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Role of the Ligand in the Formation of Short Vanadium–Vanadium Contacts. Preparation and Crystal Structure of Monomeric $\{[(Ph_2P)_2CH]_3V\}[Li(THF)_4](THF)_2$ and $[PhNC(H)NPh]_2V(TMEDA)$ and Dimeric $\{[PhNC(Me)O]_2V\}_2(TMEDA)$ (TMEDA = *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine)

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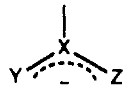
A chloride substitution reaction in *trans*-$VCl_2(TMEDA)_2$ (TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) with anionic, bidentate, bridging $[(Ph_2P)_2CH]^-$ (I), $[PhNC(H)NPh]^-$ (II), and $[PhNC(Me)O]^-$ (III) allowed the preparation and characterization of four novel V(II) complexes: monomeric $\{[(Ph_2P)_2CH]_3V\}[Li(THF)_4](THF)_2$ (**1**), $[PhNC(H)NPh]_2V(TMEDA)$ (**3**), and $(DMOB)_2V(TMEDA)$ (**5**) (DMOB = 2,6-dimethoxyphenyl) and dimeric $\{[PhNC(Me)O]_2V\}_2(TMEDA)$ (**4**). The structures of **1**, **3**, **4**, and **5** have been demonstrated by X-ray analysis. Crystal data are as follows. **1**: $C_{99}H_{111}P_6O_6VLi$, $M = 1640.69$, monoclinic, $P2_1/n$, $a = 15.496$ (2) Å, $b = 26.264$ (6) Å, $c = 24.283$ (7) Å, $\beta = 99.22$ (2)°, $V = 9755$ (4) Å^3, $Z = 4$; **3**: $C_{32}H_{38}N_6V{\cdot}C_4H_8O$, $M = 629.75$, monoclinic, $P2_1/c$, $a = 10.914$ (4) Å, $b = 21.301$ (5) Å, $c = 14.446$ (3) Å, $\beta = 91.82$ (3)°, $V = 3356.7$ (4) Å^3, $Z = 4$; **4**: $C_{38}H_{48}N_6O_4V_2$, M = 754.72, triclinic, $P1$, $a = 10.293$ (1) Å, $b = 11.323$ (1) Å, $c = 17.550$ (3) Å, $\alpha = 102.01$ (2)° $\beta = 93.02$ (2)°, $\gamma = 108.63$ (2)° $V = 1880.1$ (5) Å^3, $Z = 2$.

Introduction

Identifying the characteristics intrinsic to the ligand that promote or discourage close contacts between two transition metals is a challenging task and a significant step toward understanding the nature of the M–M interaction. Very short metal–metal multiple bonds have been found in the chemistry of divalent vanadium[1,2] and chromium,[3,4] in the presence of two or more anionic bridging ligands, that have the characteristic three-center chelating geometry and four-π-electron configuration of allylic systems (structure A). It has been argued that the existence of strong M–M multiple bonds is the factor that holds together the binuclear frame of these complexes. However, the almost invariable presence of a very characteristic molecular frame imposed by two or four chelating bridging ligands[3] suggests that the architecture of the ligand may be very important in the establishment of extremely short intermetallic contacts. For example, very short intermetallic distances are often observed in Li[5] and Cu(I)[6] derivatives, where the electronic configuration of the metal makes problematic the formation of M–M bonds. This curious behavior indicates that in some cases, the tendency of bridging ligands to impose close M–M contacts may prevail over the electrostatic repulsions between two metal cations.



A

X = RC, N, etc.
Y, Z = O, RN, R_2C, etc.

Recent work in our laboratory on the chemistry of Cr(II)[7] and Zr(III)[8] has demonstrated that bridging interactions may have a fundamental importance in determining: (i) the shape and complexity of the molecular frame (monomeric versus dimeric), (ii) the value of the M–M distance and (iii) the magnetic properties of the transition metal. Therefore, it would be desirable to evaluate the characteristics of the bridging three-center chelating ligands that are responsible for imposing close contacts between two transition metals, by examining (1) a modification of the electronic configuration of the three-center chelating ligands, (2) a variation of the size of the ligand's *bite*, and (3) a possible dependence of the molecular complexity on variations in the ligand frame.

We have recently started a synthetic study on the chemistry of divalent vanadium with the double purpose of developing its poorly known coordination chemistry[9] and trying to gain insights into the ability of vanadium to form metal–metal multiple bonds. The existence of V–V bonds is established, especially in the organometallic chemistry of divalent vanadium,[10] and a *very strong*

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V–V triple bond[1b] is thought to exist in the dimeric and diamagnetic $[V(DMOB)_2]_2$ (DMOB = 2,6-dimethoxyphenyl) derivatives.[1,2] To date, however, there is no single report of a case in which a V–V multiple bond exists between two divalent vanadium atoms in the absence of bridging ligands. Furthermore, recent theoretical work has showed that only antiferromagnetic exchange, without M–M bond, may exist at very short V–V distance (2.315 Å).[10f] Therefore, the seemingly essential presence of bridging ligands for the formation of short V–V contacts, raises questions about the real nature of the V–V interaction (multiple bond, antiferromagnetic exchange, ligand-mediated superexchange).

This paper reports the formation of four novel V(II) complexes both monomeric and dimeric, containing three anionic ligands, whose three-center chelating geometry is present along with different electronic configurations. The results of this study will be incorporated into a discussion of the role of bridging ligands in imposing a close contact between the two metals.

Experimental Section

All operations were performed under an inert atmosphere (N_2 or Ar) by using standard Schlenk techniques or in a nitrogen-filled drybox (Vacuum Atmosphere). *trans*-$(TMEDA)_2VCl_2$ was prepared according to published procedures.[9m] TMEDA was chromatographed over Al_2O_3 and distilled after refluxing over molten potassium. Phenylacetamide, *N,N'*-diphenylformamidine, 1,3-dimethoxybenzene (Aldrich), and bis(diphenylphosphino)methane (Strem) were used without further purification. Infrared spectra were recorded on a Perkin-Elmer 393 instrument from Nujol mulls prepared in a drybox. Elemental analyses were carried out at the Microanalytical Department of the Chemistry Department at the Rijksuniversiteit Groningen. Magnetic measurements were performed by using a Faraday balance (Oxford Instruments) interfaced with an Apple II computer. Calculations were carried out by standard methods, and corrections for underlying diamagnetism were applied to the data.[11]

$\{[(Ph_2P)_2CH]_3V\}[Li(THF)_4](THF)_2$ (1). A hexane solution of *n*-BuLi (4.6 mL, 1.6 M, 7.4 mmol) was added dropwise to a cooled solution (−80 °C) of bis(diphenylphosphino)methane in THF (80 mL). After being stirred for 30 min, the mixture was slowly warmed to room temperature and solid *trans*-$(TMEDA)_2VCl_2$ (0.87 g, 2.5 mmol) was added. The color turned deep green, and the stirring was continued for 10 h. Light green crystals of 1 (3.07 g, 1.9 mmol, 76%) were obtained when the resulting solution was cooled to 0 °C. Anal. Calcd (found) for $C_{99}H_{111}P_6O_6VLi$: C, 72.47 (72.10); H, 6.76 (6.37); V, 3.11 (3.26); Li, 0.43 (0.52). IR (Nujol mull, KBr, cm^{-1}): 1420 (s), 1300 (m), 1120 (s), 1080 (w), 1060 (m), 1040 (s), 1020 (m), 1000 (w), 950 (m), 900 (s), 850 (m), 800 (w), 750 (m), 740 (s), 700 (s), 695 (s), 560 (s), 540 (s), 520 (s). $\mu_{eff} = 3.62\ \mu_B$.

$\{[(Ph_2P)_2CH]_2V(py)_2\}$ (2). The addition of neat pyridine (5 mL) to a toluene suspension (30 mL) of 1 (2.14 g, 1.3 mmol) turned the color from light green to deep red. The resulting solution was refluxed for 30 min and concentrated to a small volume (10 mL). Deep red crystals of 2 separated when the solution was cooled to −30 °C (0.81 g, 0.83 mmol, 64%) Anal Calcd (found) for $C_{60}H_{52}P_4N_2V$: C, 72.85 (73.85); H, 5.33 (5.47); N, 2.87 (2.94); V, 5.23 (5.67). IR (Nujol mull, KBr, cm^{-1}): 1595 (m), 1575 (m), 1480 (m), 1460 (m), 1450 (s), 1430 (m), 1375 (m), 1295 (m), 1180 (w), 1140 (m), 1120 (s), 1090 (s), 1070 (m), 1034 (m), 890 (s), 840 (m), 835 (m), 740 (s), 730 (s), 695 (s), 660 (w). $\mu_{eff} = 3.74\ \mu_B$.

$(PhNCHNPh)_2V(TMEDA)$ (3). NaH (0.34 g, 14.2 mmol) was suspended in a solution of diphenylformamidine, PhN(H)CH=NPh (2.77 g, 14.1 mmol), in THF (75 mL). After the mixture was stirred for 15 min, *trans*-$VCl_2(TMEDA)_2$ (2.4 g, 6.92 mmol) was added to the mixture and stirring was continued for 10 h. The color of the mixture gradually turned reddish brown and a white solid (NaCl) separated. After filtration and solvent evaporation in vacuo, the residual solid was recrystallized from Et_2O (50 mL) at −30 °C, yielding brick-red crystals of 3 (2.98 g, 4.72 mmol, 68%). Anal Calcd (found) for $C_{36}H_{46}N_6OV$: C, 68.68 (68.70); H, 7.31 (7.35); N, 13.33 (12.84); V, 8.11 (8.10). IR (Nujol mull, KBr, cm^{-1}): 1670 (m), 1585 (m), 1470 (s), 1390 (m), 1465 (m), 1365 (m), 1275 (s), 1265 (s), 1210 (s), 1165 (m), 1055 (s), 1010 (m), 990 (w), 955 (m), 930 (w), 820 (w), 795 (s), 775 (s), 755 (s), 690 (s), 660 (w). $\mu_{eff} = 3.76\ \mu_B$.

Table I. Crystal Data and Structural Analysis Results

	1	3	4
formula	$C_{99}H_{111}P_6VO_6Li$	$C_{40}H_{46}N_6OV$	$C_{38}H_{48}N_6O_4V_2$
fw	1640.69	629.75	754.72
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/c$	$P1$
a, Å	15.496 (2)	10.914 (4)	10.293 (1)
b, Å	26.264 (6)	21.301 (5)	11.323 (1)
c, Å	24.283 (7)	14.446 (3)	17.550 (3)
α, deg			102.01 (2)
β, deg	99.22 (2)	91.82 (3)	93.02 (2)
γ, deg			108.63 (2)
V, Å^3	9755 (4)	3356.7	1880.1 (5)
Z	4	4	2
radiation (Mo Kα), Å	0.71073	0.71073	0.71073
T, K	130	130	130
D_{calcd}, g cm^{-3}	1.117	1.246	1.333
μ_{calcd}, cm^{-1}	2.4	3.20	5.3
R_F, R_{wF}	0.087, 0.087	0.046, 0.057	0.041, 0.046

$\{[PhNC(Me)O]_2V\}_2(TMEDA)$ (4). NaH (0.28 g, 11.6 mmol) was suspended in a solution of PhNHC(O)Me (1.5 g, 11.5 mmol) in THF (50 mL). The resulting mixture was stirred for 30 min. A red color formed upon addition of *trans*-$(TMEDA)_2VCl_2$ (1.83 g, 5.17 mmol), and stirring was continued for an additional 8 h. After solvent evaporation in vacuo, the resulting red solid was recrystallized from Et_2O (25 mL) at −30 °C, yielding large red crystals of 3 (1.31 g, 1.74 mmol, 67%). Anal. Calcd (found): C, 60.48 (59.96); H, 6.37 (6.21); N, 11.14 (10.95); V, 13.53 (13.29). IR (Nujol mull, KBr, cm^{-1}): 1550 (s), 1400 (s), 1350 (s), 1280 (m), 1235 (s), 1225 (s), 1170 (w), 1160 (w), 1150 (w), 1120 (w), 1065 (m), 1025 (s), 1010 (s), 955 (s), 925 (w), 895 (m), 820 (m), 810 (m), 790 (s), 750 (s), 695 (s), 665 (w), 655 (m). $\mu_{eff} = 0.42\ \mu_B$.

$(DMOB)_2V(TMEDA)$ (5). *trans*-$(TMEDA)_2VCl_2$ (1.46 g, 4.12 mmol) was added to a cooled (−30 °C) solution of (DMOB)Li (1.24 g, 8.6 mmol) in 30 mL of THF. A greenish brown color appeared quite rapidly. The mixture was allowed to warm slowly to room temperature and was stirred for an additional 6 h. LiCl was precipitated by adding 30 mL of ether, and red crystals of 5 (1.14 g, 2.6 mmol, 63%) were obtained upon filtration and cooling of the resulting solution to −30 °C. Anal Calcd (found) for $C_{22}H_{34}O_4N_2V$: C, 59.86 (59.65); H, 7.71 (7.78); N, 6.35 (6.33); V, 11.56 (11.62). IR (Nujol mull, KBr, cm^{-1}): 1560 (s), 1540 (s), 1430 (s), 1400 (s), 1390 (s), 1300 (m), 1280 (m), 1230 (s), 1200 (s), 1170 (s), 1150 (m), 1090 (s), 1050 (s), 1030 (m), 1010 (m), 965 (s), 930 (w), 870 (s), 800 (s), 760 (s), 720 (s), 700 (s), 600 (s), 500 (s), 470 (m), 430 (w). $\mu_{eff} = 3.59\ \mu_B$.

Thermolysis of $(DMOB)_2V(TMEDA)$. A solution of $(DMOB)_2V(TMEDA)$ (1.14 g, 2.6 mmol) in THF (50 mL) was refluxed for 8 h. The color slowly turned to green, and deep green crystals of $[(DMOB)_2V]_2(THF)_2$ separated when the solution was cooled at room temperature (0.40 g, 0.5 mmol, yield 38%). The product has been identified by comparison of the spectroscopic data with those of an analytically pure sample.

X-ray Crystallography. The crystals used for this study were selected in a drybox equipped with a microscope. Suitable crystals were glued on top of a glass fiber covered with a thin layer of silicon oil and mounted on a diffractometer (CAD-4F) equipped with a locally modified cooling device. Details on the structure determination and refinement are given in Table I. Tables of hydrogen positional and thermal parameters, extensive lists of bond distances, bond angles, and torsion angles, and tables of F_o, F_c and $\sigma(F)$ are given as supplementary material. Neutral-atom scattering factors[12] were applied to the non-hydrogen atoms, using anomalous dispersion corrections.[13] All calculations were carried out on a CDC-Cyber 962-31 computer at the University of Groningen using the program packages XTAL,[14] EUCLID[15] (calculation of geometric data), and ORTEP[16] and an extended version of the program PLUTO[17] (preparation of the illustrations).

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**

	x	*y*	*z*	U_{eq},[a] Å^2
V1	0.27379 (8)	0.14057 (5)	0.21046 (6)	0.0200 (4)
P1	0.1712 (1)	0.21879 (8)	0.21223 (9)	0.0226 (7)
P2	0.3522 (1)	0.22787 (8)	0.2252 (1)	0.0271 (7)
P3	0.4006 (1)	0.08129 (8)	0.1894 (1)	0.0318 (8)
P4	0.2810 (1)	0.12649 (8)	0.0963 (1)	0.0294 (8)
P5	0.2688 (1)	0.12036 (8)	0.3242 (1)	0.0295 (8)
P6	0.1747 (1)	0.06513 (8)	0.2280 (1)	0.0264 (7)
C13	0.2575 (5)	0.2591 (3)	0.2352 (4)	0.034 (3)
C38	0.3709 (5)	0.0871 (3)	0.1121 (4)	0.041 (3)
C63	0.1996 (5)	0.0696 (3)	0.3068 (4)	0.039 (3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_ja_i\cdot a_j$.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **3**

	x	*y*	*z*	B, Å^2
V	0.38117 (4)	0.17883 (2)	0.37152 (3)	0.822 (9)
N7	0.478 (1)	0.2582 (2)	0.3198 (1)	1.1 (1)
N9	0.579 (1)	0.1664 (2)	0.3293 (1)	1.1 (1)
N22	0.189 (1)	0.2102 (2)	0.3516 (1)	1.1 (1)
N24	0.281 (1)	0.1509 (2)	0.2455 (1)	1.1 (1)
N33	0.324 (1)	0.0868 (2)	0.4366 (1)	1.1 (1)
N36	0.438 (1)	0.1983 (2)	0.5186 (1)	1.1 (1)
C8	0.579 (1)	0.2263 (3)	0.3026 (2)	1.1 (1)
C23	0.179 (1)	0.1788 (3)	0.2723 (2)	1.2 (1)
C34	0.354 (1)	0.0914 (3)	0.5378 (2)	1.4 (1)

Compound 1. The final lattice parameters were determined by least-squares treatment, using the setting angles of 25 reflections in the range 6.66° < θ < 10.34°. Data were corrected for small decay and Lorentz polarization effects, but not for absorption. From a total of 14 850 reflections in the range 1.21° < θ < 24.50°, 7742 satisfied the $I > 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[18] Refinement resulted in the location of all the atoms, including two interstitial molecules of THF. The difference Fourier map indicated major ring disorder on one of the two THF molecules. The coordinates for the disordered THF atoms were calculated by fitting the observed peaks to two idealized THF structures. Rigid body refinements using idealized THF ring geometry were applied; refinement of the two-site occupancy factor of the disordered THF ring suggested a 50% occupancy for both sites. The hydrogen atoms of the vanadium fragment and some hydrogen atoms of the THF molecules were located in difference Fourier maps after anisotropic refinement of the non-hydrogen atoms. The remaining hydrogen atoms of the THF molecules were introduced at calculated positions (C–H = 1.0 Å) and refined with fixed geometry with respect to their carrier atoms. The failure to model the heavy conformational disorder of one of the two interstitial molecules of THF prevented an accurate solution of the structure in spite of the reasonable quality of the data set. Weights were introduced in the final refinement cycles. Refinement by *F* block-diagonal least-squares techniques, with anisotropic thermal parameters for the non hydrogen atoms and one common thermal parameter for the hydrogen atoms, converged to a final value of $R_F = 0.087$ ($R_{wF} = 0.087$). A final difference Fourier synthesis showed no unusual features, the maximum residual peak being ±0.97 e/Å^3. Crystal data and experimental details are given in Table I. Final atomic coordinates are listed in Table II. Relevant bond distances and angles are listed in Table V.

Compound 3. Cell constants and an orientation matrix for the data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range 1.0° < θ < 27.0°. From a total of 7255 reflections collected in the range 1.0° < θ < 27.0°, 5115 satisfied the $I > 3\sigma(I)$ criterion of observability. Data were collected for scale variation and Lorentz and polarization effects, but not for absorption. The structure was solved in part by direct methods.[19] The positions of the remaining atoms, including all the hydrogen atoms, were obtained from succeeding Fourier syntheses. Block-diagonal least-squares refinement on *F*, with unit weights, converted to $R_F = 0.046$ ($R_{wF} = 0.057$) using anisotropic temperature factors for the non-hydrogen atoms and isotropic fixed thermal parameters for the hydrogen atoms. In the final refinement, the hydrogen atoms were constrained at their idealized positions riding on their carrier atom (C–H = 0.96 Å). Scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_c. Final atomic coordinates are listed in Table III. Relevant bond distances and angles are listed in Table V.

Table IV. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **4**

	x	*y*	*z*	U_{eq},[a] Å^2
V1	0.13972 (5)	0.28772 (4)	0.20325 (3)	0.0139 (1)
V2	0.32353 (4)	0.49511 (4)	0.25415 (3)	0.0131 (1)
O1	0.1657 (2)	0.4547 (2)	0.1575 (1)	0.0165 (6)
O2	0.3024 (2)	0.3255 (2)	0.2956 (1)	0.0177 (6)
O3	0.0187 (2)	0.3463 (2)	0.2823 (1)	0.0200 (6)
O4	0.2618 (2)	0.2285 (2)	0.1249 (1)	0.0175 (6)
N1	0.3264 (2)	0.6457 (2)	0.1969 (1)	0.0165 (7)
N2	0.4766 (2)	0.5039 (2)	0.3455 (1)	0.0165 (7)
N3	0.1815 (2)	0.5425 (2)	0.3310 (1)	0.0158 (7)
N4	0.4376 (2)	0.4189 (2)	0.1672 (1)	0.0162 (7)
N5	0.0397 (2)	0.1980 (2)	0.1068 (1)	0.0210 (7)
N6	0.0613 (2)	0.0937 (2)	0.2299 (1)	0.0235 (7)
C2	0.2176 (3)	0.5704 (3)	0.1481 (2)	0.0173 (8)
C10	0.4214 (3)	0.3799 (3)	0.3385 (2)	0.0172 (8)
C18	0.0582 (3)	0.4575 (3)	0.3294 (2)	0.0184 (8)
C26	0.3844 (3)	0.3030 (3)	0.1221 (2)	0.0175 (8)

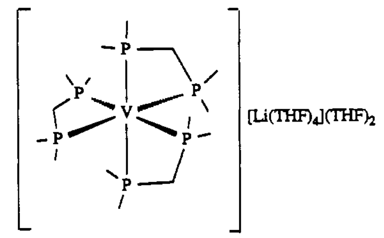
[a] $U_e = {}^1/_3\sum_i\sum_j U_{ij}a_ia_ja_i\cdot a_j$.

Compound 4. Final lattice parameters were derived from the angular setting of 22 reflections in the range 9.04° < θ < 18.44°. Data were corrected for scale variation and Lorentz and polarization effects, but not for absorption. From a total of 7767 reflections in the range 1.20° < θ < 26.0°, 5467 satisfied the $I > 2.5\sigma(I)$ criterion of observability. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86).[18] Subsequent difference Fourier syntheses gave all the hydrogen atoms. Refinement was carried out with block-diagonal least-squares techniques on *F*. Convergence to a final value of $R_F = 0.041$ ($R_{wF} = 0.046$) was reached by using anisotropic temperature factors for the non-hydrogen atoms and a common isotropic thermal factor for the hydrogen atoms. Final atomic coordinates are listed in Table IV. Relevant bond distances and angles are listed in Table V.

Results

The reaction of *trans*-(TMEDA)$_2$VCl$_2$ (TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) with 3 equiv of [(Ph$_2$P)$_2$CH]Li (eq 1) proceeded rapidly in THF, forming deep-green solutions

$$\textit{trans}\text{-(TMEDA)}_2\text{VCl}_2 + 3\ [(\text{Ph}_2\text{P})_2\text{CH}]\text{Li} \longrightarrow$$



(1)

from which the ionic {[(Ph$_2$P)$_2$CH]$_3$V}[Li(THF)$_4$](THF)$_2$ complex (**1**) was isolated in good yield as light green crystals. The high stability of **1** seems to be the driving force for its formation, since attempts to isolate any intermediate, neutral species by careful control of the reaction stoichiometry led only to variable amounts of **1** contaminated by unreacted starting *trans*-(TMEDA)$_2$VCl$_2$. The magnetic moment of **1** (μ_{eff} = 3.62 μ_B) is as expected for a high-spin V(II) species in an octahedral field.[11]

The heterobimetallic, ionic **1** can be easily transformed into a neutral species by reaction with a coordinating ligand like pyridine (eq 2). The reaction proceeds rapidly in the presence

$$\underset{\mathbf{1}}{\{[(\text{Ph}_2\text{P})_2\text{CH}]_3\text{V}\}[\text{Li(THF)}_4](\text{THF})_2} + \text{pyridine} \rightarrow \underset{\mathbf{2}}{[(\text{Ph}_2\text{P})_2\text{CH}]_2\text{V(py)}_2} \quad (2)$$

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(18) Sheldrick, G. M. SHELXS86. Program for crystal structure solution. University of Göttingen, Göttingen FRG.

(19) Computer software: SDP/PDP (Enraf-Nonius & B. A. Frenz, & Associates, Inc.).

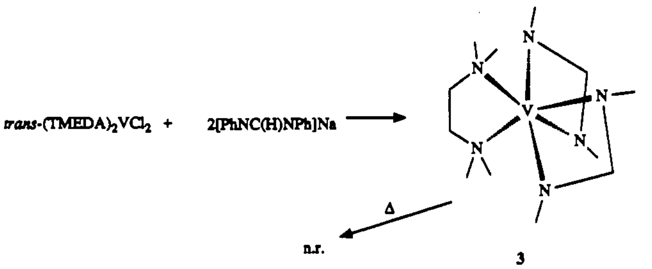
(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Table 2.2 B.

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

1		3		4	
V–P1	2.602 (6)	V–N7	2.143 (8)	V1⋯V2	2.4499 (8)
V–P2	2.593 (3)	V–N9	2.276 (13)	V1–O1	2.151 (2)
V–P3	2.620 (3)	V–N22	2.213 (13)	V1–O2	2.141 (2)
V–P4	2.817 (3)	V–N24	2.177 (7)	V1–O3	2.060 (2)
V–P5	2.826 (3)	V–N33	2.270 (6)	V1–O4	2.064 (2)
V–P6	2.584 (3)	V–N36	2.234 (4)	V2–O1	2.154 (2)
V–C13	3.185 (6)	N7–V–N9	61.0 (3)	V2–O2	2.144 (2)
V–C38	3.326 (7)	N7–V–N22	101.2 (4)	V1–N5	2.250 (2)
V–C63	3.334 (7)	N7–V–N24	99.5 (2)	V1–N6	2.243 (2)
P1–V–P2	64.76 (7)	N7–V–N33	166.3 (5)	V2–N1	2.145 (2)
P1–V–P3	162.06 (9)	N7–V–N36	93.4 (2)	V2–N2	2.152 (2)
P1–V–P4	103.92 (8)	N9–V–N22	154.6 (1)	V2–N3	2.157 (2)
P1–V–P5	91.14 (8)	N9–V–N24	101.5 (3)	V2–N4	2.177 (2)
P1–V–P6	102.81 (8)	N9–V–N33	106.6 (3)	V1–O2–V2	69.75 (6)
P2–V–P3	101.70 (8)	N9–V–N36	92.2 (4)	V1–O1–V2	69.38 (6)
P2–V–P4	99.20 (8)	N22–V–N24	61.6 (3)	O1–V1–O2	110.51 (8)
P2–V–P5	96.73 (8)	N22–V–N33	92.4 (4)	O1–V2–O2	110.24 (8)
P2–V–P6	159.0 (1)	N22–V–N36	107.6 (3)	O3–V1–O4	179.49 (8)
P3–V–P4	65.23 (8)	N24–V–N33	88.4 (2)	O2–V1–O5	166.02 (8)
P3–V–P5	102.56 (8)	N24–V–N36	164.5 (6)	O1–V1–N5	86.03 (8)
P3–V–P6	93.48 (8)	N33–V–N36	80.7 (2)	N3–V2–N4	170.43 (9)
P4–V–P5	161.62 (8)				
P4–V–P6	100.38 (8)				
P5–V–P6	65.45 (8)				

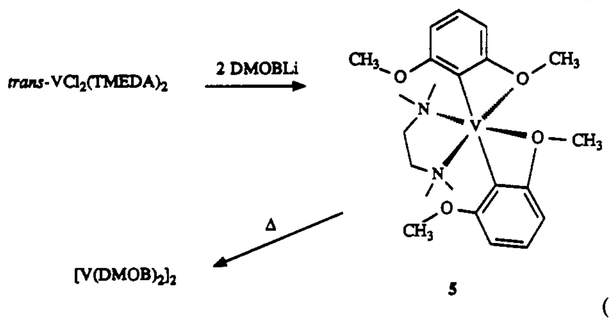
of an excess of pyridine, forming $[(Ph_2P)_2CH]_2V(py)_2$ (**2**) as a red, crystalline, analytically pure compound. That **2** is a monomer and probably octahedral is suggested by its magnetic moment ($\mu_{eff} = 3.74\ \mu_B$).

The reaction of *trans*-$(TMEDA)_2VCl_2$ with 2 equiv of [PhNC(H)NPh]Na formed the new monomeric species [PhNC(H)NPh]$_2$V(TMEDA) (**3**) (eq 3). Complex **3** is thermally stable



(3)

and failed to dimerize during attempts to remove the residual TMEDA by refluxing it for 7 days in THF. Conversely, the similarly prepared monomeric and paramagnetic $(DMOB)_2V(TMEDA)$[24] (**5**) gave a good yield of the well-known dimeric $(DMOB)_4V_2$ complex after thermolysis in THF (6 h) (eq 4).



(4)

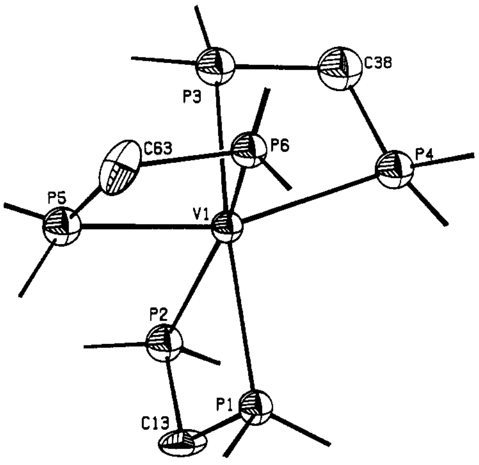


Figure 1. ORTEP plot of the core of the anion of **1**. Thermal ellipsoids are drawn at the 50% probability level. C_6H_5 rings have been deleted for clarity reasons.

The crystal structures of **1** and **3** have been determined by X-ray analysis. Complex **1** consists of two separated $\{[(Ph_2P)_2CH]_3V\}^-$ (Figure 1) and $[Li(THF)_4]^+$ units (figure 1S in the supplementary material). The overall geometry of vanadium in the anionic fragment is octahedral (average P–V–P = 65.14°), the small observed distortion probably arising from the considerable steric congestion caused by the presence of 12 phenyl rings. The three methylide fragments are coplanar with vanadium in an overall propeller-shaped geometry. The almost perfect planarity of the vanadium–phosphinomethylide rings suggests a considerable charge delocalization in each metallocycle. However, the V–C distances [average V–C = 3.281 (7) Å] are longer than the V–P distances [ranging from 2.584 (3) to 2.826 (3) Å], suggesting that the most significant bonding interaction is achieved through the phosphorus atoms. In spite of the distorted geometry, the V–P distances are quite normal and fall within the range of values observed in other phosphine containing V(II) complexes,[21-23] except two trans-positioned V–P bonds [V–P4 = 2.817 (3) Å, V–P5 = 2.826 (3) Å], which are noticeably longer, probably due to a crystal packing effect. The structure is completed by the tetrahedrally solvated $[Li(THF)_4]$ cation.

The structure of complex **3** consists of discrete monomeric units. The coordination geometry around the vanadium atom is distorted octahedral, with the two chelating formamidine ligand and the TMEDA molecule assuming an overall propeller-shaped configuration (Figure 2). The two formamidine fragments are coplanar with vanadium. In spite of the considerable differences between

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(21) Jensen, J. A.; Girolami, G. S. *Inorg. Chem.* **1989**, *28*, 2114.

(22) Hessen, B.; van Bolhuis, F.; Teuben, J. H.; Petersen, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 295.

(23) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946.

(24) Crystal data: $C_{22}H_{34}O_4N_2V$, monoclinic, $P2_1/n$, $a = 10.781$ (2) Å, $b = 15.530$ (5) Å, $c = 13.995$ (7) Å, $\beta = 99.58°$, $V = 2310.5$ (14) Å^3, $Z = 4$, $R_F = 0.109$ ($R_{wF} = 0.093$) for 785 reflections.

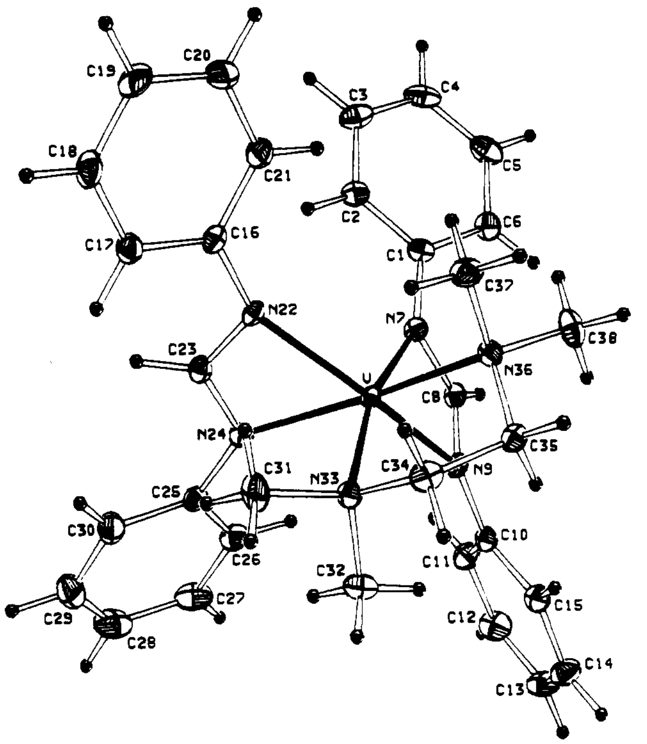
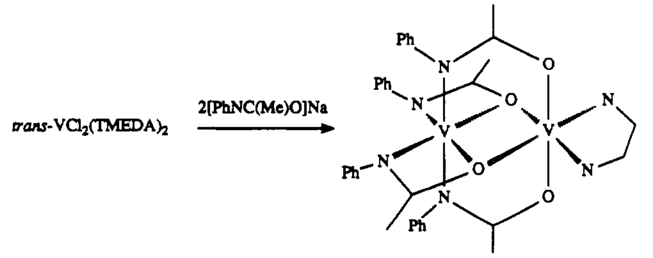


Figure 2. ORTEP plot of **3**. Thermal ellipsoids are drawn at the 50% probability level.

the electronic configurations of the formamidine and TMEDA ligands, the V–N distances in **3** [ranging from 2.143 to 2.276 (13) Å] are very comparable to those formed by the nitrogen atoms of the TMEDA molecule [2.234 (6) and 2.270 (6) Å]. This is moreover in striking contrast with the different hybridization of the two nitrogen atoms (sp^2 versus sp^3) in the two ligands and indicates the absence of a N→V π-bonding interaction with the formamidine moiety. Furthermore, the V–N distances are longer than those observed in *trans*-$[PhNC(H)NPh]_2V(pyridine)_2$,[9n] suggesting that the residual TMEDA molecule considerably increases the steric hindrance of complex **3**. The angle subtended at the carbon atom by the two formamidine nitrogen atoms [N22–C23–N24 = 116.0 (1)°] is quite normal and shows only a little contraction from the regular amplitude expected for an sp^2 carbon atom. The geometry of the TMEDA ligand is as expected.

A similar reaction of *trans*-$(TMEDA)_2VCl_2$ with $[PhNC(Me)O]Na$ (eq 5) led to the formation of the dimeric $\{[PhNC(Me)O]_4V_2(TMEDA)\}$ (**4**).



(5)

As demonstrated by X-ray analysis, the bimetallic frame of **4** consists of two inequivalent vanadium atoms linked by four acetanilide groups. The coordination geometry around each vanadium atom is distorted octahedral, the angles subtended at vanadium by the two atoms placed in trans positions being quite close to linear (ranging respectively from 170.43 to 171.44° for V2 and from 166.02 to 179.49° for V1). The overall geometry of the molecule appears to be quite similar to that observed in the triply bonded diamagnetic complex $[(DMOB)_2V]_2$ [DMOB = 2,6-dimethoxyphenyl].[1] The four acetanilide ligands are coordinated to the two metal atoms by using two different modes of ligation. Two of them work as conventional bridging three-center chelating ligands; the other two ligands (trans to each other about the intermetallic axis) show the characteristic bridging–chelating type of bonding previously observed in $[(DMOB)_2V]_2$. The particular conformation of the four acetanilide ligands is probably the result of steric congestion introduced by the residual TMEDA molecule, which forces the four phenyl rings onto the same side of the molecule. Conversely, the two different chelating modes (tridentate versus bidentate) adopted by the ligands are probably determined by the preference of vanadium for the octahedral coordination geometry, which necessarily requires that two donor atoms of the ligand be shared. This tendency is probably also responsible for the distorted-trigonal-planar coordination geometry of the bridgehead oxygen atoms. In spite of the very different coordination environment of the two metal atoms, the V1–O1–V2–O2 frame appears to be quite regular with little deviation in the V–O distances [V1–O1 = 2.151 (2) Å, V1–O2 = 2.141 (2) Å, V2–O1 = 2.154 (2) Å, V2–O2 = 2.144 (2) Å]. The angles subtended at the oxygen atoms are quite narrow [V1–O1–V2 = 69.38 (6)°, V1–O2–V2 = 69.75 (6)°] and are similar to those subtended at the square-planar phenyl carbon atom of similarly bonded DMOB ligands of the $[(DMOB)_2V]_2$ complex.[1] The geometry of the acetanilide ligands is surprisingly comparable in the two different modes of chelation (tri- and bidentate), since the angles subtended at the acetyl carbon atoms [O3–C18–N3 = 121.6 (3)°, O2–C10–N2 = 115.3 (3)°] are rather similar.

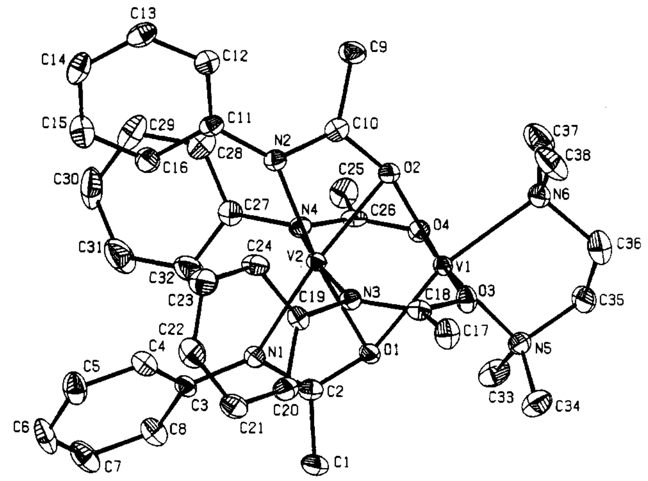
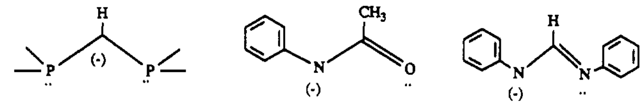


Figure 3. PLUTO plot of **4**. Thermal ellipsoids are drawn at the 50% probability level.

Chart I



I II III

Discussion

As illustrated in Chart I, the three anionic three-center chelating ligands used for this work possess considerably different electronic configurations. Due to the presence of an electron pair on the central carbon atom, the bis(diphenylphosphino)methylide ligand I[25] works exclusively as a 6-electron donor.[26] Conversely, the less bulky ligands II and III display a higher electronic flexibility, since ligand III can use four or six electrons for bonding the transition metal, depending on the ability to give π-bonds, while up to eight electrons can be used by ligand II. However, the fairly long V–N bond distances observed in complexes **3** and **4** are comparable with those formed by the TMEDA ligand and suggest

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(25) Hietkamp, S.; Stelzer, O. *Inorg. Chem.* **1984**, *23*, 258.
(26) Uson, R.; Laguna, A.; Laguna, M.; Gimeno, M. C. *J. Chem. Soc., Dalton Trans.* **1989**, 1883.

that the second lone pair of the nitrogen atom of the amido group is probably not engaged in bonding with the metal center.

Due to the fact that three-center chelating ligands with the same electronic configuration as II and III almost invariably form dimers,[3] the binuclear structure of **4** and the close structural similarity with the triply bonded $[V(DMOB)_2]_2$[1] complex are as expected. However, the V–V distance in complex **4** [V1]V2 = 2.4499 (8) Å] is considerably longer and likely not in agreement with the presence of a V–V triple bond. This idea is furtherly supported by the presence in complex **4** of a small residual paramagnetism ($\mu_{eff} = 0.42\ \mu_B$). Although this behavior might be explained by the existence of a V–V double bond with a $\sigma^2\pi^2\delta^{*2}$ electronic configuration and low-lying δ^*, we observe that it is closely related to that of a recently reported dinuclear chromium(II) complex of a three-center chelating ligand, isostructural with the well-known quadruply bonded systems, where a very low residual paramagnetism has been observed in the absence of a Cr–Cr quadruple bond.[7d] Furthermore, considering (i) that this class of ligands has a unique ability to enforce binuclear aggregation within a wide range of M–M distances and with a considerable number of transition and non transition metals,[27] (ii) that bridging interactions are capable of determining the magnetic properties of the transition metal,[7,8,10f] and (iii) that very short V–V distances can exist in the absence of V–V bonds,[10f] we suggest that the V–V distance and the magnetic properties of **4** might be nothing more than the combined result of ligand frame steric interactions between the four bridging chelating ligands and the tendency of the two vanadium atoms to achieve an octahedral coordination geometry.

Molecular geometry considerations, on the basis of the X-ray data of **3** and **4**, suggest that when the steric bulk is increased, as when II is replaced by III (complex **3**), dimerization may be achieved only against unfavorable steric interactions of the formamidine phenyl rings with the TMEDA methyl groups. Consistent with the hypothesis that the dimerization of **3** is inhibited by steric factors, the reaction of *trans*-$(TMEDA)_2VCl_2$ with DMOBLi also produces a *monomeric*[24] and paramagnetic complex, $[DMOB]_2V(TMEDA)$ (**5**). The well-known diamagnetic dimer $[V(DMOB)_2]_2$ was obtained only upon several hours of refluxing in THF, while, analogous to the case of the monomeric *trans*-$[PhNC(H)NPh]_2V(pyridine)_2$,[9n] no dimerization reaction was observed after a THF solution of **3** was refluxed for several days. It is unclear whether the reluctance of **5** to dimerize is related to a poor thermodynamic stability of the dimer compared to the monomer or to a high activation barrier provided by the dissociation of TMEDA. In any case, it is reasonable to expect that the corresponding activation energy in complex **3** will be rather comparable. Therefore, if we accept the idea that the failure of **3** to dimerize is just the result of unfavorable steric interactions, we can expect that the formation of V–V multiple bonds cannot provide the amount of energy necessary to compensate for these factors. In other words, these bonds are probably not strong. On the other hand, an hypothetical ability of vanadium to form elongated and weak V–V multiple bonds may not provide the thermodynamic driving force for the dimeric aggregation, and in any case, the existence of a M–M bond is not strictly necessary to account for the magnetic properties of the metal center.[7,8]

The different electronic configuration of $[Ph_2PCHPPh_2]^-$ (I) together with the higher steric hindrance is probably responsible for the monomeric nature of **1**, since the neutral, four-electron-donating phosphine $Ph_2PCH_2PPh_2$ (DPPM) usually works as a three-center, chelating, bridging ligand favoring the formation of binuclear species. For example, in $[(\mu\text{-DPPM})(\mu\text{-Cl})V(BH_4)]_2$[29] and $Cr_2Cl_4(DPPM)_2$,[30] there is no doubt that the particular geometry of the chelating phosphine is the most important factor promoting the dimerization, since other chelating phosphines, possessing different *bites*, do not display special bridging abilities in similar complexes.[5,9b]

In conclusion, in analogy with the case of Li and Cu(I) derivatives with similar three-center chelating ligands,[28] the particular geometry of the ligands, rather than the tendency of vanadium to form weak V–V multiple bonds, may be the predominant factor that, in complex **4**, determines the dimeric aggregation.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Nederlandse Organisatie voor Wettenschapelijk Onderzoek (The Netherlands) and the Chemistry Department at the University of Groningen are gratefully acknowledged for providing a visiting scholarship (J.J.H.E.).

Supplementary Material Available: Tables listing atomic positional parameters, temperature factors, torsion angles, bond angles and distances, and hydrogen atom positional parameters associated with complexes **1**, **3**, and **4** and drawings of the cation and anion in **1** (57 pages); tables of calculated and observed structure factors (112 pages). Ordering information is given on any current masthead page.

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