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Chemistry of the Vanadium–Carbon σ Bond. 1. Insertion of Carbon Monoxide, Isocyanides, Carbon Dioxide, and Heterocumulenes into the V–C Bond of Tris(mesityl)vanadium(III)

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Complex 1, $[V(Mes)_3(THF)]$, reacts with Bu^tNC to form the homoleptic tris(η^2-iminoacyl) complex $[V\{\eta^2\text{-}C(Mes){=}NBu^t\}_3]$ (2), while the reaction with carbon monoxide leads to the elimination of MesC(O)Mes and reduction of vanadium to a vanadium–carbonyl species. Cyclohexyl and phenyl isocyanate groups insert into the three V—Mes bonds of 1, forming the tris(amido) derivatives $[V\{O{-}C(Mes)]{=}NCy\}_3]$, (6) and $[V\{O{-}C(Mes){=}NPh\}_3]$ (7). Solvated forms of 7 were prepared, giving $[py{-}V\{O{-}C(Mes){=}NPh\}_3]$ (8) and $[MeCN{-}V\{O{-}C(Mes){=}NPh\}_3]$ (9). Complex 1 undergoes a double insertion of $CyN{=}C{=}NCy$ ($Cy = C_6H_{11}$), giving $[\{CyN{-}C(Mes){-}NCy\}_2V(Mes)]$ (10) which undergoes a further insertion of CO or Bu^tNC into the remaining V—Mes bond, forming $[\{CyN{-}C(Mes){-}NCy\}_2V\{\eta^2\text{-}C(Mes){=}O\}]$ (11) and $[\{CyN{-}C(Mes){-}NCy\}_2V\{\eta^2\text{-}C(Mes){=}NBu^t\}]$ (12), respectively. All complexes have a high-spin d^2 configuration. The structures of 1, 2, 8, and 10 have been determined by X-ray analysis. Crystallographic details: 1 is monoclinic, space group $P2_1/c$, with $a = 8.472(2)$ Å $b = 14.273(4)$ Å $c = 22.385(6)$ Å, $\alpha = \gamma = 90°$, $\beta = 97.64(3)°$, $Z = 4$, and $R = 0.057$; 2 is triclinic, space group $P\bar{1}$, with $a = 17.913(2)$ Å, $b = 13.697(2)$ Å, $c = 8.273(1)$ Å, $\alpha = 80.40(1)°$, $\beta = 80.30(1)°$, $\gamma = 88.34(1)°$, $Z = 2$, and $R = 0.070$; 8 is triclinic, space group $P\bar{1}$, with $a = 14.701(1)$ Å, $b = 14.808(1)$ Å, $c = 13.267(1)$ Å, $\alpha = 69.06(1)°$, $\beta = 73.16(1)°$, $\gamma = 81.37(1)°$, $Z = 2$, and $R = 0.062$; 10 is tetragonal, space group $P4_12_12$, with $a = 12.703(1)$ Å, $b = 12.703(1)$ Å, $c = 30.473(3)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, and $R = 0.059$.

Introduction

The insertion of organic functionalities[1] into the V–C bonds of $[V(Mes)_3(THF)]$ ($Mes \equiv 2,4,6\text{-}Me_3C_6H_2$)[2] has been used for making novel vanadium(III) organometallic derivatives. Those compounds should serve to develop an organometallic chemistry of vanadium(III) and vanadium(II) in aprotic media without the limitations derived from the use of ancillary ligands such as cyclopentadienyl.[3] At the outset, we summarize the main points of the chemistry reported in this paper, which is the first paper of this series.

(i) The starting material $[V(Mes)_3(THF)]$[2,4] is easily accessible by our method and is thermally stable.

(ii) This is the first series of insertion reactions used for making novel starting materials in vanadium chemistry.

(iii) All the reactions reported are selective, high yield, and relatively large scale. In addition, they produce crystalline solids.

In this paper we explore the reactivity of $[V(Mes)_3(THF)]$ (1) with CO, isocyanides, CO_2, and CO_2 analogues. Preliminary communications[4,5] have described some of the compounds reported here.

Results and Discussion

Our starting material for studying the chemistry of the vanadium–carbon bond is complex 1, which is synthesized by a conventional method:

$$VCl_3(THF)_3 + 3(Mes)MgBr \xrightarrow[THF]{dioxane} \underset{1}{[V(Mes)_3(THF)]} \quad (1)$$

$$Mes = 2,4,6\text{-}Me_3C_6H_2$$

Complex 1 is thermally stable but very sensitive to oxygen and any protic source. Its structure, as determined by X-ray analysis, is shown in Figure 1. The coordination

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes 1, 2, 8, and 10

	1	2	8	10
formula	$C_{31}H_{41}OV$	$C_{42}H_{60}N_3V$	$C_{53}H_{53}N_4O_3V{\cdot}C_4H_{10}O$	$C_{53}H_{77}N_4V$
cryst syst	monoclinic	triclinic	triclinic	tetragonal
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P4_12_12$
cell params at 295 K[a]				
a, Å	8.472(2)	17.913(2)	14.710(1)	12.703(1)
b, Å	14.273(4)	13.697(2)	14.808(1)	12.703(1)
c, Å	22.385(6)	8.273(1)	13.267(1)	30.475(3)
α, deg	90	80.40(1)	69.06(1)	90
β, deg	97.64(3)	80.30(1)	73.16(1)	90
γ, deg	90	88.34(1)	81.37(1)	90
V, Å^3	2682.8(12)	1972.8(4)	2580.7(4)	4917.6(7)
Z	4	2	2	4
D_{calcd}, g cm^{-3}	1.190	1.108	1.183	1.109
mol wt	480.6	657.9	919.1	821.2
cryst dimens, mm	0.34 × 0.39 × 0.70	0.35 × 0.50 × 0.56	0.20 × 0.42 × 0.55	0.38 × 0.45 × 0.48
linear abs coeff, cm^{-1}	3.76	2.71	19.77	2.30
diffractometer	Philips PW 1100	Philips PW 1100	Siemens AED	Philips PW 1100
scan type	ω	$\omega/2\theta$	$\theta/2\theta$	$\omega/2\theta$
scan width, deg	1.00	b	b	b
radiation	c	c	d	c
2θ range, deg	5–48	6–46	6–140	6–50
unique total data	4210	5510	9807	4329
criterion for observn	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	1959	3758	7551	2955
no. of variables	298	411	498	264
overdeterminn ratio	6.6	9.1	15.2	11.2
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.057	0.070	0.062	0.059
$R_w = \sum w^{1/2}\lvert\Delta F\rvert/\sum w^{1/2}\lvert F_o\rvert$	0.060	0.070	0.068	0.059
GOF = $[\sum w\lvert\Delta F\rvert^2/(N_o - N_v)]^{1/2}$	1.37	1.59	1.72	2.00

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25–30 carefully centered reflections chosen from diverse regions of reciprocal space. [b] $(\theta - 0.6)$–$[\theta + (0.6 + \Delta\theta)]$; $\Delta\theta = [(\lambda\alpha_2 - \lambda\alpha_1)/\lambda] \tan\theta$. [c] Graphite-monochromated Mo Kα (λ = 0.710 69 Å). [d] Nickel-filtered Cu Kα (λ = 1.541 78 Å).

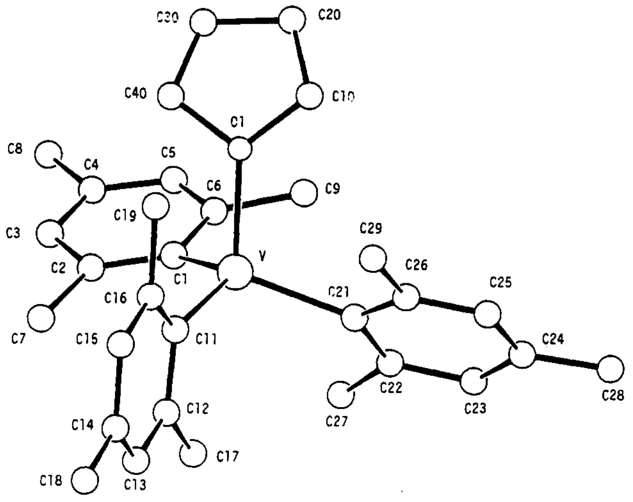
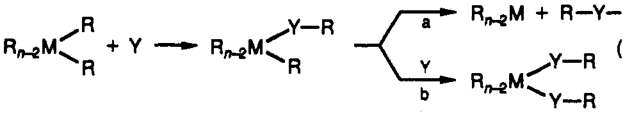


Figure 1. SCHAKAL[22] view of complex 1.

polyhedron is a trigonal pyramid with vanadium lying 0.482(1) Å from the plane through the σ-bonded carbon atoms, in the direction of the apical THF oxygen atom. The V–C bond distances compare well with those found in [V(Mes)$_4$].[6] The most relevant structural parameters are listed in Table VI. The THF is tightly bound to the metal and is not lost when 1 is recrystallized from toluene or benzene. Complex 1 has been used so far in three major classes of reactions: oxidations, reaction with protic ligands,[7] and insertion reactions.

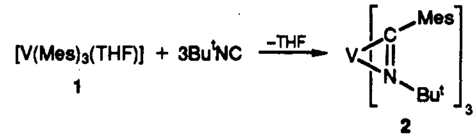
We took advantage of the presence of three V–C σ bonds in 1 to perform insertion reactions in order to prepare a variety of functionalized vanadium(III) organometallic derivatives.

Insertion reactions, when more than one migrating group is present on the metal, generally proceed through one of the two pathways in reaction 2: reductive elimination (a) or polyinsertion (b). Reaction 2b may have a limited preparative use, since it produces an uncontrolled mixture of mono-, di-, and polyinsertion compounds.


$$R_{n-2}M\langle{}^{R}_{R} + Y \longrightarrow R_{n-2}M\langle{}^{Y-R}_{R} \begin{cases} \xrightarrow{a} R_{n-2}M + R{-}Y{-}R \\ \xrightarrow[b]{Y} R_{n-2}M\langle{}^{Y-R}_{Y-R} \end{cases} \quad (2)$$

In the case of complex 1, the insertion reaction, depending on the inserting molecule, proceeded through either path a (carbon monoxide) or path b (isocyanides, CO_2, and CO_2 analogues). In the latter case, the di- or triinsertion products were obtained selectively.

(i) Reaction of [V(Mes)$_3$(THF)] (1) with CO and Bu^{t}NC. Vanadium tris(mesityl) undergoes reductive elimination when reacted with carbon monoxide, producing MesC(O)Mes and an inorganic fraction having a CO band at 1862 cm^{-1}, very probably belonging to [V(CO)$_6$].[8] The reaction of 1 with Bu^{t}NC, however, follows path b in reaction 2, and we found that insertion of isocyanide molecules occurs for all three V–C σ bonds[1,9] and the tris(iminoacyl) derivative 2 is produced exclusively.


$$\underset{\mathbf{1}}{[V(Mes)_3(THF)]} + 3Bu^tNC \xrightarrow{-THF} \underset{\mathbf{2}}{V\left[\eta^2\text{-}C(Mes){=}NBu^t\right]_3} \quad (3)$$

Complex 2, which still contains very reactive V–C bonds, is thermally stable and very reactive to oxygen and protic

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(8) [V(CO)$_6$]$^-$ is the most stable form of [V(CO)$_6$] and forms easily under many reductive conditions: Reference 3a, pp 648–651.

Table II. Fractional Atomic Coordinates (×10⁴) for Complex 1

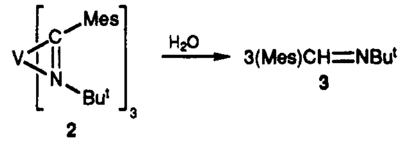
atom	*x/a*	*y/b*	*z/c*
V	6687.5(13)	2457.5(8)	553.1(5)
C1	7617(7)	2596(5)	−275(3)
C2	8315(8)	1867(4)	−570(3)
C3	8481(9)	1923(5)	−1187(3)
C4	8022(8)	2731(5)	−1515(3)
C5	7394(8)	3469(5)	−1226(3)
C6	7183(8)	3406(4)	−621(3)
C7	8936(9)	984(5)	−241(3)
C8	8227(10)	2807(6)	−2179(3)
C9	6421(10)	4247(5)	−365(3)
C11	7157(9)	1229(4)	1058(3)
C12	8703(8)	1147(5)	1360(3)
C13	9159(9)	428(5)	1759(3)
C14	8072(10)	−232(5)	1899(3)
C15	6506(10)	−200(5)	1595(3)
C16	6072(9)	526(5)	1183(3)
C17	9930(9)	1879(5)	1266(3)
C18	8541(11)	−1001(6)	2353(4)
C19	4345(10)	506(5)	885(4)
C21	6945(8)	3590(5)	1165(3)
C22	8097(8)	4316(5)	1188(3)
C23	8024(9)	5106(5)	1569(3)
C24	6802(9)	5177(5)	1928(3)
C25	5736(9)	4458(5)	1928(3)
C26	5804(8)	3674(5)	1573(3)
C27	9469(9)	4273(5)	819(3)
C28	6687(11)	6066(6)	2281(4)
C29	4656(10)	2888(5)	1645(3)
O1	4390(5)	2456(3)	106(2)
C10	3024(10)	3052(6)	188(4)
C20	2116(10)	3173(7)	−395(4)
C30	2738(13)	2453(8)	−790(4)
C40	3935(11)	1920(6)	−448(4)

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

atom	*x/a*	*y/b*	*z/c*
V	7264.2(6)	2438.6(7)	−208.0(13)
N1	7858(3)	3520(4)	−1970(6)
C1	8063(4)	4698(4)	−85(7)
C2	8711(4)	4597(4)	655(7)
C3	8978(4)	5385(5)	1219(8)
C4	8603(5)	6290(5)	1136(9)
C5	7954(5)	6367(5)	434(9)
C6	7678(4)	5612(5)	−192(8)
C7	9131(4)	3633(5)	801(9)
C8	8878(6)	7133(6)	1801(12)
C9	6977(4)	5754(5)	−990(10)
C10	7771(3)	3818(4)	−601(8)
C11	8299(5)	3936(5)	−3665(8)
N2	6177(3)	2567(4)	−629(6)
C21	5446(3)	2493(4)	2207(7)
C22	5268(4)	3372(4)	2828(7)
C23	4603(4)	3428(5)	3952(8)
C24	4127(4)	2617(6)	4526(8)
C25	4341(4)	1746(5)	4004(9)
C26	5003(4)	1654(5)	2854(8)
C27	5779(4)	4264(5)	2274(9)
C28	3400(4)	2715(7)	5691(10)
C29	5195(4)	684(5)	2297(10)
C30	6135(3)	2471(4)	951(8)
C31	5631(4)	2753(5)	−1809(8)
C32	5833(5)	2077(6)	−3019(11)
C33	5782(5)	3792(6)	−2705(11)
C34	4830(5)	2664(10)	−995(11)
N3	7694(3)	1246(3)	1092(6)
C41	8177(4)	263(4)	−1160(7)
C42	7730(4)	−448(4)	−1518(7)
C43	8063(5)	−1188(5)	−2358(8)
C44	8834(5)	−1228(6)	−2869(9)
C45	9270(4)	−493(6)	−2535(9)
C46	8969(4)	256(5)	−1707(8)
C47	6874(4)	−447(5)	−1000(10)
C48	9169(6)	−2057(7)	−3726(11)
C49	9471(4)	1034(6)	−1381(10)
C50	7821(3)	1097(4)	−401(7)
C51	7817(4)	643(5)	2714(8)
C12A[a]	7720(7)	4033(9)	−4907(16)
C13A	8876(7)	3109(9)	−4140(15)
C14A	8723(7)	4887(10)	−3726(16)
C12B	8225(19)	3179(25)	−4622(40)
C13B	9161(18)	4185(23)	−3438(37)
C14B	7963(17)	4982(22)	−4189(36)
C52A	8178(8)	−378(9)	2509(14)
C53A	8362(8)	1248(10)	3430(17)
C54A	7036(8)	512(11)	3850(17)
C52B	7569(15)	−472(17)	2753(28)
C53B	8633(13)	765(17)	2826(28)
C54B	7255(12)	1088(18)	4062(27)

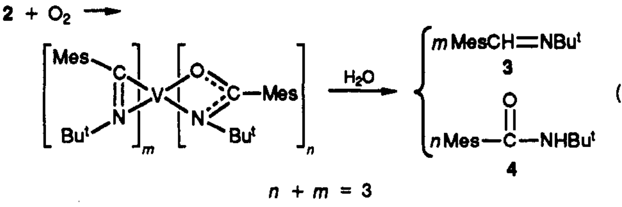
[a] The site occupation factors for the disordered methyl carbon atoms are as follows: 0.7140 and 0.2860 for C12, C13, and C14, A and B, respectively; 0.6302 and 0.3698 for C52, C53, and C54, A and B, respectively.

sources. Hydrolysis of **2** and H_2O (see the Experimental Section) produced in good yield the corresponding imine **3**.



(4)

The reaction of **2** in the air gave a mixture of **3** and **4**, as a result of oxygen insertion into some V–C bonds followed by hydrolysis of the resulting amido ligands and the unchanged iminoacyl groups.



(5)

Exhaustive oxidation of **2** using dry oxygen gave a mixture of compounds other than the expected amido derivative [V{O—C(Mes)=NBu^t}$_3$]. A homoleptic tris(amido) derivative was obtained (vide infra) via the insertion of alkyl and aryl isocyanates into the V=C bonds.

Complex **2** is paramagnetic with a μ_{eff} value of 2.60 μ_β at 288 K. The ν(C=N) band at 1566 cm^{-1} is in agreement with the η^2-bonding mode of the iminoacyl group. Complex **2** has a remarkable chemistry which will be reported in ensuing papers. Examples of homoleptic tris(η^2-iminoacyl) derivatives are rare[10] and have only been obtained in the presence of an ancillary ligand; the insertion of isocyanides into metal–aryl bonds has been reported.[9]

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Table IV. Fractional Atomic Coordinates ($\times 10^4$) for Complex 8

atom	x/a	y/b	z/c
V	1616.3(3)	2331.7(3)	866.8(4)
O1	1204(2)	3748(1)	900(2)
N1	1022(2)	2557(2)	2457(2)
C1	484(1)	4250(1)	2490(2)
C2	−373(1)	4750(1)	2327(2)
C3	−721(1)	5506(1)	2753(2)
C4	−213(1)	5761(1)	3342(2)
C5	644(1)	5261(1)	3504(2)
C6	992(1)	4505(1)	3078(2)
C7	−939(3)	4494(3)	1690(3)
C8	−575(4)	6607(3)	3759(4)
C9	1926(3)	3996(3)	3241(3)
C10	895(2)	3489(2)	1959(2)
C11	648(2)	2042(1)	3605(1)
C12	1207(2)	1279(1)	4143(1)
C13	848(2)	724(1)	5257(1)
C14	−69(2)	933(1)	5832(1)
C15	−628(2)	1696(1)	5294(1)
C16	−269(2)	2251(1)	4181(1)
O2	2196(1)	3172(1)	−760(2)
N2	3050(2)	2654(2)	452(2)
C21	3696(1)	3906(1)	−1421(1)
C22	3908(1)	4701(1)	−1217(1)
C23	4550(1)	5359(1)	−2035(1)
C24	4981(1)	5221(1)	−3058(1)
C25	4769(1)	4426(1)	−3263(1)
C26	4127(1)	3768(1)	−2445(1)
C27	3441(3)	4890(3)	−118(4)
C28	5671(3)	5938(3)	−3948(4)
C29	3934(3)	2899(3)	−2682(3)
C30	2993(2)	3210(2)	−549(2)
C31	3854(1)	2477(2)	887(2)
C32	4786(1)	2440(2)	242(2)
C33	5543(1)	2239(2)	737(2)
C34	5369(1)	2077(2)	1877(2)
C35	4437(1)	2114(2)	2522(2)
C36	3680(1)	2315(2)	2027(2)
O3	1761(2)	928(2)	1913(2)
N3	2015(2)	1173(2)	148(2)
C41	2280(1)	−503(1)	1428(2)
C42	3120(1)	−864(1)	1755(2)
C43	3353(1)	−1857(1)	2065(2)
C44	2747(1)	−2488(1)	2049(2)
C45	1907(1)	−2127(1)	1723(2)
C46	1674(1)	−1134(1)	1412(2)
C47	3813(3)	−185(3)	1734(4)
C48	3017(4)	−3562(3)	2326(5)
C49	767(3)	−770(3)	1047(3)
C50	2028(2)	553(2)	1123(2)
C51	2323(1)	983(2)	−869(1)
C52	1778(1)	1389(2)	−1642(1)
C53	2066(1)	1241(2)	−2672(1)
C54	2898(1)	686(2)	−2929(1)
C55	3442(1)	280(2)	−2156(1)
C56	3155(1)	428(2)	−1126(1)
N61	180(2)	2279(2)	829(2)
C62	−436(3)	1640(3)	1627(3)
C63	−1385(3)	1701(4)	1607(4)
C64	−1695(3)	2420(5)	784(5)
C65	−1077(3)	3071(3)	−24(4)
C66	−143(2)	2975(3)	23(3)
O1S	6413(8)	2168(10)	4452(9)
C1S	7069(7)	3544(7)	4526(8)
C2S	7087(10)	2898(11)	4040(11)
C3S	6607(13)	1231(15)	4929(15)
C4S	5730(11)	778(10)	5221(11)

The structure of **2** is given in Figure 2, and a selection of bond distances and angles is reported in Table VII. All three iminoacyl groups are η^2-bonded, giving a formally six-coordinated vanadium complex. The dihedral angles between adjacent V,C,N planes are as follows: V,N1,C10 $\wedge$ V,N2,C10, 69.1(2)°; V,N1,C10 $\wedge$ V,N3,C50, 54.5(3)°; V,N2,C30 $\wedge$ V,N3,C50, 58.9(2)°. The coordination polyhedron is a flattened trigonal prism, the dihedral angle between the N1,N2,C50 and C10,C30,N3 bases being 0.5(2)°. The vanadium atom lies approximately at the center of the prism, which shows slight distortion, the two bases being rotated by ca. 4°. The structure can alternatively be viewed as pseudo trigonal planar with each of the iminoacyl groups occupying a single coordination site. For very bulky ligands a trigonal-planar geometry was observed. The phenyl rings are nearly perpendicular to the V,C,N planes, the dihedral angles being 81.9(3)° for C1⋯C6 $\wedge$ V,N1,C10, 81.6(3)° for C21⋯C26 $\wedge$ V,N2,C30, and 84.2(3)° for C41⋯C46 $\wedge$ V,N3,C50.

Table V. Fractional Atomic Coordinates ($\times 10^4$) for Complex 10

atom	x/a	y/b	z/c
V	158.0(5)	158.0(5)	0(-)
N1	533(3)	−331(3)	655(1)
N2	−1057(3)	68(3)	424(1)
C1	1343(3)	1343(3)	0(0)
C2	1137(4)	2357(4)	150(2)
C3	1908(5)	3144(5)	146(2)
C4	2916(4)	2916(4)	0(0)
C7	61(5)	2666(4)	344(2)
C8	3774(4)	3774(4)	0(0)
C10	−456(3)	−230(4)	768(2)
C11	−878(4)	−388(4)	1225(2)
C12	−1198(4)	449(4)	1485(2)
C13	−1568(4)	249(5)	1906(2)
C14	−1612(5)	−769(5)	2078(2)
C15	−1313(5)	−1581(5)	1811(2)
C16	−949(4)	−1424(4)	1385(2)
C17	−1154(5)	1572(5)	1321(2)
C18	−1985(6)	−964(6)	2544(3)
C19	−616(5)	−2361(4)	1117(2)
C21	−2225(3)	98(4)	448(2)
C22	−2680(5)	−994(6)	418(3)
C23	−3890(6)	−974(7)	419(4)
C24	−4297(5)	−295(6)	58(3)
C25	−3848(5)	803(5)	84(3)
C26	−2633(4)	787(5)	90(2)
C31	1375(4)	−440(4)	983(2)
C32	2258(4)	−1131(5)	789(2)
C33	3180(5)	−1212(6)	1112(2)
C34	3591(5)	−143(7)	1238(2)
C35	2732(5)	545(5)	1424(2)
C36	1819(5)	641(5)	1106(2)

Table VI. Selected Bond Distances (Å) and Angles (deg) for Complex 1

V–C1	2.117(7)	V–C21	2.111(7)
V–C11	2.095(6)	V–O1	2.067(4)
C21–V–O1	108.9(2)	V–C11–C16	128.2(5)
C11–V–O1	111.1(2)	V–C11–C12	115.4(4)
C11–V–C21	107.1(3)	C12–C11–C16	115.9(6)
C1–V–O1	90.7(2)	V–C21–C26	117.5(5)
C1–V–C21	118.6(3)	V–C21–C22	126.4(5)
C1–V–C11	119.0(3)	C22–C21–C26	116.0(6)
V–C1–C6	117.1(4)	V–O1–C40	122.4(4)
V–C1–C2	124.8(5)	V–O1–C10	130.3(4)
C2–C1–C6	116.3(6)	C10–O1–C40	106.6(6)

The observed structural parameters imply only a slight contribution by an iminocarbene resonance form. This may be a key point in understanding the difference between the reactions of **1** with carbon monoxide and isocyanides. Vanadium, which is an oxophilic metal, should favor carbenoid character in the acyl via the η^2 interaction rather than in the iminoacyl. The migration of a second alkyl or aryl group is much easier to a carbenoid carbon than to a normal sp^2 carbon.[1] The reductive elimination of MesC(O)Mes and the formation of a vanadium carbonyl species as seen in the reaction with carbon monoxide can be understood on the basis of the intermediacy of a

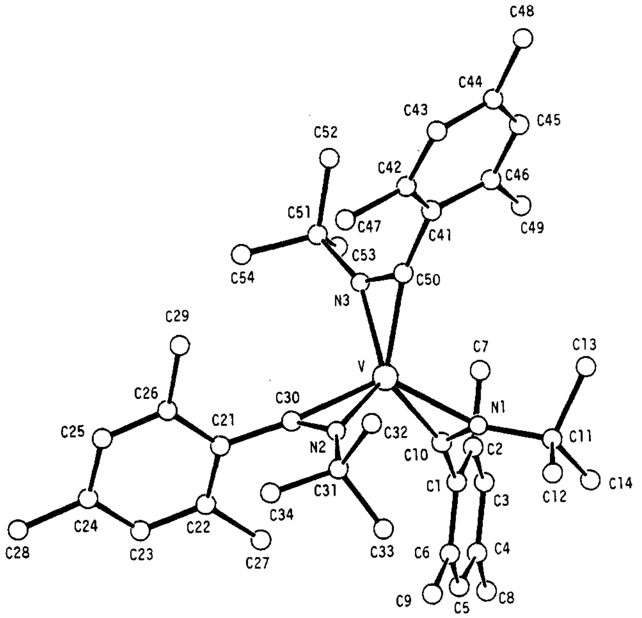


Figure 2. SCHAKAL[22] view of complex 2.

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

V–N1	2.073(5)	C1–C10	1.480(9)
V–C10	2.072(6)	N2–C30	1.280(8)
V–N2	2.032(5)	N2–C31	1.483(9)
V–C30	2.090(6)	C21–C30	1.476(8)
V–N3	2.009(5)	N3–C50	1.268(8)
V–C50	2.082(6)	N3–C51	1.500(8)
N1–C10	1.251(9)	C41–C50	1.472(8)
N1–C11	1.517(8)		
N3–V–C50	36.0(2)	C10–N1–C11	132.2(6)
C30–V–C50	120.7(2)	N1–C10–C1	132.0(6)
C30–V–N3	103.7(2)	V–C10–C1	155.0(5)
N2–V–C50	118.2(2)	V–C10–N1	72.5(4)
N2–V–N3	124.9(2)	V–N2–C31	149.8(4)
N2–V–C30	36.2(2)	V–N2–C30	74.4(3)
C10–V–C50	126.1(2)	C30–N2–C31	135.6(5)
C10–V–N3	121.7(2)	N2–C30–C21	127.5(5)
C10–V–C30	111.9(2)	V–C30–C21	162.9(4)
C10–V–N2	110.7(2)	V–C30–N2	69.4(3)
N1–V–C50	107.7(2)	V–N3–C51	150.9(4)
N1–V–N3	127.2(2)	V–N3–C50	75.1(3)
N1–V–C30	128.1(2)	C50–N3–C51	133.7(5)
N1–V–N2	105.1(2)	N3–C50–C41	131.8(5)
N1–V–C10	35.1(2)	V–C50–C41	159.3(4)
V–N1–C11	154.9(4)	V–C50–N3	68.8(3)
V–N1–C10	72.4(4)		

[V(η-COMes)] species having an acyl group with significant carbenoid character.

(ii) Reaction of 1 with CO_2 and CO_2 Analogues. Reaction of M—C functionalities with CO_2 and CO_2-like cumulenes deserves a great deal of attention in the context of carbon dioxide activation by transition metals.[11] In the case of 1 these reactions were expected to produce novel organometallic and coordination complexes of vanadium(III).

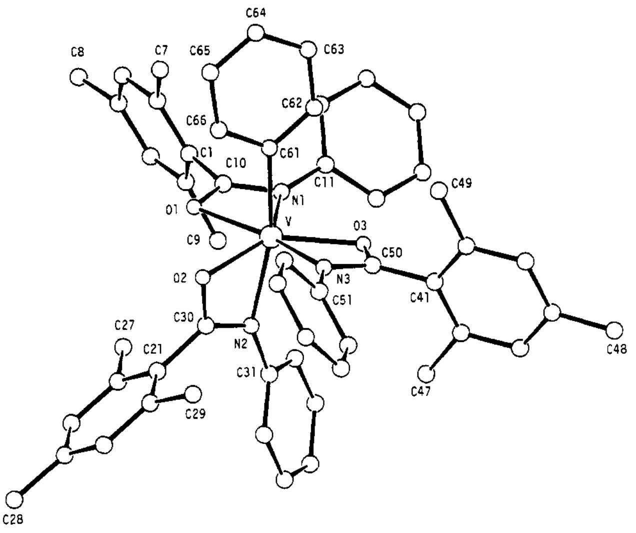


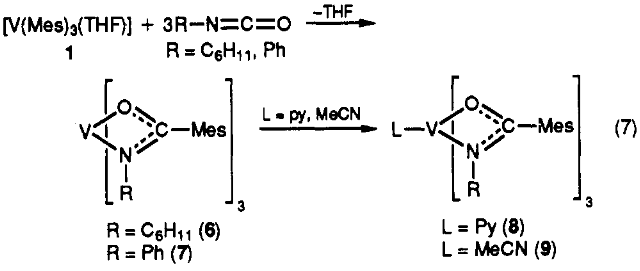
Figure 3. SCHAKAL[22] view of complex 8.

The reaction of 1 with carbon dioxide gave a high yield of a poorly soluble green solid, the analysis of which is in agreement with the tris(carboxylato) derivative 5.

$$\underset{1}{[V(Mes)_3(THF)]} + 3CO_2 \xrightarrow{-THF} \underset{5}{(1/n)[V(O_2CMes)_3]_n} \qquad (6)$$

The use of isocyanates[12] for mimicking the chemistry of CO_2 is a well-known approach, and the reactivity of 1 with isocyanates parallels that of 1 with CO_2.

Reaction 7 proceeds via path b of reaction 2, with the insertion of the isocyanate groups into all three V—C bonds forming tris(carboxamido) derivatives of vanadium(III).



Complexes 6 and 7 dissolve in hydrocarbons, giving green solutions, which become red upon addition of any coordinating agent. The pyridine and acetonitrile adducts 8 and 9 have been isolated as red crystalline solids. Complexes 6–9 have the normal paramagnetic behavior expected for a d^2 high-spin system (see Experimental Section). The structure of 8 is shown in Figure 3, and a list of selected bond distances and angles is reported in Table VIII. The bonding mode of the carboxamido ligand in 8 supports the structures proposed for 6, 7, and 9. The coordination polyhedron can be defined as a distorted pentagonal bipyramid with the N1, O1, O2, N3, and O3 atoms defining the equatorial plane and the N2 and N6 atoms occupying the apical positions. The maximum displacement of atoms from the mean equatorial plane is −0.329(3) Å for O3. The value of the N2–V–N61 angle (164.0(1)°) indicates a distortion of the bipyramid. We did not find anything peculiar in the V–O and V–N bond distances, except in the difference between equatorial and axial V–N distances. The corresponding bond distances

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[11] The use of CO_2-like molecules for mimicking the carbon dioxide behavior is well-known: Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, FRG, 1988. Darensbourg, D.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 4740. Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165. Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173. Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 792.

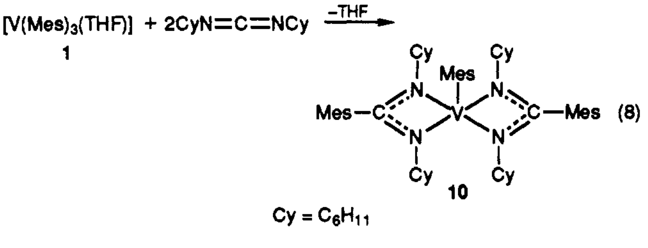
[12] Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927.

Table VIII. Selected Bond Distances (Å) and Angles (deg) for Complex 8

V–O1	2.106(2)	O2–C30	1.295(4)
V–N1	2.162(3)	N2–C30	1.307(3)
V–O2	2.065(2)	N2–C31	1.413(4)
V–N2	2.102(3)	O3–C50	1.293(4)
V–O3	2.066(3)	N3–C50	1.295(3)
V–N3	2.177(3)	N3–C51	1.408(4)
V–N61	2.142(3)	C1–C10	1.499(4)
O1–C10	1.275(3)	C21–C30	1.498(3)
N1–C10	1.311(4)	C41–C50	1.486(3)
N1–C11	1.419(3)		
N1–V–N3	140.8(1)	N2–C30–C21	128.3(3)
N1–V–O3	80.9(1)	O2–C30–C21	117.9(2)
N1–V–N2	103.8(1)	O2–C30–N2	113.7(3)
N1–V–O2	136.8(1)	V–O3–C50	95.1(2)
O1–V–N3	157.0(1)	V–N3–C51	143.4(2)
O1–V–O3	141.5(1)	V–N3–C50	90.0(2)
O1–V–N2	89.5(1)	C50–N3–C51	125.8(3)
O1–V–O2	77.5(1)	N3–C50–C41	128.4(2)
O1–V–N1	60.8(1)	O3–C50–C41	118.1(2)
N2–V–N61	164.0(1)	O3–C50–N3	113.4(3)

and angles within the three chelation rings are not significantly different from each other. The O–C and N–C sp^2 bond distances indicate a double-bond character. The chelation rings are nearly planar, with the greatest displacement (0.258(1) Å) being observed for the N2–C30–O2 ring containing the apical nitrogen atom. The dihedral angles (deg) between the chelation rings are as follows: N1···O1 ∧ N2···O2, 91.2(3); N1···O1 ∧ N3···O3, 12.5(2); N2···O2 ∧ N3···O3, 85.8(3). These values are consistent with a pentagonal pyramid. Pyridine occupies the seventh coordination site, and vanadium lies 0.201(1) Å from the plane of pyridine. The orientations of the mesityl groups are indicated by the dihedral angles (deg) they form with the corresponding chelation rings: C1···C6 ∧ N1···O1, 68.9(1); C21···C26 ∧ N2···O2, 65.6(1); C41···C46 ∧ N3···O3, 71.1(1). The dihedral angles (deg) the phenyl rings form with the chelation rings are as follows: C11···C16 ∧ N1···O1, 46.6(1); C31···C36 ∧ N2···O2, 29.7(1); C51···C36 ∧ N3···O3, 48.0(1).

The use of dicyclohexylcarbodiimide as the inserting group in the reaction with 1 is different from the previous cases in two ways: there is no oxygen atom available to interact with the oxophilic metal, and a significant steric hindrance is present.


$[V(Mes)_3(THF)]$ + 2CyN=C=NCy $\xrightarrow{-THF}$ (8)

1

10

Cy = C_6H_{11}

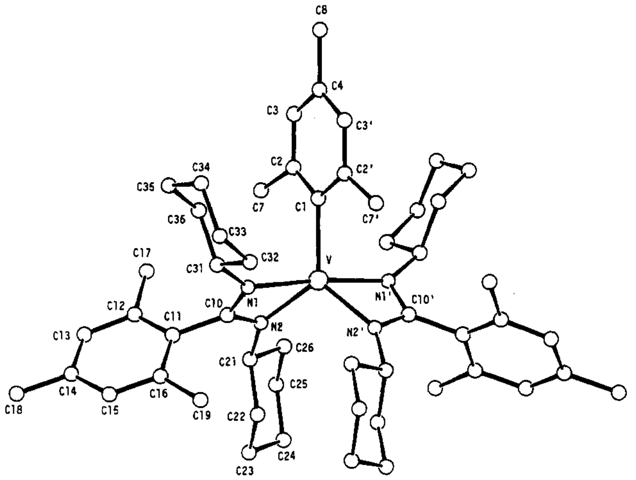


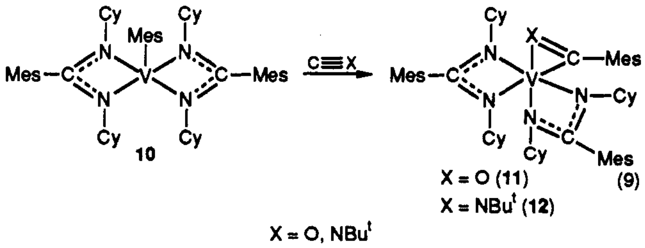
Figure 4. SCHAKAL[22] view of complex **10**. The prime indicates a transformation of *x*, *y*, −*z*.

Table IX. Selected Bond Distances (Å) and Angles (deg) for Complex 10

V1–N1	2.143(4)	N2–C10	1.351(6)
V1–N2	2.016(4)	N2–C21	1.485(5)
V1–C1	2.129(4)	C10–C11	1.506(7)
N1–C10	1.309(6)	C11–C12	1.387(7)
N1–C31	1.472(6)		
N2–V1–C1	125.5(1)	C10–N2–C21	122.3(4)
N2–V1–N2′[a]	108.9(1)	N1–C10–N2	111.4(4)
N1′–V1–C1	92.7(1)	N2–C10–C11	123.6(4)
N1′–V1–N2	112.8(1)	N1–C10–C11	124.9(4)
N1–V1–C1	92.7(1)	C10–C11–C16	117.9(4)
N1–V1–N2	63.7(1)	C10–C11–C12	122.1(4)
N1–V1–N1′	174.5(1)	C12–C11–C16	120.0(5)
V1–N1–C31	145.3(3)	N2–C21–C26	109.0(4)
V1–N1–C10	90.2(3)	N2–C21–C22	110.9(4)
C10–N1–C31	121.8(4)	N1–C31–C36	110.4(4)
V1–N2–C21	142.6(3)	N1–C31–C32	108.8(4)
V1–N2–C10	94.6(3)		

[a] The prime indicates the symmetry transformation *y*, *x*, −*z*.

Regardless of the stoichiometric ratio used, only two carbodiimide molecules insert into the V—Mes bonds of 1. The exhaustive hydrolysis of **10** in acid solution gave mesitylene and CyN=C(Mes)]—NHCy (as reported in the Experimental Section) The molecule has an imposed crystallographic C_2 symmetry (Figure 4 and Table IX) and the coordination polyhedron is a distorted trigonal bipyramid with vanadium lying on the equatorial plane defined by C1, N2, and N2′. The N1–V–N1′ angle is 174.5(1)°, and the V–N1 bond forms an angle of 30.8(1)° with the normal to the equatorial plane. This angle describes the major distortion of the bipyramid and has to be related to the narrow N···N bite (N1···N2, 2.198(5) Å). The axial V–N1 distances are significantly longer than the equatorial V–N2 ones (Table IX). This suggests a nonsymmetric π delocalization over the N–C–N unit. The coordinated mesityl ligand is rotated around the V–C bond to form a dihedral angle of 29.7(1)° with the equatorial N2,N2′,C,V plane. Vanadium lies exactly in the plane of the aromatic ring for reasons of symmetry. The mesityl substituents at the carbodiimide ligands are twisted with respect to the chelation rings by 72.0(2)°. A comparative study of Cp_2V–R and **10** should provide information on the role of ancillary ligands in the chemistry of the V–C functionality.[13] The reactivity of the V–C bond in **10** was explored using CO and Bu^{t}NC:


$\xrightarrow{C\equiv X}$ (9)

10

X = O (11)

X = NBu^t (12)

X = O, NBu^t

Complexes **11** and **12** have been isolated as crystalline solids in good yield. The structure we propose is essentially based on the analytical and IR evidence presented in the

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(13) See ref 3a, p 677.

Experimental Section; i.e, the absence of any C═X bond above 1650 cm^{-1} favors an η^2-bonding mode for the acyl 11 and the iminoacyl 12.

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. $VCl_3(THF)_3$[14] was prepared as reported. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, and ^1H NMR spectra were measured on a Bruker 200-AC instrument. Magnetic measurements were carried out with a Faraday balance.

Preparation of 1. A suspension of $VCl_3(THF)_3$ (29.31 g, 78.45 mmol) in THF (800 mL) was cooled to −40 °C. Then, a solution of MesMgBr (166 mL, 1.45 N in THF, 240.6 mmol) was added dropwise to the stirred suspension of $VCl_3(THF)_3$. The addition took 1 h and the solution became brown. The temperature was allowed to rise to room temperature; then, the solution was stirred for 2 h and became blue. Upon addition of dioxane (130 mL) white magnesium salts precipitated. The resulting suspension was stirred for 30 min at room temperature and then heated to 50 °C and filtered. A blue solution was obtained, which was concentrated to 300 mL and cooled to −30 °C. Blue crystals of $[V(Mes)_3(THF)]$ were obtained (22.6 g, 60%). An additional amount of product was obtained upon concentration of the mother liquor, but recrystallization was needed on this fraction in order to eliminate traces of the MgBrCl·dioxane adduct. Anal. Calcd for $C_{31}H_{41}OV$: C, 77.47; H, 8.60. Found: C, 77.31; H, 8.61. $\mu_{eff} = 2.65\ \mu_\beta$ at 293 K.

Reaction of 1 with CO. A THF (100 mL) solution of 1 (2.07 g, 4.3 mmol) was treated with CO in excess at room temperature. The color suddenly turned to brown. After 1 h, the solvent was evaporated to dryness and the residue treated with *n*-hexane (300 mL). A colorless solution and a black precipitate were obtained. From the solution, filtered and concentrated, a white crystalline solid corresponding to MesC(O)Mes separated (0.66 g, 40%). The black precipitate is a pyrophoric material, with an IR band at 1862 cm^{-1} (THF solution) (cf. 1859 cm^{-1} (THF solution) for $V(CO)_6^-$).[15] A total of 0.64 g of this compound was obtained.

Reaction of 1 with Bu^{t}NC: Synthesis of 2. To a THF (200 mL) solution of 1 (5.81 g, 12.11 mmol) was added Bu^{t}NC (4.10 mL, 36.29 mmol) dropwise. The mixture was stirred at room temperature for 5 h, and the color changed from blue to dark green. Then, the solvent was evaporated to dryness and the residue was washed with *n*-hexane (60 mL). Crystals suitable for X-ray analysis were obtained by recrystallization from *n*-hexane (5.26 g, 66%). Anal. Calcd for $C_{42}H_{60}N_3V$: C, 76.68: H, 9.19; N, 6.39. Found: C, 76.56; H, 9.02; N, 6.41. $\mu_{eff} = 2.60\ \mu_\beta$ at 288 K. ν(C═N) (Nujol): 1566 cm^{-1}. The complex is very soluble in toluene and THF and stable at room temperature.

Hydrolysis of 2. A THF (50 mL) solution of 1 (0.97 g, 1.47 mmol) was reacted with H_2O (9 μL, 0.5 M in THF). The color suddenly turned red. The solution was stirred for 30 min at room temperature. Then, the solvent was evaporated to dryness. *n*-Hexane (100 mL) was added, yielding a black precipitate and a colorless solution. The solution was filtered and concentrated under vacuum, giving MesCH═NBu^t as a colorless oil (0.62 g, 69%). NMR and IR spectra are in agreement with the proposed formula.

Oxidation of 2. When a THF solution of 2 was exposed to the air for 4 h, decomposition occurred. After filtration, extraction with *n*-hexane, and crystallization, MesC(O)—NHBu^t was isolated in 50% yield. The product MesCH═NBu^t, resulting from the direct protonation by water in the air, was also detected in 20% yield.

Reaction of 1 with Carbon Dioxide: Synthesis of 5. A THF (100 mL) solution of 1 (2.12 g, 4.42 mmol) was kept under a CO_2 atmosphere for 12 h at room temperature. A green solid formed, which was collected by filtration and washed with THF (1.9 g, 79.5%). Anal. Calcd for $C_{30}H_{33}O_6V$: C, 66.66; H, 6.15. Found: C, 66.52; H, 6.13. $\mu_{eff} = 2.60\ \mu_\beta$ at 293 K. The complex is very slightly soluble in THF or pyridine and stable to the air for days. The carboxylato group shows a strong and broad band (Nujol) at 1530 cm^{-1}.

Reaction of 1 with CyNCO: Synthesis of 6. To a THF (150 mL) solution of 1 (2.8 g, 5.83 mmol) was added CyNCO (2.22 mL, 17.5 mmol) at room temperature, and the color suddendly changed to light green. The solution was stirred for 30 min; then the solvent was evaporated to dryness. The residue was redissolved in *n*-hexane (75 mL), and from the solution, after filtration and concentration, a light green crystalline solid was obtained (3.66 g, 80%). Anal. Calcd for $C_{48}H_{66}N_3O_3V$: C, 73.54; H, 8.48; N, 5.36. Found: C, 73.49; H, 8.40; N, 5.35. $\mu_{eff} = 2.79\ \mu_\beta$ at 293 K.

A THF (30 mL) solution of the product $[V\{CyNC(Mes)O\}_3]$ (0.28 g, 0.357 mmol) was exposed to the air for 4 h. A black solid precipitated, and a colorless solution was obtained, which was filtered and evaporated to dryness. White crystals of Cy(H)-N—C(O)—Mes were obtained (0.24 g, 91%).

Reaction of 1 with PhNCO: Synthesis of 7. When a THF (80 mL) solution of 1 (2.62 g, 5.46 mmol) was treated with PhNCO (1.8 mL, 16.54 mmol) at room temperature, a pale red solution was obtained. The solution was stirred for 30 min at room temperature; then the solvent was evaporated to dryness and the residue heated under vacuum at 50 °C. A green solid was obtained, which was recrystallized from *n*-hexane, giving a green crystalline product (3.7 g, 88.5%). Anal. Calcd for $C_{48}H_{48}N_3O_3V$: C, 75.28; H, 6.32; N, 5.49. Found: C, 75.03; H, 6.45; N, 5.30. $\mu_{eff} = 2.72\ \mu_\beta$ at 293 K.

Synthesis of $[(L)V\{PhNC(Mes)O\}_3]$ (L = py, 8; L = MeCN, 9). To a *n*-hexane (50 mL) solution of 7 (0.62 g, 4.96 mmol) was added pyridine (0.4 mL, 4.96 mmol), and a yellow crystalline solid suddenly formed, which was collected by filtration and dried (0.55 g, 80%). The product can be recrystallized from diethyl ether. Anal. Calcd for $C_{53}H_{53}N_4O_3V$: C, 75.34; H, 6.32; N, 6.63. Found: C, 75.00; H, 6.03; N, 7.18. $\mu_{eff} = 2.51\ \mu_\beta$ at 293 K.

To a *n*-hexane (80 mL) solution of 7 (0.85 g, 1.12 mmol) was added MeCN (0.5 mL, 9.5 mmol). A yellow crystalline solid suddenly formed, which was collected by filtration and dried (0.78 g, 89%). Anal. Calcd for $C_{50}H_{51}N_4O_3V$: C, 74.42; H, 6.37; N, 6.94. Found: C, 74.64; H, 6.42; H, 7.05. $\mu_{eff} = 2.61\ \mu_\beta$ at 288 K. ν(CN) (Nujol): 2286 cm^{-1}. The solution is green in noncoordinating solvents, but it turns red in ligating solvents such as THF. Evaporation of a THF solution to dryness gave back the green unsolvated starting material.

Reaction of 1 with Dicyclohexylcarbodiimide: Synthesis of 10. Dicyclohexylcarbodiimide (2.15 g, 10.42 mmol) was added to a THF (150 mL) solution of 1 (2.44 g, 5.08 mmol) at room temperature. The resulting orange solution was stirred for 30 min at room temperature and then evaporated to dryness. An orange residue was obtained, which was dissolved in *n*-hexane (150 mL), and the solution was filtered. From the solution, upon concentration, an orange product separated (3.67 g, 88%). The same compound is obtained when an excess of carbodiimide is used. The complex is very soluble in THF or toluene and less soluble in *n*-hexane or diethyl ether. A strong broad band was observed for the N═C═N fragment at 1509 cm^{-1} in the IR spectrum. Anal. Calcd for $C_{53}H_{77}N_4V$: C, 77.52; H, 9.45; N, 6.82. Found: C, 77.39; H, 9.50; N, 6.86. $\mu_{eff} = 2.49\ \mu_\beta$ at 293 K.

Hydrolysis of 10. Complex 10 (0.10 g) was dissolved in $CDCl_3$ (0.4 mL); then aqueous HCl (32%, 0.05 mL) was added. The solution was stirred for 5 min and then introduced into an NMR tube. The NMR spectrum showed the presence of mesitylene and $[Mes—C(NHCy)_2]^+$ in a 1/2 ratio. This solution, treated with NaOH in excess, gave CyN═C(Mes)—NHCy, detected in the NMR spectrum. The same product was obtained when a solution of 10 (0.10 g) in *n*-hexane (30 mL) was allowed to decompose in the air overnight. The organic material crystallized upon concentration of the solution.

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Reaction of 10 with CO: Synthesis of 11. A THF (75 mL) solution of **10** (1.19 g, 1.45 mmol) was treated with CO in excess at room temperature. The resulting green solution was stirred for 30 min; then the solvent was evaporated to dryness, the residue extracted with *n*-hexane (30 mL), and the solution filtered. Concentration and cooling of the solution at −30 °C gave a green solid (1.0 g, 81%). Anal. Calcd for $C_{54}H_{77}N_4OV$: C, 76.38: H, 9.14: N, 6.60. Found: C, 76.59; H, 10.04; N, 6.27. $\mu_{eff} = 2.76\ \mu_B$ at 293 K. ν(CO) (Nujol): 1640 cm^{-1} (m). $\nu(CN_2)$ (Nujol): 1509 cm^{-1}.

Reaction of 10 with Bu^{t}NC: Synthesis of 12. Bu^{t}NC (0.23 mL, 2.03 mmol) was added to a THF (100 mL) solution of **10** (1.62 g, 1.97 mmol). The resulting yellow solution was stirred for 1 h and then evaporated to dryness, the residue redissolved in *n*-hexane (50 mL), and the solution filtered. Concentration and cooling of the solution gave a yellow crystalline product (1.26 g, 71%). Anal. Calcd for $C_{58}H_{86}N_5V$: C, 77.04; H, 9.59; N, 7.74. Found: C, 77.30; H, 9.83; N, 7.50. $\mu_{eff} = 2.56\ \mu_B$ at 293 K. $\nu(CN_2)$ (Nujol): 1500 cm^{-1}(s).

Crystal Structure Determination of Complexes 1, 2, 8, and 10. The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[16] Crystal data and details associated with data collection are given in Table I. The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[17] and the absolute scale was established by the Wilson method.[18] No correction for absorption was applied. The function minimized during the full-matrix least-squares refinement was $\sum w|\Delta F|^2$ with unit weights for complexes **2** and **10**. For complexes **1** and **8** a weighting scheme based on counting statistics[17] was applied. Scattering factors for neutral atoms were taken from ref 19a for non-hydrogen atoms and from ref 20 for H. Anomalous scattering corrections were included in all structure factor calculations.[19b] Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Solution and refinement were based on the observed reflections. The structures of complexes **1** and **2** were solved by the heavy-atom method, starting from a three-dimensional Patterson map. The structures of complexes **8** and **10** were solved by direct methods using SHELX-76[17] and SHELX-86,[21] respectively. Refinement was done first isotropically and then anisotropically for all the non-H atoms except the C12, C13, C14, C52, C53, and C54 methyl carbons for the two *tert*-butyl groups in complex **2** and the diethyl ether solvent of crystallization in complex **8**. The methyl carbons were found to be disordered over two positions (A and B) isotropically refined with site occupation factors given in Table IV. The abnormally high values reached by the thermal parameters of the diethyl ether atoms (complex **8**) could not be explained in terms of statistical distribution, attempts to split these atoms into "partial" atoms being unsuccessful. Refinement was then carried out isotropically for them. The hydrogen atoms associated with these groups were ignored as well as those associated with the C8 methyl carbons (complex **2**), which have to be considered as disordered for symmetry requirements, the C8 carbon lying on a crystallographic 2-fold axis. All the other hydrogen atoms for complexes **1**, **2**, **8**, and **10**, 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. During the refinement of complex **8** all the phenyl and mesityl rings were constrained to be regular hexagons (C=C = 1.395 Å). In the final cycle of refinement no parameter shifted by more than 0.1 times its standard deviation. The final difference maps showed no unusual features, with no significant peak above the general background.

Final atomic coordinates are listed in Tables II–V for non-H atoms and selected interatomic distances and angles in Tables VI–IX.

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Supplementary Material Available: Listings of unrefined hydrogen coordinates (Tables S1–S4), thermal parameters (Tables S5–S8), and bond distances and angles (Tables S9–S12) for 1, 2, 8, and 10 (15 pages). Order information is given on any current masthead page.

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