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Organometallic Chemistry of Vanadium(III) Based on the Vanadium–Dibenzotetramethyltetraaza[14]annulene Moiety: Synthesis, Structural Studies by X-ray and ^{1}H NMR Spectroscopy, and Reactivity of Vanadium–Carbon Functionalities

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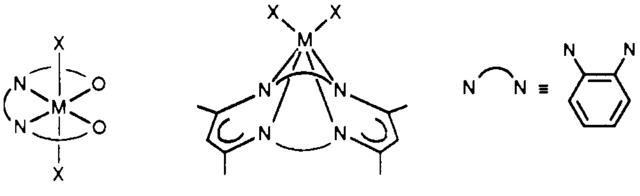
Reaction of VCl$_3$(THF)$_3$ with tmtaaLi$_2$ gave the monochloro derivative [(tmtaa)V(Cl)] (**1**). It was converted by conventional methods into the corresponding alkyl and aryl derivatives [(tmtaa)V(R)] [R = Me (**2**), CH$_2$Ph (**3**), Ph (**4**), 2,4,6-Me$_3$C$_6$H$_2$ = Mes (**5**)]. A nonconventional synthetic route leading to the [(tmtaa)V^{III}] organometallic derivatives uses [(tmtaa)V(O)] (**6**) as starting material. The structures of **1**, **4**, and **5** have been determined by an X-ray analysis. In addition, they have been inspected in solution, though they are paramagnetic, by ^{1}H NMR spectroscopy. The V–R bond does not behave normally in the reaction with carbon monoxide. Such a reaction led to the deoxygenation of the acyl or ketone intermediate, forming **6**. An indirect proof of the occurrence of the insertion reaction into a V–C bond was obtained in the reaction of **3** with C$_6$H$_{11}$NC, leading to [(tmtaa)V–C(NC$_6$H$_{11}$)CH$_2$Ph] (**13**). Crystallographic details are as follows: **1**, space group $P2_1/n$, monoclinic, a = 8.558 (2) Å, b = 20.451 (5) Å, c = 13.514 (3) Å, $\alpha = \gamma = 90°$, β = 93.06 (2)°, Z = 4, and R = 0.072 for 1327 independent observed reflections; **4**, space group $P\bar{1}$, triclinic, a = 9.597 (2) Å, b = 10.635 (2) Å, c = 12.296 (2) Å, α = 82.48 (2)°, β = 68.14 (1)°, γ = 80.07 (1)°, Z = 2, and R = 0.042 for 2151 independent observed reflections; **5**, space group $P\bar{1}$, triclinic, a = 12.671 (4) Å, b = 13.501 (5) Å, c = 14.613 (4) Å, α = 113.58 (3)°, β = 93.80 (3)°, γ = 109.79 (3)°, Z = 2, and R = 0.075 for 3116 independent observed reflections.

Introduction

Rarely do we take advantage of the chemical environments provided by a multidentate ligand for introducing and studying the chemistry of organic functionalities at a metal center as in the case of cobalt(III), where a variety of coordination environments reminiscent of the structure of vitamin B$_{12}$ have been considered.[1] For example, the organometallic chemistry of early transition metals has been largely confined to the use of cyclopentadienyl[2] and more recently alkoxides as ancillary ligands.[3] Rather recently we used tetradentate Schiff bases (SB)[4,5] and the dibenzotetramethyltetraaza[14]annulene (tmtaa) dianion for studying M–C functionalities[6,7] in the area of early transition metals. The major difference existing between those two classes of tetradentate ligands remains in their conformation.[6-8] In the tetradentate Schiff base derivatives a potential hexacoordinate metal has the two additional reactive sites or functionalities trans to each other, while in the case of tmtaa bonded to early transition metals they are cis.



[M(SB)X$_2$] [M(tmtaa)X$_2$]

SB = salen, salophen, acacen;
tmtaa = dibenzotetramethyltetraaza[14]annulene

This is a crucial geometrical factor for having a metal-controlled intramolecular reactivity assisted by two coordination sites. In addition, the tmtaa ligand provides a sort of cavity, which should be an additional factor for controlling the reactivity at the metal. The present paper reports some vanadium(III) derivatives [(tmtaa)V(X)] (X = Cl, R, Ar) which should be considered as starting materials for lower oxidation states of vanadium[9] and for studying the V–C bond chemistry in a macrocyclic environment. Some recent interesting reports[10,11] deal with the synthesis of early-transition-metal–tmtaa complexes, though none of them with their organometallic derivatization.

Experimental Section

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The syntheses of VCl$_3$(THF)$_3$,[12] tmtaaH$_2$,[13] and [VO(tmtaa)][14] (THF = tetrahydrofuran) were carried out as reported in the literature. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer, and ^{1}H NMR spectra using a 200-AC Brucker instrument.

Preparation of [(tmtaa)V(Cl)] (1). A benzene (400 mL) solution of tmtaaH$_2$ (15.4 g, 44.7 mmol) was reacted with LiMe (1.65 M in Et$_2$O, 89.5 mmol). The final red solution was kept on stirring for 1 h, and then

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$VCl_3(THF)_3$ (16.7 g, 44.7 mmol) was added. The suspension was refluxed overnight, and then the solid was extracted using the mother liquor. A light brown crystalline solid (60%) was isolated and dried in vacuo. Anal. Calcd for [(tmtaa)V(Cl)], $C_{22}H_{22}ClN_4V$: C, 61.25; H, 5.10; N, 13.00. Found: C, 61.49; H, 5.20; N, 12.67. The solid recrystallized from toluene gave crystals suitable for X-ray analysis. Anal. Calcd for $[(tmtaa)V(Cl)]\cdot 0.5C_7H_8$, $C_{25.5}H_{26}ClN_4V$: C, 64.49; H, 5.48; N, 11.80. Found: C, 64.84; H, 5.89; N, 11.70. ^1H NMR (C_6D_6, room temperature): δ 93.09 (bs, 12 H, Me), 41.55 (s, 2 H, CH), −8.84 (s, 4 H, Ph), −9.22 (s, 4 H, Ph). ^1H NMR (CD_2Cl_2, room temperature): δ 94.09 (bs, 12 H, Me), 43.54 (bs, 2 H, CH), −8.00 (bs, 4 H, Ph), −8.86 (bs, 4 H, Ph). ^1H NMR (CD_2Cl_2, 248 K): δ 114.5 (bm, 12 H, Me), 52.50 (s, 2 H, CH), −10.83 (bm, 8 H, Ph). $\mu_{eff} = 2.75\ \mu_B$ at 293 K.

Preparation of [(tmtaa)V(Cl)]·0.5Li$_2$(μ-Cl)$_2$(THF)$_4$ (1a). TmtaaH$_2$ (26.22 g, 76.22 mmol) was dissolved in THF (300 mL), and then LiMe (100 mL, 1.59 M in Et_2O, 159 mmol) was added dropwise under stirring, resulting in a green solution. The color turned suddenly to red. The solution was stirred for 3 h at room temperature, and then $VCl_3(THF)_3$ (28.47 g, 76.22 mmol) was added. The color turned to brown, and a brown solid formed. The suspension refluxed for 1 h and then cooled and filtered gave a brown beige solid (39.40 g, 83%). Anal. Calcd for $[(tmtaa)V(Cl)]\cdot 0.5Li_2(\mu\text{-}Cl)_2(THF)_4$, $C_{30}H_{38}Cl_2LiN_4O_2V$: C, 58.55; H, 6.18; N, 9.10. Found: C, 58.19; H, 6.38; N, 9.03. $\mu_{eff} = 2.70\ \mu_B$ at 293 K. The THF extraction gave crystals of **1**$\cdot 0.5Li_2(\mu\text{-}Cl)_2(THF)_4$. It is isostructural with the titanium analogue, crystallizing with the same form of LiCl. The structure of the [V(tmtaa)Cl] moiety is the same shown in Figure 1 for the salt-free form.

Preparation of [(tmtaa)V(Me)] (2). A benzene (300 mL) suspension of **1** (3.05 g, 7.08 mmol) was slowly reacted at 10 °C with LiMe (1.66 M in Et_2O, 7.4 mmol). The color turned suddenly to red. The temperature was allowed to rise slowly to 25 °C, and then the suspension was stirred for 12 h. The solid (LiCl and a bit of the final product) was filtered out, and the concentrated solution gave a crystalline red solid (55%). Anal. Calcd for [(tmtaa)V(Me)], $C_{23}H_{25}N_4V$: C, 67.64; H, 6.13; N, 13.72. Found: C, 67.45; H, 6.03; N, 13.81. ^1H NMR (C_6D_6, room temperature): δ 134.76 (bm, 15 H, Me), 41.27 (bs, 2 H, CH), −15.90 (s, 4 H, Ph), −18.64 (s, 4 H, Ph). ^1H NMR (CD_2Cl_2, room temperature): δ 133.68 (bm, 15 H, Me), 41.28 (s, 2 H, CH), −15.62 (s, 4 H, Ph), −17.91 (s, 4 H, Ph). ^1H NMR (CD_2Cl_2, 248 K): δ 166.04 (bm, 15 H, Me), 48.03 (bs, 2 H, CH), −19.92 (s, 4 H, Ph), −22.39 (s, 4 H, Ph). $\mu_{eff} = 2.87\ \mu_B$ at 291 K. The synthesis can be equally well carried out using MeMgI.

Preparation of [(tmtaa)V(CH$_2$Ph)] (3). A benzene (300 mL) suspension of **1** (5.34 g, 12.39 mmol) was reacted at 10 °C with a THF solution of $PhCH_2MgBr$ (14 mL, 12.9 mmol). The suspension was heated up to 20 °C and stirred for 4 h. The solid was filtered out from the red solution, and by evaporation of the solvent to 100 mL and addition of Et_2O (150 mL), a red-brown crystalline solid formed (47%). The solid can be recrystallized from a THF/Et_2O mixture. Anal. Calcd for [(tmtaa)V(CH$_2$Ph)], $C_{29}H_{29}N_4V$: C, 71.90; H, 5.99; N, 11.57. Found: C, 71.35; H, 6.08; N, 10.88. $\mu_{eff} = 2.57\ \mu_B$ at 291 K.

Preparation of [(tmtaa)V(Ph)] (4). Method A. To a THF (150 mL) brown suspension of **1** (1.71 g, 3.97 mmol) at −25 °C was added a THF solution of PhMgBr (0.97 M, 4.14 mL, 4.01 mmol). The solution was warmed to room temperature while being stirred and then concentrated to 75 mL with diethyl ether (30 mL) added. The solid was filtered out and the solution cooled down to −25 °C for 24 h. A brown product formed containing white impurities (magnesium salts). After filtration and standing for 48 h at −25 °C, a brown crystalline pure product was collected (34%). Anal. Calcd for [(tmtaa)V(Ph)], $C_{28}H_{27}N_4V$: C, 71.48; H, 5.75; N, 11.91. Found: C, 70.98; H, 5.66; N, 11.67. $\mu_{eff} = 2.85\ \mu_B$ at 291.5 K.

Method B. In a 500-mL flask containing a THF (100 mL) green suspension of [(tmtaa)VO] (**6**) (1.98 g, 4.81 mmol) at −25 °C was added a solution of PhMgBr (1.43 M, 7.00 mL, 10.00 mmol). The solution was allowed to reach room temperature while being stirred for 12 h and became dark brown. It was filtered and cooled to −25 °C. After standing for 48 h at −25 °C, a brown microcrystalline product was collected, which was recrystallized from a THF/ether mixture (44%). Anal. Calcd for **4**, $C_{28}H_{27}N_4V$: C, 71.48; H, 5.75; N, 11.91. Found: C, 71.02; H, 5.60; N, 11.98.

Preparation of [(tmtaa)V(Mes)] (5). Method A. A solution of MesMgBr (1.22 M, 4.80 mL, 5.86 mmol) was added to a brown suspension of **1** (2.53 g, 5.86 mmol) in THF (200 mL) at −25 °C. The suspension was warmed to room temperature and the solvent evaporated to 80 mL. Diethyl ether (30 mL) was added, and then the suspension was cooled to −25 °C for 48 h. A brown product crystallized along with some white crystalline material. This solid was filtered out, and then diethyl ether (10 mL) was added again. On standing for 48 h at −25 °C, a brown-red crystalline product formed (33%). Crystal were suitable for an X-ray analysis. Anal. Calcd for $[(tmtaa)V(Mes)]\cdot 0.5[MgCl_{1.56}Br_{0.44}(THF)_4]\cdot THF$, $C_{43}H_{57}Br_{0.22}Cl_{0.78}Mg_{0.5}N_4O_3V$: C, 65.69; H, 7.26; Br, 2.24; Cl, 3.52; N, 7.13. Found: C, 65.31; H, 7.15; Br, 2.69; Cl, 3.39; N, 7.29. $\mu_{eff} = 2.87\ \mu_B$ at 288.9 K.

Method B. A THF (200 mL) suspension of [(tmtaa)VO] (3.45 g, 8.38 mmol) was reacted at −25 °C with a solution of MesMgBr (1.22 M, 13.80 mL, 16.84 mmol). The solution was allowed to reach room temperature while being stirred for 12 h; the color turned to brown-red. The solution was concentrated to 100 mL, combined with diethyl ether (20 mL), and then cooled to −25 °C. After standing for 48 h at −25 °C, a brown-red microcrystalline product formed (43%). Anal. Calcd for **5**, $C_{31}H_{33}N_4V$: C, 72.64; H, 6.44; N, 10.94. Found: C, 72.00; H, 6.15; N, 10.98. $\mu_{eff} = 2.84\ \mu_B$ at 289.5 K. ^1H NMR (C_6D_6): δ 119.71 (vbs, 12 H, tmtaa Me), 108.36 (bs, 3 H, *p*-Me from Mes), 87.3 (bs, 6 H, *o*-Me from Mes), 40.50 (bs, 2 H, CH), 16.88 (bs, 2 H, Mes), −14.76 (bs, 4 H, Ph), −16.89 (bs, 4 H, Ph).

Preparation of [(tmtaa)V(η^5-C$_5$H$_5$)] (9). To a THF (200 mL) suspension of **1** (4.58 g, 10.62 mmol) was slowly added a THF solution (10 mL, 10.9 mmol) of C_5H_5Na. The resulting green suspension was stirred overnight, and then NaCl and some green product were filtered out. The solution was evaporated to 50 mL and then Et_2O (150 mL) added. A crystalline green solid was obtained (76%). Anal. Calcd for [(tmtaa)V(η^5-C$_5$H$_5$)], $C_{27}H_{27}N_4V$: C, 70.74; H, 5.90; N, 12.22. Found: C, 70.63; H, 6.00; N, 11.98.

Reaction of [(tmtaa)V–R] with Molecular Oxygen. A THF (100 mL) solution of [(tmtaa)V–R] (R = Ph, CH$_2$Ph, Mes) was reacted with O_2 dried for a long time over P_2O_5. The color of the solution turned from red-brown to green. Partial evaporation of the solvent resulted in the formation of the microcrystalline [VO(tmtaa)] (>90%). The GC–MS of the mother solution showed the presence of R–R (>60%).

Reaction of 3 with Carbon Monoxide. A THF (100 mL) solution of **3** (1.05 g, 2.17 mmol) was allowed to stand in a carbon monoxide atmosphere. The color changed from deep red beige to brown while a green solid formed. The suspension was kept under CO for 12 h, the solution partially evaporated, and then the microcrystalline solid collected (84%) and shown to be compound **6**. The absorption of CO controlled in a gas-volumetric apparatus corresponds to a V:CO molar ratio of 1:1.05. The CG–MS spectra of the solution showed a large variety of organic compounds, among them 1,3-diphenylacetone, 2-phenylpropanal, and some 1,2-diphenylethane. Very similar results have been obtained from the reaction of **4** and **5** with carbon monoxide.

Reaction of 3 with Cyclohexyl Isocyanide. To a THF (100 mL) solution of **3** (1.07 g, 2.21 mmol) was added neat $C_6H_{11}NC$ (2.20 mmol). The color of the solution changed slowly from red to brown. The solvent was entirely evaporated and then the solid dissolved in toluene (30 mL). *n*-Hexane (10 mL) was added, and the resulting solution cooled at 0 °C for 24 h gave a black microcrystalline solid (68%). Anal. Calcd for $C_{36}H_{40}N_5V$: C, 72.85; H, 6.75; N, 11.80. Found: C, 72.38; H, 6.56; N, 11.69. $\mu_{eff} = 2.73\ \mu_B$ at 193 K. The IR spectrum does not show any band above 1600 cm^{-1}.

Collection and Reduction of X-ray Data. Suitable single crystals of $[(tmtaa)V(Cl)]\cdot{}^1/_2MePh$ (**1**), [(tmtaa)V(Ph)] (**4**), and $[(tmtaa)V(Mes)]\cdot 0.5[MgCl_{1.56}Br_{0.44}(THF)_4]\cdot THF$ (**5**) were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with data collection are given in Table I. The reduced cells were obtained with use of TRACER.[15] Data were collected at room temperature (298 K). The structure amplitudes were obtained after the usual Lorentz and polarization corrections, and the absolute scale was established by the Wilson method.[16] The crystal quality was tested by ψ scans, showing that crystal absorption effects could be neglected for **4** and **5**. The corresponding data were corrected for absorption using a semiempirical method.[17] The function minimized during the least-squares refinement was $\sum w|\Delta F_o|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$ on the basis of the counting statistics. Anomalous scattering corrections were included in all structure factor calculations.[18b] Scattering factors for neutral atoms were taken from ref 18a for non-hydrogen atoms and from ref 19 for H. Among the low-angle reflections no corrections for secondary extinction were deemed necessary.

Solution and Refinement. [(tmtaa)V(Cl)]·0.5C$_7$H$_8$ (1). The structure was solved by the heavy-atom method starting from a three-dimensional

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds **1**, **4**, and **5**

compd	**1**	**4**	**5**
chem formula	$C_{22}H_{22}ClN_4V\cdot{}^1/_2C_7H_8$	$C_{28}H_{27}N_4V$	$C_{31}H_{35}N_4V\cdot0.5[MgCl_{1.56}Br_{0.44}(C_4H_8O)_4]\cdot C_4H_8O$
a, Å	8.558 (2)	9.597 (2)	12.671 (4)
b, Å	20.451 (5)	10.635 (2)	13.501 (5)
c, Å	13.514 (3)	12.296 (2)	14.613 (4)
α, deg	90	82.48 (2)	113.58 (3)
β, deg	93.06 (2)	68.14 (1)	93.80 (3)
γ, deg	90	80.07 (2)	109.79 (3)
V, Å^3	2361.8 (10)	1144.2 (4)	2096.0 (15)
Z	4	2	2
fw	474.9	470.5	788.3
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, °C	23	23	23
λ, Å	0.710 69	1.541 78	1.541 78
ρ_{calc}, g cm^{-3}	1.336	1.365	1.249
μ, cm^{-1}	5.39	38.22	31.02
transm coeff	1.00–0.88	1.00–0.63	1.00–0.73
R^a	0.072	0.042	0.075
$R_w{}^b$	0.109	0.046	0.100

$^a R = \sum|\Delta F|/\sum|F_o|$. $^b R_w = [\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2}$.

Table II. Refined Atomic Coordinates (with Esd's) for the [(tmtaa)V(Cl)] Unit (**1**)

atom	*x*	*y*	*z*
V	359 (2)	1591 (1)	965 (2)
Cl	−585 (5)	2593 (2)	1166 (3)
N1	2126 (12)	1518 (5)	1991 (8)
N2	1936 (11)	1619 (5)	−69 (7)
N3	−829 (11)	1098 (5)	−131 (7)
N4	−615 (11)	983 (5)	1930 (7)
C1	4725 (15)	1212 (7)	2725 (11)
C2	3637 (17)	1413 (6)	1869 (11)
C3	4257 (14)	1429 (6)	937 (12)
C4	3494 (16)	1534 (6)	27 (10)
C5	4497 (16)	1500 (7)	−835 (11)
C6	1072 (16)	1689 (6)	−999 (9)
C7	1525 (17)	2063 (7)	−1796 (12)
C8	534 (22)	2127 (7)	−2640 (11)
C9	−960 (20)	1866 (8)	−2634 (11)
C10	−1442 (15)	1515 (7)	−1846 (10)
C11	−425 (16)	1419 (6)	−1028 (10)
C12	−2217 (15)	171 (7)	−1001 (10)
C13	−1656 (13)	549 (7)	−89 (10)
C14	−1956 (15)	257 (6)	805 (11)
C15	−1466 (15)	439 (8)	1757 (10)
C16	−1733 (17)	−54 (7)	2585 (10)
C17	−57 (15)	1218 (7)	2894 (9)
C18	−944 (16)	1257 (8)	3729 (11)
C19	−372 (21)	1532 (9)	4562 (11)
C20	1120 (23)	1800 (8)	4576 (12)
C21	1979 (16)	1795 (7)	3766 (12)
C22	1409 (15)	1499 (6)	2928 (10)

Table III. Refined Atomic Coordinates (with Esd's) for the [(tmtaa)V(Ph)] Unit (**4**)

atom	*x*	*y*	*z*
V	295 (1)	1515 (1)	7253 (1)
N1	−1678 (4)	1932 (3)	8574 (3)
N2	416 (3)	−297 (3)	7938 (3)
N3	1457 (3)	646 (3)	5760 (3)
N4	−757 (3)	2846 (3)	6403 (3)
C1	−4139 (4)	1537 (4)	10144 (4)
C2	−2514 (5)	1129 (4)	9391 (4)
C3	−1976 (5)	−162 (4)	9521 (4)
C4	−627 (5)	−861 (4)	8848 (4)
C5	−483 (5)	−2290 (4)	9156 (4)
C6	1813 (4)	−961 (4)	7212 (4)
C7	2697 (5)	−1939 (4)	7617 (4)
C8	4108 (5)	−2458 (4)	6864 (4)
C9	4626 (5)	−1986 (4)	5719 (4)
C10	3795 (5)	−993 (4)	5304 (4)
C11	2382 (4)	−462 (4)	6022 (4)
C12	2246 (5)	215 (4)	3638 (4)
C13	1360 (4)	976 (4)	4690 (4)
C14	340 (5)	2019 (4)	4512 (4)
C15	−691 (4)	2871 (4)	5287 (4)
C16	−1819 (5)	3769 (4)	4853 (4)
C17	−1687 (4)	3754 (4)	7212 (4)
C18	−1947 (4)	5064 (4)	6963 (4)
C19	−2659 (5)	5868 (4)	7860 (4)
C20	−3120 (5)	5395 (4)	9023 (4)
C21	−2851 (4)	4088 (4)	9287 (4)
C22	−2177 (4)	3257 (4)	8409 (4)
C23	1877 (4)	2405 (4)	7536 (3)
C24	3295 (4)	1769 (4)	7513 (4)
C25	4355 (5)	2394 (4)	7655 (4)
C26	4067 (5)	3666 (4)	7819 (4)
C27	2685 (5)	4323 (5)	7874 (5)
C28	1614 (5)	3705 (4)	7736 (4)

Patterson map. Refinement was first isotropically and then anisotropically for non-hydrogen atoms, by full-matrix least squares for the four complexes. The toluene solvent molecule was found to be disordered over two positions around a center of symmetry with the methyl carbon of each one being coincident with the *para*-carbon of the other, as often happens for crystallized toluene. The five independent carbons were refined isotropically giving site occupation factors for 1.0 for C1 and C3 and 0.5 for C2, C4, and C5. Restraints were put on the C–C interatomic distances [C–C = 1.39 (1) Å]. All the hydrogen atoms were located from difference Fourier maps and introduced in the subsequent refinement as fixed atom contributions with isotropic *U*'s fixed at 0.05 Å^2. The final difference maps showed no unusual features, with no significant peak above the general background. All calculations were carried out using SHELX76.[20] Final atomic coordinates are listed in Table II, and selected bond distances and angles in Table V.

[(tmtaa)V(Ph)] (4). The SHELXTL program was used for all calculations.[21] The structure was solved by direct methods. Refinement was first isotropically and then anisotropically for non-hydrogen atoms. All the hydrogen atoms were put in geometrically calculated positions and introduced as fixed contributors prior to the final refinement. The final difference maps showed no unusual features, with no significant peak above the general background. Final atomic coordinates are listed in Table III, and selected bond distances and angles in Table V.

[(tmtaa)V(Mes)]·0.5[MgCl$_{1.56}$Br$_{0.44}$(THF)$_4$]·THF (5). The structure was solved by the heavy-atom method and refined anisotropically for all the non-hydrogen atoms, with the exception of the THF molecules. All the carbon atoms of the two independent coordinated THF molecules were found to be disordered over two positions. The molecules were modeled successfully by allowing the occupancy to refine to 0.6/0.4 for each pair of carbon atoms. The magnesium atom lies on a center of symmetry. The Cl:Br ratio, which is in good agreement with the ele-

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

Table IV. Refined Atomic Coordinates (with Esd's) for the [(tmtaa)V(Mes)] Unit (**5**)

atom	*x*	*y*	*z*
V	6832 (1)	10179 (1)	3270 (1)
N1	7992 (5)	11858 (5)	3973 (4)
N2	7697 (5)	9826 (5)	4213 (4)
N3	5516 (5)	8940 (5)	3405 (4)
N4	5785 (5)	11001 (5)	3248 (4)
C1	9499 (7)	13702 (7)	5348 (6)
C2	8825 (6)	12399 (7)	4813 (5)
C3	9085 (6)	11767 (7)	5316 (5)
C4	8547 (6)	10580 (7)	5059 (5)
C5	8909 (6)	10206 (7)	5829 (6)
C6	7132 (6)	8608 (7)	3890 (5)
C7	7695 (7)	7881 (7)	3882 (6)
C8	7059 (8)	6667 (8)	3455 (7)
C9	5900 (8)	6189 (8)	3030 (7)
C10	5337 (7)	6899 (7)	3016 (6)
C11	5938 (6)	8115 (6)	3454 (5)
C12	3692 (7)	8051 (7)	3875 (6)
C13	4488 (6)	8938 (6)	3588 (5)
C14	4141 (6)	9792 (6)	3569 (6)
C15	4735 (6)	10796 (7)	3444 (6)
C16	4204 (7)	11688 (8)	3631 (8)
C17	6445 (6)	11993 (7)	3076 (6)
C18	6002 (7)	12399 (7)	2472 (6)
C19	6752 (8)	13291 (7)	2294 (6)
C20	7936 (8)	13752 (7)	2678 (6)
C21	8371 (7)	13320 (7)	3263 (6)
C22	7649 (6)	12457 (6)	3475 (5)
C23	7144 (7)	9486 (6)	1810 (5)
C24	8256 (7)	9652 (7)	1652 (5)
C25	8434 (7)	9183 (7)	660 (6)
C26	7561 (9)	8576 (8)	-199 (6)
C27	6486 (9)	8422 (8)	-57 (6)
C28	6243 (7)	8854 (7)	911 (6)
C29	5004 (8)	8650 (9)	977 (7)
C30	9324 (7)	10344 (9)	2529 (6)
C31	7794 (11)	8102 (9)	-1260 (7)

Table V. Selected Bond Distances (Å) and Angles (deg) for Complexes **1**, **4**, and **5** (X = Cl for Complex **1**, X = C23 for Complexes **4** and **5**)

complex	1	4	5
V-N1	2.007 (10)	2.007 (3)	2.008 (5)
V-N2	2.000 (10)	2.002 (3)	2.002 (8)
V-N3	2.017 (10)	2.008 (3)	2.009 (6)
V-N4	2.011 (10)	2.005 (3)	2.002 (8)
V-X	2.221 (5)	2.073 (5)	2.085 (7)
N3-V-N4	87.7 (4)	90.6 (1)	88.2 (3)
N2-V-N4	142.0 (4)	145.4 (2)	141.7 (2)
N2-V-N3	80.4 (4)	81.3 (1)	80.1 (3)
N1-V-N4	80.1 (4)	80.4 (1)	80.5 (3)
N1-V-N3	143.2 (4)	148.9 (2)	145.5 (2)
N1-V-N2	88.2 (4)	89.3 (1)	88.8 (2)
N4-V-X	109.2 (3)	105.9 (2)	108.4 (3)
N3-V-X	112.4 (3)	104.5 (2)	109.7 (3)
N2-V-X	108.7 (3)	108.7 (2)	109.9 (3)
N1-V-X	104.4 (3)	106.6 (2)	104.8 (3)

mental analysis, was found by considering the same site to be occupied by chlorine and bromine and allowing the occupancy of the two "partial" atoms to refind to 0.78/0.22, respectively. All the hydrogen atoms were put in geometrically calculated positions and introduced as fixed contributors prior to the final refinement. The final difference maps showed no unusual features, with no significant peak above the general background. All calculations were carried out using SHELXTL.[21] Final atomic coordinates are listed in Table IV, and selected bond distances and angles in Table V.

Results and Discussion

The synthesis of **1**, which is the parent compound allowing the access to lower oxidation states of vanadium and to the organometallic functionalization, was performed as reported in eq 1.

$$\mathrm{tmtaaH_2} \xrightarrow[-\mathrm{CH_4,\ THF}]{\mathrm{LiMe,}} \mathrm{tmtaaLi_2} \xrightarrow[-\mathrm{LiCl,\ THF}]{\mathrm{VCl_3(THF)_3}} \underset{\mathbf{1}}{[\mathrm{V(tmtaa)Cl}]} \qquad (1)$$

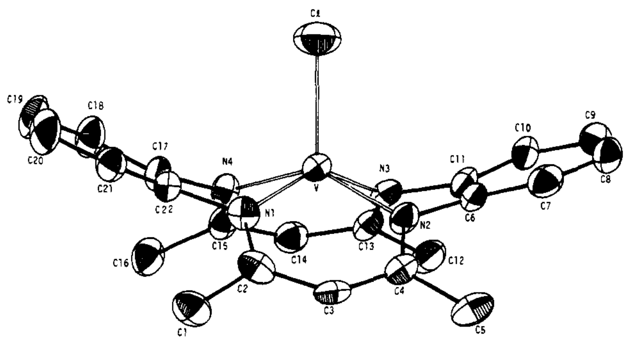

Figure 1. ORTEP drawing for complex **1** (30% probability ellipsoids).

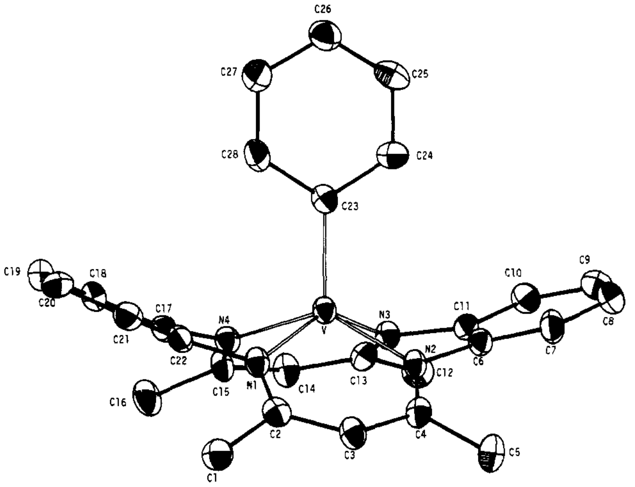

Figure 2. ORTEP drawing for complex **4** (30% probability ellipsoids).

The lithiation of tmtaaH_2 has to be done using preferentially LiMe, rather than alkali hydrides or LiBu, incomplete metalation or byproducts being observed in the latter case. When the entire sequence (1) is carried out in benzene or toluene, complex **1** was isolated with benzene or toluene of crystallization. The use of THF in reaction **1** led to the isolation of **1** cocrystallizing with LiCl, the final compound having the stoichiometry [V(tmtaa)-Cl]·0.5[$Li_2(\mu\text{-}Cl)_2(THF)_4$].[23] Complex **1** was characterized by an X-ray analysis, and its structure shown in Figure 1. It will be discussed jointly with that of **4** and **5**. The characterization of **1** in solution was conveniently carried out by ^1H NMR spectroscopy (see Experimental Section).

The alkylation of **1** was carried out using Grignard reagents:

$$\underset{\mathbf{1}}{[\mathrm{V(tmtaa)Cl}]} + \mathrm{RMgX} \xrightarrow{-\mathrm{MgXCl}} [\mathrm{V(tmtaa)R}] \qquad (2)$$
$$\begin{array}{l} \mathrm{R = Me}\ (\mathbf{2}) \\ \mathrm{R = CH_2Ph}\ (\mathbf{3}) \\ \mathrm{R = Ph}\ (\mathbf{4}) \\ \mathrm{R = Mes}\ (\mathbf{5}) \end{array}$$
$$\mathrm{Mes} \equiv 2,4,6\text{-}\mathrm{Me_3C_6H_2}$$

The only serious problem of reaction 2 is how to make free the organometallic derivatives **2**–**5** from magnesium halides, this being the major reason for some low yields reported. The structure of complexes **4** and **5** was confirmed by an X-ray analysis; pictures of **4** and **5** are given in Figures 2 and 3. Depending on the solubility, ^1H NMR spectroscopy might be used for their characterization. Significant spectra were obtained for **2** and **5** (see Experimental Section). The best solvent for such an inspection is CH_2Cl_2, but a rather fast reaction is observed with the organometallic derivative being converted back to the original chloride, **1**. The normal experimental procedures gave saltfree **2**–**4**, while **5** crystallized with magnesium halides (see Experi-

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(23) This form of complex **1** is isostructural with the titanium analogue [Ti(tmtaa)Cl]·0.5[$Li_2(\mu\text{-}Cl)_2(THF)_4$]: Floriani, C.; Chiesi-Villa, A. Unpublished results.

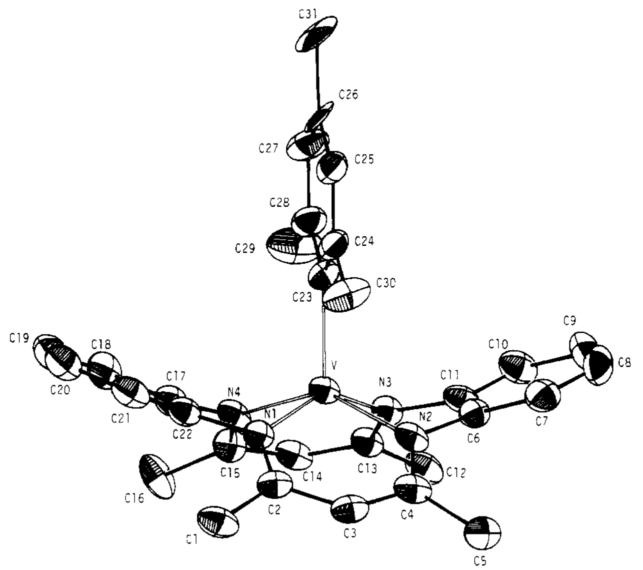


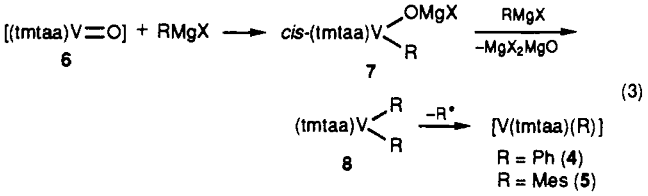
Figure 3. ORTEP drawing for complex **5** (30% probability ellipsoids).

mental Section), and the X-ray analysis was performed on such a species.

An alternative and rather unconventional route to the organometallic derivatives was considered by using [VO(tmtaa)] (**6**) as starting material, a very convenient synthesis being available for it.[14]

The reductive alkylation of **6**, though quite unusual, opens the possibility of using metal–oxo derivatives as starting materials for organometallic derivatization. Their use in this context emphasizes the analogy between related functional groups[24] like V=O and ketones,[25,11b] carboxylic acids, and inorganic equivalents like $[(8\text{-quinolinato})_2V(O)OH]$.[26]

The alkylation of **6** by using PhMgBr or MesMgBr led to **4** and **5** in a better yield than in reaction 2.



Reaction 3 requires the use of 2 equiv of Grignard reagent per vanadium. The proposed pathway seems quite plausible including the formation of an intermediate vanadium(IV) dialkyl. Its reductive decomposition to a vanadium(III) alkyl is quite in line with the instability of vanadium(IV) dialkyl derivatives of vanadocene.[27] The cis arrangement of the two alkyls in the proposed intermediate is reasonably proved by the structure of [*cis*-$(PhCH_2)_2Zr(\text{tmtaa})$],[7] and the reactivity of **6**, like that in reaction 3, was recently observed in case of the analogous titanyl [TiO(tmtaa)] complex.[11c] A single π-organometallic residue bonded to the $[(\text{tmtaa})V^{III}]$ moiety was so far reported. Reaction of cpNa with **1**,[6] or vanadocene with tmtaaH_2,[28] led to the same η^5-bonded cyclopentadienyl derivative, **9**.

$$\underset{\mathbf{1}}{[(\text{tmtaa})V(Cl)]} + \text{cpNa} \xrightarrow[-\text{NaCl}]{} \underset{\mathbf{9}}{[(\text{tmtaa})V(\eta^5\text{-}C_5H_5)]} \quad (4)$$

Table VI. Comparison of the Most Relevant Structural Parameters for Complexes **1**, **4**, and **5**

(a) Dihedral Angles between Significant Planes[a] (deg)

	1	4	5
N1,N2,N3,N4 Λ N1,C_3,N2	146.8 (5)	151.0 (1)	146.7 (2)
N1,N2,N3,N4 Λ N3,C_3,N4	147.6 (3)	153.1 (2)	147.1 (2)
N1,N2,N3,N4 Λ N1,C_6,N4	157.5 (4)	164.3 (1)	161.3 (2)
N1,N2,N3,N4 Λ N2,C_6,N3	162.3 (3)	160.0 (1)	160.9 (2)
N1,C_6,N4 Λ N2,C_6,N3	142.5 (3)	144.4 (1)	142.2 (2)
C6···C11 Λ C17···C22	138.0 (4)	138.7 (1)	137.3 (2)
N1,C_3,N2 Λ N3,C_3,N4	114.4 (5)	124.1 (2)	113.8 (2)
N1,N2,N3,N4 Λ C23···C28		85.7 (1)	86.7 (3)

(b) Out-of-Plane Distances for Vanadium (Å)

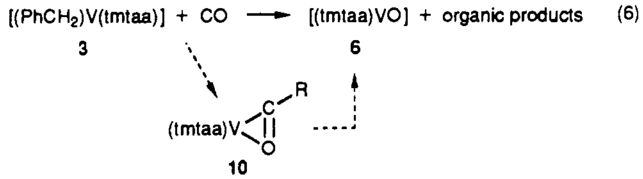
	1	4	5
N1,N2,N3,N4	0.644 (2)	0.570 (1)	0.626 (2)
N1,C_3,N2	0.167 (2)	0.138 (1)	0.181 (2)
N3,C_3,N4	0.152 (2)	0.074 (1)	0.176 (1)
C23···C28		0.093 (1)	0.035 (2)

[a] N1,C_3,N2 defines the plane through atoms N1, C2, C3, C4, and N2. N3,C_3,N4 defines the plane through atoms N3, C13, C14, C15, and N4. N1,C_6,N4 defines the plane through atoms N4, C17, C18, C19, C20, C21, C22, and N1. N2,C_6,N3 defines the plane through atoms N2, C6, C7, C8, C9, C10, C11, and N3. C6···C11, C17···C22, and C23···C28 refer to the planes through the aromatic rings.

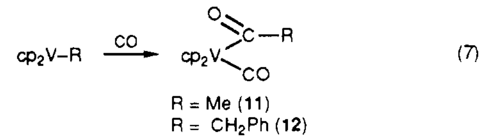
The structure of **9** has been recently solved by Cotton.[28] The alkyl derivatives **2–5** are extremely sensitive to molecular oxygen, and they react forming the oxovanadium complex, **6**.

$$[(\text{tmtaa})V(R)] + {}^1\!/_2O_2 \rightarrow$$
$$R = CH_2Ph\ (\mathbf{4})$$
$$R = Ph\ (\mathbf{5})$$
$$\underset{\mathbf{6}}{[(\text{tmtaa})VO]} + R\text{–}R + \text{byproducts} \quad (5)$$

The significant amount of the coupled organic radical found seems to exclude, at least partially, that the generation of **6** goes through the insertion of dioxygen into the V–C bond but rather to a sort of labilization of such a bond by the interaction of V(III) with dioxygen. The high oxophilicity of vanadium is responsible for an unusual pathway in the insertion of carbon monoxide exemplified by its reaction with **3**.



Complex **3** absorbs CO in a 1:1 molar ratio at room temperature. The same results have been obtained at lower temperatures. The intermediacy of the acyl derivative is supported by the presence of $(Ph_2CH_2)_2CO$ and Ph_2CH_2CHO among many other organic products derived from reaction 6. Formation of **6** is rather intriguing: it may come directly from the deoxygenation of **10** or the elimination of an acyl radical from **10** generates a vanadium(II), which is well-known as a deoxygenating agent.[29] Reaction 6 emphasizes the major difference of chemical reactivity between the V–R functionality, when bonded to the [(tmtaa)V] or the $[cp_2V]$ fragment.[25] In the latter case the reaction led to the corresponding acyl carbonyl derivatives,[30] **11** and **12**.



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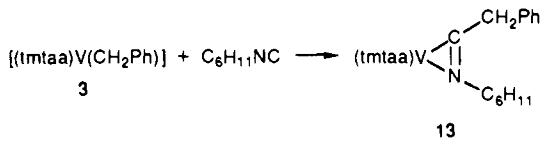
An indirect proof of the intermediacy of the acyl in the carbon monoxide reaction was obtained from the reaction of **3** with cyclohexyl isocyanide, leading to the corresponding iminoacyl, which was isolated as a crystalline solid.



(8)

The η^2-bonding mode is confirmed by the rather low C=N stretching value, which was not observed above 1600 cm^{-1}.[31]

The structures of **1**, **4**, and **5** are shown in Figures 1–3. A selection of structural parameters in Tables V and VI allows the comparison of the structures. The ligand tmtaa maintains its usual saddle-shape conformation,[6-11] which remains almost unchanged for the three compounds. Therefore the cavity where the additional functionality (Cl, Ph, Mes) is located does not change significantly (Table VI). The four N-donor atoms define a perfect plane in **1**, and they show some significant tetrahedral distortions in **4** and **5**. The vanadium V–N4 out of plane distances are rather close. The V–N distances are not affected by the change in the axial ligand. V–Cl and V–C are close to those found in the vanadium(III)–Schiff base complexes[4] (Table V). The most significant difference between **4** and **5** consists in the orientation of the phenyl ring, which, for steric reasons, is rotated by **5** by 90° with respect to **4** (Figures 2 and 3).

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-28470.90) for financial support.

Supplementary Material Available: Listings of unrefined hydrogen coordinates (Tables SI–SIII), thermal parameters (Tables SIV–SVI), bond distances and angles (Tables SVII–SIX), complete crystallographic data (Table SX), and positional parameters and equivalent isotropic thermal parameters with esd's (Tables SXI–SXIII) (23 pages); listings of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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Reduction of Biscarborane: Molecular Structures of $[(15\text{-crown-}5)_3Na_2](C_2B_{10}H_{11})_2$ and $[P(C_6H_5)_3CH_3]_2[\mu\text{-}9,10\text{-}CH\text{-}(\mu\text{-}9',10'\text{-}CH\text{-}\textit{nido}\text{-}7'\text{-}CB_{10}H_{11})\text{-}\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]$

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Received July 11, 1991

The synthesis, characterization, and elucidation of the structures of $[(15\text{-crown-}5)_3Na_2](C_2B_{10}H_{11})_2$ ($[(15\text{-crown-}5)_3Na_2]$(**1**)) and $[P(C_6H_5)_3CH_3]_2[\mu$-9,10-CH-(μ-9′,10′-CH-*nido*-7′-$CB_{10}H_{11}$)-*nido*-7-$CB_{10}H_{11}]$ ($[P(C_6H_5)_3CH_3]_2$(**2**)) are described. A comparison is made between the solid-state structures of the anion, **1**, in $[(15\text{-crown-}5)_3Na_2]$(**1**) and $[P(C_6H_5)_3CH_3]_2$(**1**). The structure of the cation $[(15\text{-crown-}5)_3Na_2]^{2+}$, described in detail, represents the first structural characterization of a 3:2 15-crown-5:Na "club sandwich" complex. $[(15\text{-crown-}5)_3Na_2](C_2B_{10}H_{11})_2$ crystallized in the triclinic space group $P\bar{1}$ with $a = 12.411$ (1), $b = 14.676$ (2), and $c = 14.988$ (2) Å, $\alpha = 101.371$ (3), $\beta = 96.222$ (3), and $\gamma = 91.549$ (4)°, $V = 2657$ Å^3, and $Z = 2$. Data were collected at 128 K on a modified Picker FACS-1 diffractometer using Mo Kα radiation, to a maximum $2\theta = 56°$, giving 12 832 unique reflections. The structure was solved by direct methods. The final discrepancy indices were $R = 0.057$ and $R_w = 0.062$ for 5012 independent reflections with $I > 3\sigma(I)$. The protonation of the species formed by the reduction of biscarborane by 4 equiv or an excess of sodium naphthalide resulted in the formation of Na_2(**2**). $[P(C_6H_5)_3CH_3]_2$(**2**) crystallized in the monoclinic space group $P2_1/n$ with $a = 11.429$ (3), $b = 15.075$ (4), and $c = 16.520$ (4) Å, $\beta = 119.648$ (8)°, $V = 2474$ Å^3, and $Z = 2$. Data were collected on a Huber diffractometer (constructed at UCLA) using Mo Kα radiation, to a maximum $2\theta = 50°$, giving 4368 unique reflections. The structure was solved by direct methods (MULTAN80). The final discrepancy indices were $R = 0.070$ and $R_w = 0.101$ for 3264 independent reflections with $I > 3\sigma(I)$.

The isomers of *closo*-$C_2B_{10}H_{12}$ have been reduced by sodium or sodium naphthalide solution to yield $[\textit{nido}\text{-}C_2B_{10}H_{12}]^{2-}$ species[1-3] which, in turn, have been employed in the synthesis of numerous metallacarboranes.[4-8] The oxidation of the $[\textit{nido}\text{-}C_2B_{10}H_{12}]^{2-}$ anions derived from *closo*-1,12-$C_2B_{10}H_{12}$, *closo*-1,7-$C_2B_{10}H_{12}$, and *closo*-1,2-$C_2B_{10}H_{12}$ has resulted in the formation of *closo*-1,7-$C_2B_{10}H_{12}$, *closo*-1,2-$C_2B_{10}H_{12}$, and *closo*-1,2-$C_2B_{10}H_{12}$, respectively, indicating a preference for the carbon atoms to approach one another during the oxidation process.[9] The protonation of the $[\textit{nido}\text{-}C_2B_{10}H_{12}]^{2-}$ anion prepared via the reduction of *closo*-1,2-$C_2B_{10}H_{12}$ has resulted in the formation of two isomers:[9] a kinetic product, $[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{13}]^-$, and a thermodynamic product, $[(\mu\text{-}9,10\text{-}CH_2)\text{-}\textit{nido}\text{-}7\text{-}CB_{10}H_{11}]^-$. However, the analogous chemistry involving the reduction of biscarborane[10] has not been investigated. Presented herein are details which concern the chemistry of the products obtained upon reduction of biscarborane, the initial results of which were reported elsewhere.[11]

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