	6259(3)	−345(1)	1022(26)
C66	5590(1)	6412(3)	−60(1)	862(19)

Reaction of 1 with $PhCH_2Cl$: Synthesis of 18. To a THF (150 mL) solution of 1 (3.572 g, 5.43 mmol) was added $PhCH_2Cl$ (0.63 mL, 5.46 mmol). The color turned suddenly red. The solution was stirred for 2 h and concentrated to dryness. The residue was dissolved in *n*-hexane (250 mL) and the solution filtered. Upon concentration of the solution dark red crystals were obtained (2.93 g, 78%). Anal. Calcd: C, 72.76; H, 8.72; N, 6.06. Found: C, 72.96; H, 8.46; N, 5.96. μ_{eff}: 1.46 μ_B. The same product was obtained when 3 equiv of $PhCH_2Cl$ was employed and when acyl chlorides such as PhCOCl and PPh_2Cl were used.

Reaction of 1 with PhSSPh: Synthesis of 19. To a THF (100 mL) solution of 1 (1.026 g, 1.56 mmol) was added PhSSPh (0.17 g, 0.78 mmol) at room temperature. The color suddenly turned red. After 30 min of stirring at room temperature, the solvent was evaporated to dryness; the residue was dissolved in *n*-hexane (75 mL) and the solution filtered. Concentration of the solution yielded the product as red crystals (0.91 g, 76%). Anal. Calcd for $C_{48}H_{65}N_3SV$: C, 75.16; H, 8.54; N, 5.48. Found: C, 75.61; H, 8.72; N, 5.40. μ_{eff}: 1.48 μ_B.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for Complex 2

V–O1	1.949(3)	N3–C51	1.492(5)
V–O3	1.938(3)	C1–C10	1.499(5)
V–N1	2.349(5)	O1–C55	1.293(5)
V–N2	2.267(4)	O2–C55	1.212(6)
V–N3	2.000(4)	O3–C56	1.279(5)
V–C30	2.023(5)	O4–C56	1.217(6)
N1–C10	1.287(6)	C10–C55	1.526(6)
N1–C31	1.514(6)	C11–C20	1.490(5)
N2–C20	1.279(6)	C20–C56	1.529(6)
N2–C41	1.522(6)	C21–C30	1.484(6)
N3–C30	1.277(6)		
N3–V–C30	37.0(2)	V–N1–C10	110.7(3)
N2–V–C30	104.8(2)	C10–N1–C31	125.3(4)
N2–V–N3	141.0(2)	V–N2–C41	123.4(3)
N1–V–C30	145.3(2)	V–N2–C20	111.5(3)
N1–V–N3	109.0(1)	C20–N2–C41	124.8(4)
N1–V–N2	109.8(1)	V–N3–C51	154.6(3)
O3–V–C30	97.5(2)	V–N3–C30	72.5(3)
O3–V–N3	97.5(1)	C30–N3–C51	132.9(4)
O3–V–N2	76.1(1)	N3–C30–C21	132.3(4)
O3–V–N1	93.2(1)	V–C30–C21	157.2(3)
O1–V–C30	99.9(1)	V–C30–N3	70.5(3)
O1–V–N3	98.8(1)	O2–C55–C10	119.7(4)
O1–V–N2	95.5(1)	O1–C55–C10	115.3(4)
O1–V–N1	74.6(1)	O1–C55–O2	125.0(4)
O1–V–O3	162.2(1)	O4–C56–C20	119.5(4)
V–O1–C55	124.1(3)	O3–C56–C20	115.5(4)
V–O3–C56	121.9(3)	O3–C56–O4	124.9(4)
V–N1–C31	124.0(3)		

Table IX. Selected Bond Distances (Å) and Angles (deg) for Complex 3

V1–N1	2.154(6)	N3–C30	1.270(10)
V1–N2	2.039(7)	N3–C51	1.483(11)
V1–N3	2.150(7)	N4–C55	1.343(10)
V1–N4	1.993(6)	N4–C56	1.462(9)
V1–C20	2.059(8)	O1–C55	1.259(9)
V1–C30	2.045(7)	C1–C10	1.505(7)
N1–C10	1.312(9)	C10–C55	1.475(10)
N1–C31	1.517(9)	C11–C20	1.490(10)
N2–C20	1.276(10)	C21–C30	1.469(7)
N2–C41	1.485(11)		
C20–V1–C30	130.6(3)	V1–N2–C41	154.8(6)
N4–V1–C30	114.2(3)	V1–N2–C20	72.7(4)
N4–V1–C20	115.1(3)	C20–N2–C41	132.5(7)
N3–V1–C30	35.1(3)	V1–N3–C51	161.9(5)
N3–V1–C20	130.5(3)	V1–N3–C30	67.9(4)
N3–V1–N4	98.9(3)	C30–N3–C51	130.2(7)
N2–V1–C30	119.2(3)	V1–N4–C56	121.7(5)
N2–V1–C20	36.3(3)	V1–N4–C55	118.7(5)
N2–V1–N4	110.0(3)	C55–N4–C56	119.6(6)
N2–V1–N3	99.9(3)	N2–C20–C11	130.5(7)
N1–V1–C30	96.2(3)	V1–C20–C11	158.5(5)
N1–V1–C20	97.6(3)	V1–C20–N2	71.0(4)
N1–V1–N4	77.5(2)	N3–C30–C21	131.4(7)
N1–V1–N3	125.3(2)	V1–C30–C21	151.7(5)
N1–V1–N2	133.1(2)	V1–C30–N3	76.9(4)
V1–N1–C31	123.7(4)	N4–C55–C10	114.3(6)
V1–N1–C10	113.5(5)	O1–C55–C10	118.7(7)
C10–N1–C31	122.4(6)	O1–C55–N4	126.9(7)

Crystal Structure Determination of Complexes 2, 3, 6, 17, 18, and 19. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[21] Crystal data and details associated with data collection are given in Table I. The intensity background individual reflection profiles of the crystals were analyzed.[22] The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[23] and the absolute

(21) Lawton, S. L.; Jacobson, R. A. TRACER, a Cell Reduction Program; Ames Laboratory. Iowa State University of Science and Technology: Ames, IA, 1965.
(22) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

Table X. Selected Bond Distances (Å) and Angles (deg) for Complex 6

V1–N1	2.027(4)	N3–C30	1.262(7)
V1–N2	2.104(5)	N3–C51	1.514(7)
V1–N3	2.164(4)	N4–C55	1.376(7)
V1–N4	1.993(4)	N4–C56	1.509(6)
V1–C20	2.041(6)	N5–C60	1.144(9)
V1–C30	2.063(5)	C1–C10	1.524(7)
N1–C10	1.352(7)	C10–C55	1.384(9)
N1–C31	1.512(6)	C11–C20	1.505(7)
N2–C20	1.273(7)	C21–C30	1.491(7)
N2–C41	1.512(8)	C55–C60	1.429(8)
C20–V1–C30	124.7(2)	C20–N2–C41	131.3(5)
N4–V1–C30	93.9(2)	V1–N3–C51	163.9(4)
N4–V1–C20	98.5(2)	V1–N3–C30	68.3(3)
N3–V1–C30	34.6(2)	C30–N3–C51	127.7(5)
N3–V1–C20	128.2(2)	V1–N4–C56	129.3(3)
N3–V1–N4	122.5(2)	V1–N4–C55	113.8(3)
N2–V1–C30	107.5(2)	C55–N4–C56	116.6(4)
N2–V1–C20	35.7(2)	N1–C10–C1	130.0(4)
N2–V1–N4	133.7(2)	C1–C10–C55	116.3(4)
N2–V1–N3	95.4(2)	N1–C10–C55	113.6(4)
N1–V1–C30	117.5(2)	N2–C20–C11	133.5(5)
N1–V1–C20	117.7(2)	V1–C20–C11	151.5(4)
N1–V1–N4	79.2(2)	V1–C20–N2	74.8(3)
N1–V1–N3	101.1(2)	N3–C30–C21	133.6(4)
N1–V1–N2	121.6(2)	V1–C30–C21	149.2(3)
V1–N1–C31	123.5(3)	V1–C30–N3	77.1(3)
V1–N1–C10	115.6(4)	N4–C55–C10	117.5(4)
C10–N1–C31	120.8(4)	C10–C55–C60	116.8(5)
V1–N2–C41	159.1(4)	N4–C55–C60	125.6(5)
V1–N2–C20	69.5(3)	N5–C60–C55	178.7(7)

Table XI. Selected Bond Distances (Å) and Angles (deg) for Complex 17

V1–V2	2.460(1)	N1–C21	1.475(6)
V1–N1	1.875(4)	N2–C20	1.489(6)
V1–N3	1.845(4)	N2–C31	1.492(6)
V1–N4	1.871(4)	N3–C41	1.471(6)
V1–C9	2.045(5)	N4–C51	1.470(6)
V2–N2	1.858(4)	C1–C10	1.533(6)
V2–N3	1.862(4)	C6–C9	1.478(6)
V2–N4	1.840(4)	C11–C20	1.538(7)
V2–C19	2.058(5)	C16–C19	1.478(6)
N1–C10	1.481(6)		
N4–V1–C9	117.3(2)	N2–V2–N4	115.8(2)
N3–V1–C9	102.8(2)	N2–V2–N3	117.6(2)
N3–V1–N4	96.6(2)	V1–N1–C21	135.8(3)
N1–V1–C9	103.0(2)	V1–N1–C10	109.2(3)
N1–V1–N4	120.1(2)	C10–N1–C21	114.8(4)
N1–V1–N3	116.1(2)	V2–N2–C31	135.7(3)
V2–V1–C9	122.7(1)	V2–N2–C20	110.2(3)
V2–V1–N4	47.9(1)	C20–N2–C31	114.0(4)
V2–V1–N3	48.7(1)	V1–N3–V2	83.1(2)
V2–V1–N1	133.3(1)	V2–N3–C41	139.2(3)
V1–V2–C19	122.0(1)	V1–N3–C41	137.1(3)
V1–V2–N4	49.0(1)	V1–N4–V2	83.0(2)
V1–V2–N3	48.1(1)	V2–N4–C51	137.1(3)
V1–V2–N2	134.7(1)	V1–N4–C51	139.4(3)
N4–V2–C19	105.4(2)	V1–C9–C6	97.5(3)
N3–V2–C19	118.1(2)	N1–C10–C1	112.7(4)
N3–V2–N4	97.1(2)	V2–C19–C16	98.8(3)
N2–V2–C19	102.8(2)	N2–C20–C11	112.9(4)

scale was established by the Wilson method.[24] Data for complexes **2** and **19** were corrected for absorption using ABSORB.[25] The function minimized during the full-matrix least-squares refinement was $\Sigma w|\Delta F|^2$. For all complexes a weighting scheme based on counting statistics[23] was applied. Scattering factors for neutral atoms were taken from ref 26a for non-hydrogen atoms and from ref 27 for H. Anomalous scattering corrections were included in all structure factor calculations.[26b] Among the low-angle reflections no correction for secondary extinction was deemed necessary.

(23) Data reduction, structure solution, and refinement were carried out on a Gould 32/77 computer using: Sheldrick, G. SHELX-76 System of Crystallographic Computer Programs; University of Cambridge: Cambridge, England, 1976.
(24) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151.

Table XII. Selected Bond Distances (Å) and Angles (deg) for Complex 18

V–Cl1	2.385(2)	N1–C31	1.498(8)
V–N1	2.029(5)	N2–C20	1.249(6)
V–N2	2.149(4)	N2–C41	1.492(8)
V–N3	2.007(5)	N3–C30	1.263(7)
V–C10	2.085(5)	N3–C51	1.502(7)
V–C20	2.032(4)	C1–C10	1.484(6)
V–C30	2.017(4)	C11–C20	1.476(5)
N1–C10	1.259(7)	C21–C30	1.486(5)
C20–V–C30	89.6(2)	Cl1–V–N1	100.0(1)
C10–V–C30	97.3(2)	V–N1–C31	152.9(4)
C10–V–C20	112.1(2)	V–N1–C10	74.6(3)
N3–V–C30	36.6(2)	C10–N1–C31	132.5(5)
N3–V–C20	120.5(2)	V–N2–C41	160.1(4)
N3–V–C10	100.9(2)	V–N2–C20	67.6(3)
N2–V–C30	123.6(2)	C20–N2–C41	131.6(5)
N2–V–C20	34.6(2)	V–N3–C51	152.7(4)
N2–V–C10	98.5(2)	V–N3–C30	72.1(3)
N2–V–N3	154.0(2)	C30–N3–C51	134.8(5)
N1–V–C30	124.3(2)	N1–C10–C1	132.5(4)
N1–V–C20	127.7(2)	V–C10–C1	157.7(3)
N1–V–C10	35.6(2)	V–C10–N1	69.8(3)
N1–V–N3	108.2(2)	N2–C20–C11	135.7(4)
N1–V–N2	97.7(2)	V–C20–C11	146.4(3)
Cl1–V–C30	116.3(2)	V–C20–N2	77.8(3)
Cl1–V–C20	97.1(1)	N3–C30–C21	136.9(4)
Cl1–V–C10	135.6(1)	V–C30–C21	150.3(3)
Cl1–V–N3	91.4(2)	V–C30–N3	71.3(3)
Cl1–V–N2	86.7(1)		

Table XIII. Selected Bond Distances (Å) and Angles (deg) for Complex 19

V–S1	2.378(1)	N1–C31	1.507(5)
V–N1	2.068(2)	N2–C20	1.253(5)
V–N2	2.182(4)	N2–C41	1.509(5)
V–N3	2.084(4)	N3–C30	1.245(5)
V–C10	2.107(4)	N3–C51	1.505(5)
V–C20	2.043(4)	C1–C10	1.510(4)
V–C30	2.055(4)	C11–C20	1.492(4)
S1–C61	1.786(4)	C21–C30	1.503(5)
N1–C10	1.254(6)		
C20–V–C30	90.6(2)	S1–V–N1	105.0(1)
C10–V–C30	96.6(2)	V–S1–C61	118.8(1)
C10–V–C20	106.8(2)	V–N1–C31	151.5(3)
N3–V–C30	35.0(1)	V–N1–C10	74.3(2)
N3–V–C20	123.1(1)	C10–N1–C31	134.3(4)
N3–V–C10	97.3(1)	V–N2–C41	163.5(2)
N2–V–C30	124.7(1)	V–N2–C20	66.8(2)
N2–V–C20	34.3(1)	C20–N2–C41	129.7(3)
N2–V–C10	97.1(1)	V–N3–C51	154.9(3)
N2–V–N3	156.6(1)	V–N3–C30	71.3(2)
N1–V–C30	121.3(2)	C30–N3–C51	133.1(3)
N1–V–C20	125.5(2)	N1–C10–C1	132.3(3)
N1–V–C10	34.9(2)	V–C10–C1	156.8(3)
N1–V–N3	103.5(1)	V–C10–N1	70.8(2)
N1–V–N2	98.8(1)	N2–C20–C11	137.3(3)
S1–V–C30	106.7(1)	V–C20–C11	143.8(3)
S1–V–C20	105.9(1)	V–C20–N2	78.9(2)
S1–V–ClO	139.3(1)	N3–C30–C21	137.8(4)
S1–V–N3	84.5(1)	V–C30–C21	147.7(3)
S1–V–N2	96.3(1)	V–C30–N3	73.7(2)

Solution and refinement were based on the observed reflections. The structure of complex **2** was solved by the heavy-atom method starting from a three-dimensional Patterson map. The structures of complexes **3**, **6**, **17**, **18**, and **19** were solved by direct methods

(25) Ugozzoli, F. ABSORB, a Program for F_o Absorption Correction. In *Comput. Chem.* **1987**, *11*, 109.
(26) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99. (b) *Ibid.*, p 149.
(27) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

using SHELX-86.[28] Refinement was first performed isotropically and then anisotropically for all the non-H atoms except for the C1S, C2S, and C3S carbon atoms of hexane solvent in complex **6** and the C54 methyl carbon in complex **17**, which were refined isotropically. The hexane molecule (complex **6**) lies on a center of symmetry and shows a very high thermal motion, as often happens in situations such as this. All the hydrogen atoms for the complexes **2**, **3**, **6**, **17**, **18**, and **19**, either located from difference maps or put in geometrically calculated positions, were introduced in the refinement as fixed contributors with isotropic *U*'s fixed at 0.08 Å^2. The hydrogen atoms associated with the hexane solvent in complex **6** were ignored. During the refinement all the mesityl and phenyl rings were constrained to be regular hexagons (C–C = 1.395 Å). In the final cycle of refinements no parameter shifted by more than 0.1 times its standard deviation. The final difference maps showed no unusual feature, with no significant peak above the general background. For complex **6** a complete refinement performed on a set of data corrected for absorption[25] was discarded, resulting in final values significantly higher than those corresponding to the original set: $R = 0.067$, $R_G = 0.093$ vs $R = 0.060$, $R_G = 0.079$ ($R_G = [\sum w|\Delta F|^2/\sum|F_o|^2]^{1/2}$).

Final atomic coordinates are listed in Tables II–VII for non-H atoms and in Tables S1–S6 for hydrogens. Thermal parameters are given in Tables S7–S12[29] and selected interatomic distances and angles in Tables VIII–XIII.

Acknowledgment. We thank the "Fonds National Suisse de la Recherche Scientifique" (Grant No. 20-28470-90), the "Fondation Herbette" (University of Lausanne), and the U.S. Navy (Grant No. N00014-89-J-1810) for financial support.

Supplementary Material Available: Listings of unrefined hydrogen coordinates (Tables SI–SVI), thermal parameters (Tables SVII–SXII), and bond distances and angles (Tables SXIII–SXVIII) for complexes **2**, **3**, **6**, **17**, **18**, and **19** and ORTEP drawings for complexes **2**, **3**, **6**, **18**, and **19** (28 pages). Ordering information is given on any current masthead page.

OM920620B

(28) Sheldrick, G. SHELX-86, a FORTRAN-77 Program for the Solution of Crystal Structure from Diffraction Data; University of Cambridge: Cambridge, England, 1986.

(29) See paragraph at the end of the paper regarding supplementary material.

(30) Keller, E., SCHAKAL 88B/V16, a FORTRAN Program for the Graphical Representation of Molecular and Crystallographic Models; Kristallographisches Institut der Universitaet: Freiburg, FRG.

(31) Johnson, C. K. ORTEP; Report ORNL-3794; Oak Ridge National Laboratories: Oak Ridge, TN, 1965.