Synthesis and Characterization of Vanadium(V) Mono-, Bis-, Tris-, and Tetrakis(phosphoraniminato) Complexes

Arnis Aistars, Robert J. Doedens, and Nancy M. Doherty*

Department of Chemistry, University of California, Irvine, California 92717

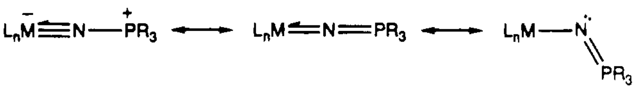
Received September 17, 1993®

$V(NSiMe_3)Cl_3$ reacts with organophosphorane dichlorides (PCl_2Ph_3, PCl_2MePh_2, PCl_2Me_2Ph, PCl_2Me_3) in dichloromethane to form vanadium(V) phosphoraniminato complexes, $V(NPR_3)Cl_4$, in excellent yield. Subsequent addition of 1 or 2 equiv of $Me_3SiNPPh_3$ to the (triphenylphosphoraniminato)vanadium compound, $V(NPPh_3)Cl_4$, produces the bis- and tris(phosphoraniminato)vanadium(V) complexes, $V(NPPh_3)_2Cl_3$ and $V(NPPh_3)_3Cl_2$, respectively. Further addition of $Me_3SiNPPh_3$ to the tris(phosphoraniminato)vanadium(V) complex produces only a small equilibrium concentration of the tetrakis(phosphoraniminato) species; however, this compound is isolated in good yield from an unusual reaction between $V(NPPh_3)_nCl_{5-n}$ ($n = 1-3$) and NH_3. An acetonitrile solvate of $[V(NPPh_3)_4]Cl$ has been structurally characterized and is found to consist of $[V(NPPh_3)_4]^+$ cations and chloride anions. ^{31}P and ^{51}V NMR spectra of this compound show a well-resolved vanadium−phosphorus coupling and support the existence of an analogous four-coordinate structure in solution.

Introduction

Phosphoraniminates (NPR_3^-) are potentially useful and versatile ligands for transition-metal complexes in high oxidation states.[1−3] Like oxo, imido, and nitrido ligands,[4] phosphoraniminates can stabilize electron-poor metals by π-donation, providing up to a total of six electrons to a metal center. Changes in the steric and electronic properties of NPR_3^- are possible by variation of the R groups, as is also the case for imido ligands.[4,5] Phosphoraniminato ligands are unusual, however, in that they offer considerable flexibility as donors, as suggested by some of the possible resonance structures for $MNPR_3$[3,6] (Scheme 1). They are also unique among good π-donor ligands in that they are monoanionic (cf. O^{2-}, NR^{2-}, and N^{3-}). This feature could be useful in the synthesis of high oxidation state transition-metal complexes. Because each NPR_3^- replaces only one halide (or other monoanionic ligand) at a metal center, phosphoraniminates offer the possibility of introducing a π-donor ligand into a metal coordination sphere without changing the number of anionic ligands.

Scheme 1



We began exploring the synthesis and chemistry of transition-metal phosphoraniminato complexes as part of our studies of the chemistry of metal-bound nitrogen atoms.[1,2] For example, we previously reported that $V(NPMePh_2)Cl_4$ can be prepared in good yield from $V(NSiMe_3)Cl_3$ and PCl_2MePh_2.[1] $V(NPMePh_2)Cl_4$ can be viewed as an analogue of VCl_5, the unknown/unstable homoleptic chloride of vanadium(V),[7] suggesting that it might be possible to replace additional chloro ligands with phosphoraniminato groups. To explore such ideas and to examine variation of the phosphoraniminato ligand, we prepared and characterized a series of vanadium(V) complexes containing one, two, three, or four phosphoraniminato ligands as described herein.

Experimental Section

General Procedures. All reactions and manipulations were performed under standard anhydrous and anaerobic conditions using appropriately dried reagent grade solvents and chemicals.[8] $V(NSiMe_3)Cl_3$,[9] PCl_2R_3 reagents,[10,11] and $Me_3SiNPPh_3$[12] were prepared using literature procedures. Ammonia (Aldrich) was used as received. NMR spectra were recorded on General Electric OMEGA500, GN500, and QE300 and on Bruker AC300 and WM250 spectrometers at ambient temperatures. Chemical shifts are reported relative to $\delta = 0$ for $SiMe_4$ (for ^1H NMR data listed below), external 85% H_3PO_4 (for ^{31}P NMR data given in Table 1), or external $V(O)Cl_3$ (for ^{51}V NMR data given in Table 1); coupling constants and peak half-widths are reported in hertz. Infrared spectra were recorded on a Mattson Galaxy 5030 FT-IR spectrometer either as films on KBr plates or as KBr pellets and are reported in cm^{-1}. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory.

$V(NPPh_3)Cl_4$ (1a). A solution of PCl_2Ph_3 (0.828 g, 2.48 mmol) in dichloromethane (7 mL) was quickly added to a stirred solution of $V(NSiMe_3)Cl_3$ (0.615 g, 2.52 mmol) in dichloromethane (3 mL) at room

---

® Abstract published in *Advance ACS Abstracts,* August 1, 1994.

(1) Schomber, B. M.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4488−4490.

(2) Lichtenhan, J. D.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1992**, *31*, 2893−2900, 4210−4212.

(3) Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, *8*, 707−726 and references therein.

(4) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(5) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123−175.

(6) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 2, pp 122−125.

(7) See, for example: Pershina, V.; Sepp, W. D.; Fricke, B.; Rosen, A. *J. Chem. Phys.* **1992**, *96*, 8367−8378. Blayden, H. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 1147−1148 and references therein.

(8) Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; Kreiger: Malaber, FL, 1982. *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(9) Critchlow, S. C.; Lerchen, M. E.; Smith, R. C.; Doherty, N. M. *J. Am. Chem. Soc.* **1988**, *110*, 8071−8075.

(10) Appel, R.; Schöler, H. *Chem. Ber.* **1977**, *110*, 2382−2384.

(11) Pure PCl_2R_3 reagents are required in order to synthesize clean samples of **1a−d** and to isolate these compounds in good yield. We prepared the reagents according to the procedure in ref 10 and then purified the soluble compounds by repeated recrystallization from acetonitrile/diethyl ether (PCl_2Ph_3) or acetonitrile (PCl_2MePh_2 and PCl_2Me_2Ph) and the insoluble compound (PCl_2Me_3) by repeated washing with dichloromethane and then acetonitrile.

(12) Birkofer, L.; Ritter, A.; Richter, P. *Chem. Ber.* **1963**, *96*, 2750−2757.

0020-1669/94/1333-4360$04.50/0

temperature, resulting in an immediate color change from orange to burgundy. The solvent volume was reduced to approximately 5 mL and the sample stirred at −80 °C for 1 h, resulting in formation of a dark maroon crystalline solid that was collected by filtration, washed with pentane (ca. 2 mL), and dried under vacuum, yielding 0.820 g of **1a** (71%). ^{1}H NMR (CD_2Cl_2): 7.95 (m, 9 H), 7.78 (m, 6 H). ^{1}H NMR (CD_3CN): 7.95 (dd, J_{HH} = 8, J_{PH} = 14, 6 H), 7.82 (t, J_{HH} = 8, 3 H), 7.66 (td, J_{HH} = 8, J_{PH} = 4, 6 H). IR: 1585, 1483, 1447, 1262, 1122, 1023, 997, 799, 728 , 686, 524. Anal. Calcd for $C_{18}H_{15}Cl_4NPV$: C, 46.09; H, 3.22; N, 2.99. Found: C, 45.80; H, 3.29; N, 2.97.

V(NPMePh$_2$)Cl$_4$ (1b).[1] The procedure for **1a** was followed using 0.433 g of PCl_2MePh_2 (1.60 mmol) and 0.389 g of $V(NSiMe_3)Cl_3$ (1.59 mmol) and yielding 0.506 g of dark maroon crystalline **1b** (78%). ^{1}H NMR (CD_2Cl_2): 8.00 (t, J_{HH} = 7, 4 H), 7.92 (t, J_{HH} = 7, 2 H), 7.78 (m, 4 H), 2.88 (d, J_{PH} = 12, 3 H). ^{1}H NMR (CD_3CN): 8.12 (dd, J_{HH} = 8, J_{PH} = 14, 4 H), 7.91 (t, J_{HH} = 8, 2 H), 7.77 (m, 4 H), 3.00 (d, J_{PH} = 14, 3 H). IR: 1429, 1395, 1128, 1082, 1015, 991, 885, 741, 670.

V(NPMe$_2$Ph)Cl$_4$ (1c). The procedure for **1a** was followed using 0.086 g of PCl_2Me_2Ph (0.411 mmol) and 0.096 g of $V(NSiMe_3)Cl_3$ (0.394 mmol) and yielding 0.170 g of dark maroon crystalline solids **1c** (79%). ^{1}H NMR (CD_3CN): 8.14 (dd, J_{HH} = 8, J_{PH} = 14, 2 H), 7.88 (t, J_{HH} = 7, 1 H), 7.76 (td, J_{HH} = 8, J_{PH} = 4, 2 H), 2.64 (d, J_{PH} = 13, 6 H). IR: 1438, 1413, 1305, 1132, 1090, 996, 943, 872, 750, 692. Anal. Calcd for $C_8H_{11}Cl_4NPV$: C, 27.86; H, 3.21; N, 4.06. Found: C, 27.79; H, 3.50; N, 3.92.

V(NPMe$_3$)Cl$_4$ (1d). A suspension of PCl_2Me_3 (0.107 g, 0.728 mmol) in dichloromethane (5 mL) was added dropwise to a stirred solution of $V(NSiMe_3)Cl_3$ (0.175 g, 0.716 mmol) in dichloromethane (5 mL) cooled to −80 °C. An immediate color change from orange to burgundy occurred, and the precipitation of dark solids was observed. The mixture was allowed to warm to room temperature, and the solids were collected by filtration, washed with dichloromethane (ca. 2 mL), and dried under vacuum, yielding 0.148 g of dark brown **1d** (73%). ^{1}H NMR (CD_3CN): 2.23 (br). IR: 1115, 1039, 953, 862, 765.

[V(NPPh$_3$)Cl$_5$]$^-$. Samples of **1a** (18.2 mg, 0.039 mmol) and PCl_2Ph_3 (8.2 mg, 0.025 mmol) were dissolved in 0.40 mL of CD_3CN in an NMR tube and allowed to react at room temperature for several days, producing a mixture containing the acetonitrile adduct of **1a**, $[V(NPPh_3)Cl_5]^-$, and PCl_2Ph_3, with the ratio of $[V(NPPh_3)Cl_5]^-$ to **1a** increasing slowly over time, consistent with the reaction shown in eq 1. ^{31}P NMR: δ 66 sharp, $PCl_2Ph_3 \rightleftharpoons [PClPh_3]^+ + Cl^-$;[13−16] δ 48 broad,

$$V(NPPh_3)Cl_4(NCMe) + PCl_2Ph_3 \rightarrow [V(NPPh_3)Cl_5][PClPh_3] + MeCN \quad (1)$$

$V(NPPh_3)Cl_4(NCCD_3)$; $[V(NPPh_3)Cl_5]^-$ was not detected due to its low concentration and the signal/noise of the spectrum.[17] ^{51}V NMR: δ 357, $\nu_{1/2}$ = 550 Hz, $[V(NPPh_3)Cl_5]^-$; δ 123, $\nu_{1/2}$ = 650 Hz, $V(NPPh_3)Cl_4(NCCD_3)$.

V(NPPh$_3$)$_2$Cl$_3$[18] (2). A solution of $Me_3SiNPPh_3$ (0.120 g, 0.343 mmol) in dichloromethane (3 mL) was added to a stirred solution of **1a** (0.158 g, 0.337 mmol) in dichloromethane (3 mL). Within a few minutes, the burgundy-colored solution turned orange and dark orange solid began to form. The solvent volume was reduced by half, and the solid was collected by filtration and dried under vacuum to yield 0.175 g of dark orange crystalline **2** (77%). ^{1}H NMR (CD_2Cl_2): 7.62 (m, 18 H), 7.42 (td, J_{HH} = 8, J_{PH} = 3, 12 H). IR: 1439, 1177, 1165, 1160, 1114, 1102, 1080, 1070, 1025, 996, 723, 691, 539, 531, 523. Anal. Calcd for $C_{36}H_{30}Cl_3N_2P_2V \cdot CH_2Cl_2$: C, 55.91; H, 4.06; N, 3.52. Found: C, 55.19; H, 4.37; N, 3.89.

V(NPPh$_3$)$_3$Cl$_2$ (3). Dichloromethane (10 mL) was vacuum-transferred onto a mixture of **2** (0.237 g, 0.334 mmol) and $Me_3SiNPPh_3$ (0.206 g, 0.589 mmol) at −80 °C. When the mixture was warmed to room temperature, reaction of sparingly soluble **2** and soluble $Me_3SiNPPh_3$ produced an orange solution that was stirred for 30 min. The solvent volume was reduced to 5 mL, 10 mL of pentane was added, and the mixture was stirred for 20 min, resulting in formation of a yellow solid **3** in a pale yellow solution. The solid was collected by filtration, washed with pentane (3 × 3 mL), and dried under vacuum, yielding 0.253 g of amber **3** (76%). ^{1}H NMR (CD_2Cl_2 or CD_3CN): 7.59 (t, J_{HH} = 8, 9 H), 7.42 (dd, J_{HH} = 8, J_{PH} = 13, 18 H), 7.32 (CD_2Cl_2) or 7.35 (CD_3CN) (td, J_{HH} = 8, J_{PH} = 3, 18 H). IR: 1482, 1437, 1088, 1025, 996, 754, 721, 690, 525. Anal. Calcd for $C_{54}H_{45}Cl_2N_3P_3V \cdot CH_2Cl_2$: C, 63.79; H, 4.57; N, 4.06. Found: C, 63.51; H, 4.83; N, 3.90.

[V(NPPh$_3$)$_4$]Cl (4). A burgundy-colored solution of **1a** (0.228 g, 0.486 mmol) in dichloromethane (15 mL) was stirred under an excess of NH_3 at 1 atm pressure. Within a few minutes, the solution became yellow with a fine brown precipitate. This solid, which can be shown to contain NH_4Cl as well was other unidentified materials, was removed by filtration, and the solvent was removed from the filtrate under vacuum to produce 0.110 g of **4** as a yellow powder (76% based on $NPPh_3$ groups available in **1a**). ^{1}H NMR: 7.45 (CD_2Cl_2) or 7.48 (CD_3CN) (m, 36 H), 7.12 (CD_2Cl_2) or 7.17 (CD_3CN) (td, J_{HH} = 8, J_{PH} = 3, 24 H). IR: 1482, 1436, 1110, 1089, 1025, 996, 718, 692, 530. Anal. Calcd for $C_{72}H_{60}ClN_4P_4V$: C, 72.58; H, 5.08; N, 4.70. Found: C, 71.80; H, 5.27; N, 4.66. Crystals of **4·4MeCN** used for an X-ray diffraction experiment were prepared by slow crystallization at 0 °C from a saturated acetonitrile solution prepared at room temperature. Crystallographic data collection and structure solution were performed as previously described;[2] details are provided as supplementary material.

Results

Mono(phosphoraniminato)vanadium(V) Complexes. Rapid formation of vanadium(V) phosphoraniminato complexes occurs upon reaction of $V(NSiMe_3)Cl_3$ with dichlorophosphoranes accompanied by elimination of chlorotrimethylsilane (eq 2). The

$$\begin{aligned} &V(NSiMe_3)Cl_3 + PCl_2R_3 \rightarrow \\ &\qquad V(NPR_3)Cl_4 \quad + \quad Me_3SiCl \quad (2) \\ &\qquad NPR_3 = NPPh_3,\ \mathbf{1a} \\ &\qquad NPR_3 = NPMePh_2,\ \mathbf{1b} \\ &\qquad NPR_3 = NPMe_2Ph,\ \mathbf{1c} \\ &\qquad NPR_3 = NPMe_3,\ \mathbf{1d} \end{aligned}$$

yield and purity of the products **1a−d** is critically dependent on the purity of the PCl_2R_3 reagents employed.

The dark maroon crystalline solids isolated from these reactions are only sparingly (**1d**) to moderately (**1a**) soluble in dichloromethane but are extremely soluble in acetonitrile. The poor solubility of **1** in noncoordinating solvents is likely due to these compounds adopting dimeric chloro-bridged structures (Figure 1), analogous to those determined by crystallographic studies of related niobium and tantalum complexes, $[Nb(NPPh_3)Cl_4]_2$[19] and $[Ta(NPPh_3)Cl_4]_2$.[20] In contrast, compounds **1a−d**

---

(13) PCl_2Ph_3 has been shown to exist in an ionized form in acetonitrile and chlorocarbon solutions by a variety of spectroscopic techniques and physical measurements. An early suggestion in the literature that $[PCl_3Ph_3]^-$ is the anion formed[14] has been supplanted by further experiments supporting ionization in the sense of $[PClPh_3]Cl$[15,16] and attributing the single ^{31}P NMR signal observed for PCl_2Ph_3 in acetonitrile solution to the $[PClPh_3]^+$ cation.[15]

(14) Beveridge, A. D.; Harris, G. S.; Inglis, F. *J. Chem. Soc. A* **1966**, 520−528.

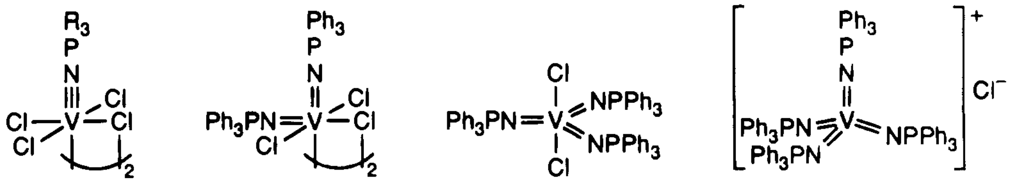
(15) Wiley, G. A.; Stine, W. R. *Tetrahedron Lett.* **1967**, 2321−2324.

(16) Harris, G. S.; Ali, M. F. *Tetrahedron Lett.* **1968**, 37−38. Lynch, R. J.; Waddington, T. C. *Adv. Nucl. Quadrupole Reson.* **1974**, *7*, 37−48. Sergienko, L. M.; Ratovskii, G. V.; Dmietriev, V. I.; Timokhin, B. V. *Zh. Obshch. Khim.* **1979**, *49*, 317−329.

(17) For some of compounds in this system, we are unable to obtain ^{31}P NMR signals for samples for which we can obtain good ^{51}V NMR data. This can be readily explained. The receptivity of ^{51}V is roughly a factor of 10 better than that of ^{31}P (see: Ebsworth, E. A. V.; Rankin, D. W. H.; Cradock, S. *Structural Methods in Inorganic Chemistry*; Blackwell Scientific: Oxford, England, 1987; Tables 2.1−2.2). Additionally, the peak shapes and couplings in this system conspire to make it difficult to observe ^{31}P NMR signals. For example, whereas moderately broad well-shaped peaks are observed in the ^{51}V NMR spectra for **1a−d** and **3**, very broad, flattened ^{31}P NMR signals are observed due to unresolved coupling to the vanadium ($I = {}^{7}/_{2}$) which is capable of splitting each ^{31}P peak into eight equal intensity lines.

(18) Choukroun, R.; Gervais, D.; Dilworth, J. R. *Transition Met. Chem. (London)* **1979**, *4*, 249−251.

(19) Bezler, H.; Strähle, J. *Z. Naturforsch.* **1979**, *34B*, 1199−1202.



1 **2** **3** **4**

Figure 1. Proposed coordination geometries for $V(NPPh_3)Cl_4$ (**1a**), $V(NPPh_3)_2Cl_3$ (**2**), and $V(NPPh_3)_3Cl_2$ (**3**) and coordination geometry for $V(NPPh_3)_4Cl$ (**4**) as discussed in the text.

Table 1. $^{31}P\{^1H\}$ and ^{51}V NMR Data for **1**–**4**

	$\delta(^{31}P\{^1H\})$		$\delta(^{51}V)$	
	CD_2Cl_2	CD_3CN	CD_2Cl_2	CD_3CN
$V(NPPh_3)Cl_4$ (**1a**)[a]	48	48	228	123
$V(NPMePh_2)Cl_4$ (**1b**)[a]	57	54	243	130
$V(NPMe_2Ph)Cl_4$ (**1c**)[a,b]		65		134
$V(NPMe_3)Cl_4$ (**1d**)[a,b]		79		137
$V(NPPh_3)_2Cl_3$ (**2**)[b]			−225	
$V(NPPh_3)_3Cl_2$ (**3**)[a]	19	19	−344	−345
$[V(NPPh_3)_4]Cl$ (**4**)[c]	6	7	−454	−453

[a] Flat-topped ^{31}P NMR signals 500–600 Hz in width; ^{51}V NMR signals with $\nu_{1/2}$ = 400–800 Hz. [b] Some chemical shift data were not obtained because of poor solubility. [c] Well-resolved multiplets with $^2J_{VP}$ = 120 Hz (Figure 3).

are quite soluble in coordinating solvents because of the formation of monomeric Lewis base adducts. We have previously reported spectroscopic and structural characterization of solvent adducts $V(NPMePh_2)Cl_4(NCMe)$[1] and $V(NPMePh_2)Cl_4(THF)$.[21] The structural data clearly indicate that the single phosphoraniminato ligand stabilizes vanadium(V) by functioning as a triply-bonded π-donor ligand.

The ^1H NMR spectra for **1a**–**d** in CD_2Cl_2 or CD_3CN show the expected phenyl and methyl signals. First-order phenyl patterns with well-resolved proton–proton and proton–phosphorus couplings are observed in CD_3CN solution. Multinuclear NMR data for **1a**–**d** are summarized in Table 1. The ^{31}P NMR spectra of **1a**–**d** show unusually broad resonances due to unresolved coupling of the phosphorus to vanadium (we have no evidence for phosphorus–nitrogen coupling in these compounds). The ^{31}P NMR signals shift upfield as phosphoraniminato phenyl groups are "replaced" with methyl groups (**1a** → **1d**), analogous to the chemical shift trend in the starting dichlorophosphoranes.[10] In contrast, changing the groups on the phosphoraniminato ligand has little effect on the ^{51}V NMR spectra, although the ^{51}V NMR chemical shifts are sensitive to solvent, consistent with adduct formation in coordinating solvents.

Attempts to extend the chemistry in reaction 1 to a more diverse group of phosphorus(V) chlorides have thus far not been encouraging. For example, no reaction has been observed between $V(NSiMe_3)Cl_3$ and $[P(N)Cl_2]_3$, even under forcing conditions. The initially surprising difference in reactivity of PCl_2R_3 versus $[P(N)Cl_2]_3$ may have its origin in the availability of free chloride ions from these reagents. PCl_2R_3 has solution behavior consistent with access to $[PClR_3]Cl$,[13] whereas $[P(N)Cl_2]_3$ undergoes dissociation of chloride[22] only at temperatures well above those needed for thermal decomposition of $V(NSiMe_3)Cl_3$.

One of the reasons for our interest in phosphoraniminato complexes has been the possibility of using reactivity of their N—P bonds for the synthesis of metallonitride complexes.[2,23] We therefore examined the reaction of **1a** with pyridine to see if the known vanadium nitride $[V(N)Cl_2(py)_2]_\infty$[9] would form. Addition of 2 equiv of pyridine to a CD_3CN solution of **1a** initially produces a complex mixture which includes a ^{51}V NMR signal at δ −69, consistent with generation of a small amount of soluble monomeric $V(N)Cl_2(py)_2$ in the reaction.[24] After several days, the NMR spectra of the mixture simplify, showing two soluble vanadium species, the acetonitrile adduct of **1a** and a new complex with a ^{51}V NMR signal at δ 357, as well as a significant amount of solid. The ^{51}V NMR signal at δ 357 has been assigned to $[V(NPPh_3)Cl_5]^-$ on the basis of the observation of this signal in the reaction of **1a** with PCl_2Ph_3 (see Experimental Section) and by analogy to the known niobium and tantalum complexes, $[M(NPPh_3)Cl_5]^-$.[25] Formation of a similar mixture containing the acetonitrile adduct of **1a**, $[V(NPPh_3)Cl_5]^-$, and solids is observed upon reaction of $[V(N)Cl_2(py)]_\infty$ and 1 equiv of PCl_2Ph_3 in CD_3CN over several days. In other words, the vanadium(V) nitrido compound combines with the phosphorus(V) reagent PCl_2Ph_3 to yield vanadium(V) phosphoraniminato products. Note that formation of a reduced vanadium(IV) phosphoraniminato compound from a vanadium(V) nitride plus phosphine (i.e., phosphorus(III)) was recently reported.[26]

The observations described above indicate the two reactions, $[V(N)Cl_2(py)_2]_\infty + PCl_2Ph_3$ and $V(NPPh_3)Cl_4$ + 2py, produce similar mixtures. The identity of all the species present in these mixtures cannot be unequivocally determined because solids are present in all cases and because $[V(N)Cl_2(py)_2]_\infty$ undergoes decomposition in CD_3CN on the time scale of the reactions. Nonetheless, the NMR data suggest that the following reactions are important in describing this chemistry:

$$V(N)Cl_2(py)_2 + PCl_2Ph_3 + MeCN \rightleftharpoons V(NPPh_3)Cl_4(NCMe) + 2py \quad (3)$$

$$V(NPPh_3)Cl_4(NCMe) + Cl^- \rightarrow [V(NPPh_3)Cl_5]^- + MeCN \quad (4)$$

The species in reaction 3 are either identified in or added to both mixtures, suggesting that reversible interconversion of the vanadium phosphoraniminato and nitrido compounds occurs, albeit in a complex reactive mixture. The source of the Cl^- in

---

(20) Bezler, H.; Strähle, J. *Z. Naturforsch.* **1983**, *38B*, 317–320.

(21) Schomber, B. M. Ph.D. Dissertation, University of Washington, 1990.

(22) See, for example: Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.

(23) Gibson, V. C.; Williams, D. N.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1989**, 1863–1864.

(24) When $[V(N)Cl_2(py)_2]_\infty$ is placed in CD_3CN, a ^{51}V NMR signal is observed at δ −69 attributed to a small amount of soluble monomeric $V(N)Cl_2(py)_2$ present in solution: Aistars, A.; Killeen, K. A.; Schomber, B. M.; Doherty, N. M. Work in progress. Compare, for example, the ^{51}V NMR signals at δ −65 and −64 reported for soluble monomeric $V(N)Cl_2(4\text{-Etpy})_2$ and $V(N)Cl_2(4\text{-}t\text{-Bupy})_2$, respectively.[9]

(25) The niobium and tantalum anions $[M(NPPh_3)Cl_5]^-$ were produced by reactions of the azido compounds $[M(N_3)Cl_5]^-$ with PPh_3: Dübgen, R.; Müller, U.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1980**, *471*, 89–101.

(26) Hills, A.; Hughes, D. L.; Leigh, G. J.; Prieto-Alcón, R. *J. Chem. Soc., Dalton Trans.* **1993**, 3609–3617.

reaction 4 is likely PCl_2Ph_3,[13–16] although the possibility of Cl^- generated by the decomposition of vanadium compounds such as $V(N)Cl_2(py)_2$ cannot be ruled out.

Poly(phosphoraniminato)vanadium Complexes. Stepwise replacement of two of the chloro ligands in $V(NPPh_3)Cl_4$ (**1a**) with phosphoraniminato ligands can be accomplished in good yield by reaction with 1−2 equiv of the *N*-(trimethylsilyl)triphenylphosphinimine (eq 5). Compound **2** has previously

$$\underset{\mathbf{1a}}{\mathrm{V(NPPh_3)Cl_4}} \xrightarrow[+\mathrm{Me_3SiNPPh_3}]{-\mathrm{Me_3SiCl}} \underset{\mathbf{2}}{\mathrm{V(NPPh_3)_2Cl_3}} \xrightarrow[+\mathrm{Me_3SiNPPh_3}]{-\mathrm{Me_3SiCl}} \underset{\mathbf{3}}{\mathrm{V(NPPh_3)_3Cl_2}} \quad (5)$$

been reported as the product of the reaction of oxovanadium trichloride with $Me_3SiNPPh_3$ in dichloromethane,[18] although in our hands this reaction produces several vanadium-containing species, including **3**.

Dark orange **2** is only very sparingly soluble in dichloromethane and, surprisingly, insoluble in coordinating solvents such as acetonitrile. We attribute the poor solubility to adoption of a dimeric chloro-bridged structure that is apparently not broken up by coordinating solvents. In contrast, the related niobium(V) bis(phosphoraniminato) compound, $Nb(NPPh_3)_2Cl_3$, has been shown to possess a five-coordinate distorted trigonal bipyramidal structure in the solid state.[27] Figure 1 shows a possible dimeric structure for **2**. We expect a cis relationship between two multiply-bonded phosphoraniminato ligands at a six-coordinate d^0 vanadium(V) center, allowing the maximum of three V−N π-bonds.[28] However, we have no information on the placement of the proposed chloro bridges relative to the phosphoraniminato ligands, in part because we have been unable to detect ^{31}P NMR signal(s) for **2** due to its poor solubility.[29]

In contrast to **2**, yellow **3** is readily soluble in both coordinating and noncoordinating solvents. This solubility and the observation that there is no change in the ^{51}V NMR signal for **3** on going from CD_2Cl_2 to CD_3CN (Table 1) suggest that **3** adopts a monomeric structure that cannot coordinate acetonitrile due to the steric and electronic demands of three triphenylphosphoraniminato ligands. A trigonal bipyramidal structure with the more electronegative chloro ligands in the axial positions as preferred in such d^0 compounds[30] and the bulky phosphoraniminato ligands in the equatorial positions (Figure 1) is consistent with the spectral data for **3** and would permit maximum π-donation (a total of four V−N π-bonds) from the phosphoraniminato ligands to the d^0 metal.[31]

Our initial attempts to place additional phosphoraniminato ligands on vanadium(V) focused on the reaction of **1a** with excess $Me_3SiNPPh_3$, but the tris(phosphoraniminato) compound (**3**) was the sole product isolated. Nonetheless, the tetrakis(triphenylphosphoraniminato)vanadium complex can be prepared by reaction of **1a**, **2**, or **3** with excess ammonia (eq 6).

$$\underset{\mathbf{1a,\ 2,\ 3}}{\mathrm{V(NPPh_3)_{\mathit{n}}Cl_{-\mathit{n}}}} \xrightarrow{\text{excess }\mathrm{NH_3}} \underset{\mathbf{4}}{\mathrm{[V(NPPh_3)_4]Cl}} \quad (6)$$

Table 2. Crystallographic Data for $[V(NPPh_3)_4]Cl{\cdot}4MeCN$ (**4·4MeCN**)

formula	$C_{80}H_{72}ClN_8P_4V$	fw	1355.00
a, Å	14.599(3)	space group	$P\bar{1}$
b, Å	14.598(3)	*T*, K	163
c, Å	18.368(4)	λ, Å	0.710 73
α, deg	89.14(3)	ϱ_{calcd}, g cm^{-3}	1.266
β, deg	68.72(3)	μ, mm^{-1}	0.308
γ, deg	77.75(3)	trasm coeff	0.931−1.000
V, Å^3	3556.3(13)	$R(F_o)^a$	0.0604
Z	2	$R_w(F_o)^b$	0.0704

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w^{-1} = \sigma^2|F_o| + 0.0004|F_o|^2$.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Selected Atoms of **4·4MeCN**

	x	*y*	*z*	*U*(eq)^a
V(1)	3332(0.7)	2247(0.6)	3102(0.5)	17(1)
Cl(1)	820(1.1)	8802(1.1)	1193(0.9)	38(1)
P(1)	3659(1.1)	2913(1.0)	1400(0.8)	23(1)
P(2)	4228(1.1)	3621(1.0)	3984(0.9)	23(1)
P(3)	1019(1.1)	2304(1.0)	4139(0.8)	20(1)
P(4)	4584(1.1)	131(1.0)	2920(0.8)	21(1)
N(1)	3109(3)	2808(3)	2302(3)	24(2)
N(2)	3793(3)	3004(3)	3565(3)	30(2)
N(3)	2207(3)	2013(3)	3789(3)	23(2)
N(4)	4241(3)	1189(3)	2757(3)	24(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

These reactions produce **4** in high yield based on the number of $NPPh_3$ groups available in the starting material; however, there is substantial loss of vanadium in these reactions. Ammonium chloride has been identified as a byproduct of reaction 6, although we have been unable to satisfactorily quantify its formation or identify the vanadium-containing coproduct(s).

Yellow **4** crystallizes from acetonitrile as a tetrasolvate, $[V(NPPh_3)_4]Cl{\cdot}4MeCN$, for which the solid state structure has been determined by X-ray crystallography (Tables 2 and 3). The asymmetric unit contains one $[V(NPPh_3)_4]^+$ cation (Figure 2), one chloride anion, and four acetonitrile molecules. The vanadium−nitrogen distances in **4** (Table 4) are the same within experimental error and are in the range expected for approximately V=N double bonds.[32] Likewise, the four nitrogen−phosphorus distances are the same within experimental error and very close to the standard 1.55 Å distance usually quoted for N=P double bonds.[33] In contrast, the VNP angles in $[V(NPPh_3)_4]^+$ range from quite bent to almost linear (Table 4).

---

(27) Weller, F.; Nusshär, D.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1992**, *615*, 7−10.

(28) In general, two multiply-bonded ligands at a six-coordinate d^0 metal center adopt a cis relationship.[4] This is the case for the structurally characterized octahedral bis(phosphoraniminato) complexes $W(NPR_3)_2F_4$: Roesky, H. W.; Katti, K. V.; Seseke, U.; Scholz, U.; Herbst, R.; Egert, E.; Sheldrick, G. M. *Z. Naturforsch.* **1986**, *41B*, 1509−1512. Roesky, H. W.; Seseke, U.; Noltemeyer, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1309−1310.

(29) The solubility of **2** is sufficiently poor that no ^{31}P NMR signal can detected for a saturated CH_2Cl_2/CD_2Cl_2 solution in a 10-mm NMR tube at 202-MHz observation frequency.[17] In contrast, a ^{51}V NMR signal attributed to **2** is detected for saturated CD_2Cl_2 solutions in 5-mm NMR tubes at 123-MHz observation frequency.

(30) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Chapters 14 and 17.

(31) The D_{3d} structure of **3** results in symmetry-allowed overlap of four of the five empty metal d orbitals (all except the d_{z^2} orbital that is used in σ-bonding with the axial ligands) with symmetry-adapted combinations of the six filled nitrogen p_π orbitals on the three phosphoraniminato ligands, resulting in a total of four $V{-}NPPh_3$ π bonds and a formally 18-electron complex.

(32) See discussion and references in: Haddad, T. S.; Aistars, A.; Ziller, J. W.; Doherty, N. M. *Organometallics* **1993**, *12*, 2420−2422.

(33) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, England, 1984; pp 871−875.

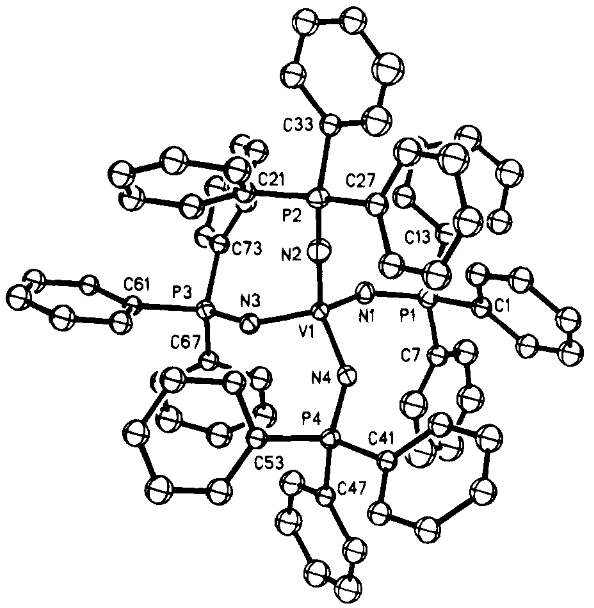


Figure 2. Drawing of the cation $[V(NPPh_3)_4]^+$ in the structure of $[V(NPPh_3)_4]Cl{\cdot}4MeCN$ with 50% thermal ellipsoids for non-hydrogen atoms.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[V(NPPh_3)_4]^+$ in **4**·**4MeCN**

V(1)—N(1)	1.771(5)	N(1)—P(1)	1.578(4)
V(1)—N(2)	1.776(6)	N(2)—P(2)	1.557(6)
V(1)—N(3)	1.768(4)	N(3)—P(3)	1.578(4)
V(1)—N(4)	1.760(4)	N(4)—P(4)	1.580(5)
V(1)—N(1)—P(1)	141.0(3)	V(1)—N(3)—P(3)	146.2(3)
V(1)—N(2)—P(2)	177.0(3)	V(1)—N(4)—P(4)	145.8(3)

We have previously argued that variations in the VNP angles arise from crystal packing forces rather than variations in the V—N and N—P bonding[1] and suggest that the same effect is operating here. Comparable structures have been reported for analogous tantalum(V),[34] molybdenum(VI),[35] and tungsten(VI)[36] tetrakis(phosphoraniminato) cations, $[M(NPPh_3)_4]^{n+}$.

NMR spectral data for **4** indicate the existence of an analogous four-coordinate tetrahedral structure for $[V(NPPh_3)_4]^+$ in solution. The ^{31}P NMR spectrum shows an eight-line pattern consistent with coupling to a single vanadium ($I = {}^7/_2$), and the ^{51}V NMR signal appears as a binomial quintet, indicating coupling to four equivalent phosphorus nuclei (Figure 3 and Table 1). The observation of well-resolved two-bond coupling (J_{VP} = 120 Hz) between the vanadium and phosphorus nuclei is unusual and likely due to the high symmetry of the cation.[37]

The tetrahedral structure of **4** is presumably enforced by the steric demands of placing four triphenylphosphoraniminato ligands around a single metal center. Nonetheless, **4** undergoes ligand exchange reactions, suggesting that five-coordinate species are accessible: **4** reacts with **1a** or **2**, producing **3** as the major vanadium-containing product in solution, presumably via ligand-bridged intermediates.[38]

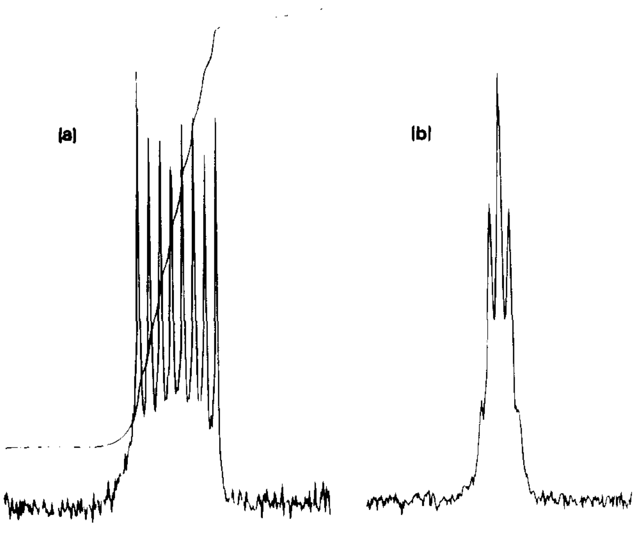


Figure 3. (a) ^{31}P NMR and (b) ^{51}V NMR spectra of $[V(NPPh_3)_4]Cl$ in CD_2Cl_2.

The steric demands of placing four triphenylphosphoraniminato ligands around a single metal center could also explain why **4** cannot be prepared from **3** plus 1 equiv of *N*-(trimethylsilyl)triphenylphosphinimine. This reaction produces only a small equilibrium concentration of **4** (eq 6), and **4** reacts rapidly with chlorotrimethylsilane to yield **3** (reverse of eq 7).

$$\underset{\mathbf{3}}{V(NPPh_3)_3Cl_2} + Me_3SiNPPh_3 \xrightleftharpoons{K = 3 \times 10^{-3}} \underset{\mathbf{4}}{[V(NPPh_3)_4]Cl} + Me_3SiCl \quad (7)$$

Discussion

Vanadium(V) mono-, bis-, tris-, and tetrakis(phosphoraniminato) complexes (Figure 1) have been prepared using the reactivity of the nitrogen—silicon bonds in both vanadium silylimido compounds and *N*-silylphosphinimine reagents. Specifically, the silylimido ligand in $V(NSiMe_3)Cl_3$ is converted to a phosphoraniminato ligand by reaction with an organophosphorane dichloride in chemistry closely related to the various condensation reactions of silylimido complexes that we have previously reported.[1,2,9,39] Subsequent replacement of chloro ligands with phosphoraniminato ligands using $Me_3SiNPPh_3$ is common for the synthesis of such compounds,[2,3,6,18,27,34-36] although substitution of the fourth phosphoraniminato ligand into the vanadium(V) coordination sphere involves an unfavorable equilibrium.

The tetrakis(phosphoraniminato)vanadium compound **4** is instead isolated by an unusual reaction of the mono-, bis-, or tris(triphenylphosphoraniminato)vanadium compound with excess NH_3. Ammonia apparently promotes phosphoraniminato ligand transfer between metal centers in a net reaction favoring formation of **4**. In contrast, ligand redistribution between **4** and **2** or **1** favors formation of the intermediate species, **3**. Overall, these reactions indicate that exchange of phosphoraniminato ligands between metal centers is facile in this system.

In contrast to the lability of the V—N bonds of **1**—**4**, reactivity at their N—P bonds is limited. The mono(phosphoraniminato) compound **1a** can be argued to undergo chemistry at its N—P

---

(34) Nusshär, D.; Weller, F.; Neuhaus, A.; Frenking, G.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1992**, *615*, 86—92.

(35) Nusshär, D.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 507—512.

(36) Rentschler, E.; Nusshär, D.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 999—1003.

(37) Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33—83. In contrast, observation of one-bond vanadium—phosphorus coupling is quite common.

(38) Ligand redistribution reactions involving coordinatively unsaturated d^0 metal centers are very common and thought to occur via dinuclear diligand-bridged species. We have found numerous examples of such reactions for vanadium(V) compounds: Killeen, K. A.; Doherty, N. M. Work in progress.

(39) Doherty, N. M.; Critchlow, S. C. *J. Am. Chem. Soc.* **1987**, *109*, 7906—7908. Hoffman, N. W.; Prokopuk, N.; Robbins, M. J.; Jones, C. M.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4177—4181.

bond on the basis of the detection of a small amount of V(N)-$Cl_2(py)_2$ in mixtures of **1a** plus pyridine, although this reaction and related mixtures ultimately yield phosphoraniminato complexes as the favored soluble vanadium-containing species. We have not yet observed any reactivity at the N—P bonds in the bis-, tris-, or tetrakis(phosphoraniminato) complexes. This fits with the expectation that as the number of phosphoraniminato ligands at the metal increases, the opportunity for each ligand to engage in metal—nitrogen π-bonding decreases, resulting in increased phosphorus—nitrogen π-bonding, as illustrated in the resonance structures in Scheme 1, and, thus, lower N—P reactivity.

The coordination number also decreases as the number of phosphoraniminato ligands about the vanadium(V) center increases, from 6 for **1** (and, tentatively, **2**) to 5 for **3** and 4 for **4**. This is consistent both with increasing steric bulk in the metal coordination sphere and with increasing electronic saturation upon placement of additional multiply-bonding ligands at the metal center. Thus, phosphoraniminates offer the possibility of introducing π-donor ligands into metal coordination spheres without changing the number of anionic ligands, however only up to the point where steric and electronic crowding dictate loss of one (or more[35,36]) of the anionic ligands.

Acknowledgment. We gratefully acknowledge support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society. N.M.D. thanks the Alfred P. Sloan Research Foundation for a fellowship (1990—3) used in partial support of this work.

Supplementary Material Available: Tables giving structure determination summary, atomic coordinates and equivalent isotropic displacement coefficients, interatomic distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients and a packing diagram of the unit cell for **4·4MeCN** (14 pages). Ordering information is given on any current masthead page.