# Vanadium and niobium diamidophosphine complexes and their reactivity

**Michael P. Shaver, Robert K. Thomson, Brian O. Patrick, and Michael D. Fryzuk**

**Abstract:** The tridentate ligand precursors $R'P(CH_2SiMe_2NR'')_2$ ($^{R'R''}$[NPN]: R′ = Cy, Ph; R″ = Ph, Mes, Me) were prepared from metathesis reactions of a lithiated amine, chloro(chloromethyl)dimethylsilane, the appropriate 1° phosphine, and *n*-butyl lithium and were isolated as solvent adducts. Metathesis between $^{CyPh}[NPN]Li_2(OEt_2)$, **2**, and $VCl_3(THF)_3$ afforded $(^{CyPh}[NPN]VCl)_2$, **7**, whose solid-state structure was established by X-ray crystallography. Reduction attempts of the $(^{R'R''}[NPN]VCl)_2$ species with $KC_8$ incorporated molecular nitrogen but were complicated by imide formation and ligand decomposition. Metathesis of **2** with $NbCl_2Me_3$ afforded the highly unstable complex $^{CyPh}[NPN]NbMe_3$, **15**. Attempts to hydrogenate this species were unsuccessful.

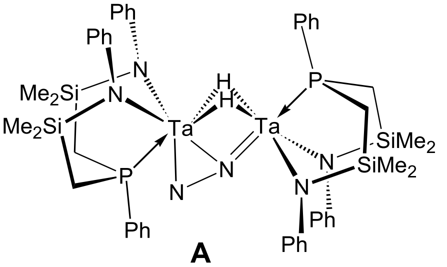
*Key words:* vanadium, niobium, metathesis, coordination chemistry, reduction, hydrogenation.

**Résumé :** Les précurseurs de ligand $R'P(CH_2SiMe_2NR'')_2$ ($^{R'R''}$[NPN] : R′ = Cy, Ph; R″ = Ph, Mes, Me) ont été préparé des réactions de métathèse du amine lithié correspondant, chloro(chloromethyl)dimethylsilane, le phosphine correspondant et *n*-butyl lithium. Les ligands ont été isolés comme adducts de solvant de selde dilithium. Les réactions de métathèse du $^{CyPh}[NPN]Li_2(OEt_2)$, **2**, avec $VCl_3(THF)_3$ ont donné $(^{CyPh}[NPN]VCl)_2$, **7**, dont de la structure d'état solide a été établie par crystallographie de rayons-X. Les tentatives de réduction de l'espèce $(^{R'R''}[NPN]VCl)_2$ avec $KC_8$ a incorporé l'azote moléculaire mais a été compliquée par la formation d'imide et la décomposition de ligand. Les réactions de métathèse de **2** avec $NbCl_2Me_3$ ont donné le complexe extrêmement instable $^{CyPh}[NPN]NbMe_3$, **15**. Les tentatives de hydrogéner était infructueux.

*Mots clés :* vanadium, niobium, la métathèse, la chimie de coordination, la réduction, l'hydrogénation.

## Introduction

Recent work from our laboratory has focused on the chemistry of tantalum dinitrogen complexes stabilized by the [NPN] ligand, where [NPN] = $PhP(CH_2SiMe_2NPh)_2$ (1–4). One of the most intriguing species is $([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1\text{-}\eta^2\text{-}N_2)$, **A**, with a side-on, end-on bound dinitrogen unit. This complex has displayed remarkable reactivity with simple organometallic hydride reagents. The coordination chemistry of [NPN] with Ta — the heaviest member of group 5 — piqued our interest in the lighter elements of this group, namely V and Nb. In this manuscript we explore some of our successes and failures in trying to extend dinitrogen chemistry to low valent vanadium and niobium [NPN] complexes.



**A**

## Experimental

### General information

Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen by means of standard Schlenk or glovebox techniques (Vacuum Atmospheres HE-553-2 glovebox equipped with an MO-40-2H purification system and a –40 °C freezer). Thick-walled Pyrex reaction vessels with 5 or 10 mm Teflon needle valves and ground glass joints were used to maintain an inert atmosphere at pressures between $10^{-6}$ and 4 atm (1 atm = 101.325 kPa). Hexanes and toluene were purchased anhydrous from Aldrich and further dried by passage through a tower of alumina and degassed by passage through a tower of Q-5 catalyst under a positive pressure of nitrogen (5). Anhydrous diethyl ether, tetrahydrofuran (THF), benzene, and hexamethyldisiloxane (HMDS) were stored over sieves and distilled from sodium benzophenone ketyl under argon. Nitrogen was dried and deoxygenated by passage through a column containing activated molecular sieves and MnO. Deuterated benzene was dried by refluxing with molten potassium metal in a sealed vessel under partial pressure, then trap-to-trap distilled, and degassed by freeze-pump-thaw three times. Unless otherwise stated, $^1H$, $^{31}P\{^1H\}$, and $^7Li$

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NMR spectra were recorded on a Bruker AMX-500 instrument operating at 500.1 MHz for $^1$H spectra. $^1$H NMR spectra were referenced to internal $C_6D_5H$ (7.15 ppm), $^{31}P\{^1H\}$ NMR spectra to external $P(OMe)_3$ (141.0 ppm with respect to 85% $H_3PO_4$ at 0.0 ppm), and $^7Li\{^1H\}$ NMR spectra to a 0.3 mol $L^{-1}$ LiCl solution in MeOH (0.00 ppm). Elemental analyses were performed in the departmental facility; mass spectra were recorded on a Kratos MS 50. Clusters assigned to specific ions show appropriate isotopic distribution patterns, as calculated for the atoms present. $NbCl_5$ was purchased from Strem Chemicals and used without further purification. Anhydrous $ZnCl_2$ was purchased from Aldrich and dried by refluxing in excess $SOCl_2$ under $N_2$. $MeNH_3^+Cl^-$ was purchased from Fisher Chemicals and recrystallized out of hot ethanol and dried in vacuo prior to use. The reagents $PhNH_2$, $ClSiMe_2CH_2Cl$, $CyPH_2$, $MesNH_2$ ($MesNH_2$ = 2,4,6-$Me_3C_6H_2NH_2$), and $PhPCl_2$ were purchased from Aldrich and purified by standard procedures (6). Solutions of MeLi (1.4 mol $L^{-1}$ in diethylether) and $^n$BuLi (1.6 mol $L^{-1}$ in hexanes) were obtained from Acros Organics and used as received. The compounds $PhPH_2$ (7), $^{PhPh}[NPN]Li_2(THF)_2$ (2), $^{CyPh}[NPN]Li_2(OEt_2)$ (8), $VCl_3(THF)_3$ (9), $KC_8$ (10), and $NbCl_2Me_3$ (11) were prepared by literature methods.

Crystallographic data[2] for compounds **4** and **7** appear in Tables 1 and 2, respectively. All measurements were made on a Rigaku–ADSC CCD area detector with graphite monochromated Mo Kα radiation. The data were processed (12) and corrected for Lorentz and polarization effects. The structure was solved by direct methods (13) and expanded by using Fourier (14) techniques. All nonhydrogen atoms were refined with anisotropic thermal parameters. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International tables for X-ray crystallography (15, 16).

**Table 1.** Crystallographic data and details of refinement for $^{CyMes}[NPN]Li_2(THF)$, **4**.

| | |
|---|---|
| Empirical formula | $C_{34}H_{57}Li_2N_2OPSi_2$ |
| Formula weight | 610.86 |
| Crystal system | Monoclinic |
| Space group | $P2_1/a$ |
| $a, b, c$ (Å) | 19.597(1), 8.9414(4), 21.492(2) |
| β (°) | 105.846(3) |
| $V$ (Å$^3$) | 3623.0(4) |
| $Z$ | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.120 |
| μ (Mo Kα) (cm$^{-1}$) | 1.69 |
| $T$ (K) | 173±1 |
| 2θ range (°) | 55.7 |
| Total reflections | 34 076 |
| Unique reflections | 8455 |
| Parameters | 508 |
| $R_1{}^a$ | 0.086 |
| $R_w{}^a$ | 0.109 |
| Goodness-of-fit | 0.87 |

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2)^{1/2}$.

**Table 2.** Crystallographic data and details of refinement for $(^{CyPh}[NPN]VCl)_2$, **7**.

| | |
|---|---|
| Empirical formula | $C_{24}H_{37}N_2PClSi_2V$ |
| Formula weight | 1054.22 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a, b, c$ (Å) | 10.2811(5), 11.4776(4), 13.3016(6) |
| α, β, γ (°) | 103.948(3), 111.556(1), 92.914(3) |
| $V$ (Å$^3$) | 1399.8(1) |
| $Z$ | 1 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.250 |
| μ (Mo Kα) (cm$^{-1}$) | 6.06 |
| $T$ (K) | 173 ± 1 |
| 2θ range (°) | 55.8 |
| Total reflections | 12 014 |
| Unique reflections | 5342 |
| Parameters | 280 |
| $R_1{}^a$ | 0.047 |
| $R_w{}^a$ | 0.095 |
| Goodness-of-fit | 1.48 |

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2)^{1/2}$.

### $^{CyMes}[NPN]Li_2(THF)$ (4)

A 300 mL ethereal solution containing 12.1 mL (11.640 g, 86.1 mmol) of $MesNH_2$ was cooled to –78 °C in a dry ice – isopropanol slush bath. A solution of 1.6 mol $L^{-1}$ $^n$BuLi in hexanes was added dropwise via syringe. After 30 min at –78 °C, the solution was warmed to room temperature (r.t.) and stirred for 60 min. Upon recooling the solution to –78 °C, 11.4 mL (12.320 g, 86.1 mmol) of $ClSiMe_2CH_2Cl$ was added and stirred for 30 min. After warming to r.t. and stirring for an additional 30 min, the solution was cooled to 0 °C and 5.8 mL (43.1 mmol) of $CyPH_2$ and 107.6 mL (172.2 mmol) of $^n$BuLi was added consecutively via syringe. This solution was stirred for 30 min and allowed to warm to r.t. The resulting white suspension was concentrated in vacuo, and the white residue was dissolved in toluene (32 g) and filtered through Celite. Removal of toluene in vacuo yielded a foamy white solid, which was dissolved in hexanes (150 mL). Addition of 5.25 mL (0.0647 mol) of THF caused $^{CyMes}[NPN]Li_2(THF)$ (**4**) to precipitate as a white microcrystalline solid, which was collected on a frit and dried under vacuum (79% yield). The other ligand precursors, $^{PhMes}[NPN]Li_2(diox)_2$ (**3**), $^{PhMe}[NPN]Li_2(diox)_2$ (**5**), and $^{CyMe}[NPN]Li_2(diox)$ (**6**) (diox = dioxane) were synthesized using the appropriate phosphines and amines in an analogous manner. Precipitation of **3**, **5**, and **6** was accomplished by addition of 3 equiv of dioxane to a hexanes solution of each product. Recovered yields were 81%, 74%, and 66%, respectively. For the *N*-

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[2] Supplementary data (crystallographic data (excluding structure factors) for $^{CyMes}[NPN]Li_2(THF)$, **4**, and $(^{CyPh}[NPN]VCl)_2$, **7**, may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 211498 and 211499, respectively, contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

methyl derivatives, $MeNH_3^+Cl^-$ was used to prepare the lithium amide, and an additional equivalent of $^n$BuLi was used. **3**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: 0.22, 0.33 (s, 12H total, Si-C$H_3$), 2.20 (s, 18H, NPh-C$H_3$), 3.17 (s, 16H, dioxane), 0.89, 1.28 (m, 4H, P-C$H_2$), 7.15, 7.24, 7.61 (m, 5H, P-Ph-*H*), 6.80 (s, 4H, NPh-*m*-*H*). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –34.1 (q, $^1J_{PLi}$ = 18.9 Hz). $^7$Li{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –0.7 (s, 1Li), –0.8 (d, $^1J_{PLi}$ = 18.9 Hz, 1Li). Anal. calcd. for $C_{38}H_{59}Li_2N_2O_4PSi_2$ (%): C 64.38, H 8.39, N 3.95; found: C 64.54, H 8.49, N 3.86. **4**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: 0.21, 0.35 (s, 12H total, Si-C$H_3$), 2.20 (s, 18H, NPh-C$H_3$), 1.13, 2.96 (s, 8H, THF), 0.85, 0.97 (m, 4H, P-C$H_2$), 1.22, 1.38, 1.68, 1.77, 1.91 (m, 11H, P-$C_6H_{11}$), 6.82 (s, 4H, NPh-*m*-*H*). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –30.2 (s). $^7$Li{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –0.8 (s, 2 Li). Anal. calcd. for $C_{34}H_{57}Li_2N_2OPSi_2$ (%): C 66.85, H 9.41, N 4.59; found: C 66.98, H 9.60, N 4.39. **5**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: –0.09, –0.10 (s, 12H total, Si-C$H_3$), 2.83 (s, 6H, N-C$H_3$), 3.57 (s, 16H, dioxane), 0.89, 0.91 (m, 4H, P-C$H_2$), 7.15, 7.22, 7.49 (m, 5H, P-Ph-*H*). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –37.5 (q, $^1J_{PLi}$ = 26.6 Hz). $^7$Li{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –1.4 (s, 1 Li), –1.5 (d, $^1J_{PLi}$ = 26.6 Hz, 1 Li). Anal. calcd. for $C_{22}H_{43}Li_2N_2O_4PSi_2$ (%): C 52.78, H 8.66, N 5.60; found: C 52.52, H 8.41, N 5.75. **6**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: 0.35 (s, 12H total, Si-C$H_3$), 3.42 (s, 8H, dioxane), 0.88, 1.22 (m, 4H, P-C$H_2$), 1.68, 1.79, 1.94 (m, 11H, P-$C_6H_{11}$), 3.02 (s, 6H, N-C$H_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –36.1 (s). $^7$Li{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –1.1 (s, 1 Li). Anal. calcd. for $C_{18}H_{41}Li_2N_2O_2PSi_2$ (%): C 51.65, H 9.87, N 6.69; found: C 51.93, H 9.85, N 6.60.

### ($^{CyPh}$[NPN]VCl)$_2$ (7)

An ethereal solution (100 mL) of $^{CyPh}$[NPN]$Li_2(OEt_2)$ (3.00 g, 4.23 mmol) maintained at –78 °C was added via cannula to a 3:1 mixture of $Et_2O$ and THF containing $VCl_3(THF)_3$ (1.58 g, 4.23 mmol). After the addition, the solution was warmed to r.t. and stirred for 90 min. Upon removal of volatiles, the resultant brick-red powder was dissolved in toluene (100 mL); the solution was filtered through Celite to remove LiCl, and the toluene was removed in vacuo. The brick-red powder was washed with pentane and dried under vacuum (75.8%, 1.69 g). Crystals of **7** suitable for X-ray diffraction were grown from a concentrated solution of layered benzene–HMDS. The compounds ($^{PhPh}$[NPN]VCl)$_2$, **8**, ($^{CyMes}$[NPN]VCl)$_2$, **9**, ($^{PhMes}$[NPN]VCl)$_2$, **10**, ($^{CyMe}$[NPN]VCl)$_2$, **11**, and ($^{PhMe}$[NPN]VCl)$_2$, **12**, were prepared analogously. **7**: EI-MS *m*/*z* (%): 526 ([M$^+$] $^{CyPh}$[NPN]VCl, 100). Anal. calcd. for $C_{48}H_{74}Cl_2N_4P_2Si_4V_2$ (%): C 54.69, H 7.08, N 5.31; found: C 54.97, H 7.26, N 5.05. **8**: EI-MS *m*/*z* (%): 520 ([M$^+$] $^{PhPh}$[NPN]VCl, 100). Anal. calcd. for $C_{48}H_{62}Cl_2N_4P_2Si_4V_2$ (%): C 55.32, H 6.00, N 5.38; found: C 55.50, H 5.88, N 5.10. **9**: EI-MS *m*/*z* (%): 610 ([M$^+$] $^{CyMes}$[NPN]VCl, 100). Anal. calcd. for $C_{60}H_{98}Cl_2N_4P_2Si_4V_2$ (%): C 58.95, H 8.08, N 4.58; found: C 58.97, H 8.26, N 4.55. **10**: EI-MS *m*/*z* (%): 604 ([M$^+$] $^{PhMes}$[NPN]VCl, 100). Anal. calcd. for $C_{60}H_{86}Cl_2N_4P_2Si_4V_2$ (%): C 59.54, H 7.16, N 4.63; found: C 59.37, H 7.00, N 4.39. **11**: EI-MS *m*/*z* (%): 402 ([M$^+$] $^{CyMe}$[NPN]VCl, 100). Anal. calcd. for $C_{28}H_{66}Cl_2N_4P_2Si_4V_2$ (%): C 41.73, H 8.25, N 6.95; found: C 41.90, H 8.02, N 6.85. **12**: EI-MS *m*/*z* (%): 396 ([M$^+$] $^{PhMe}$[NPN]VCl, 100). Anal. calcd. for $C_{28}H_{54}Cl_2N_4P_2Si_4V_2$ (%): C 42.36, H 6.86, N 7.06; found: C 42.09, H 6.89, N 6.90.

### Reduction of 7 with 2.2 $KC_8$ under 4 atm $N_2$

A thick-walled reaction vessel was charged with a magnetic stir bar, 0.218 g (0.413 mmol) of **7**, and 0.056 g (0.909 mmol) of $KC_8$. $Et_2O$ (50 mL) was vacuum transferred into the flask, frozen at –196 °C, and charged with 4 atm of $N_2$. The brick-red solution turned deep purple upon warming to r.t. The reaction was stirred for 24 h. Filtration through Celite and removal of solvent gave a waxy purple, pentane-soluble solid. EI-MS *m*/*z* (%): 505 ([M$^+$]: $^{CyPh}$[NPN]V≡N, 100), 491 ($^{CyPh}$[NPN]V, 22).

### Reduction of 7 with 3.3 $KC_8$ under 4 atm $N_2$

Diethylether (50 mL) was vacuum transferred into a thick-walled reaction vessel charged with a magnetic stir bar, 0.218 g (0.413 mmol) of **7**, and 0.084 g (1.364 mmol) of $KC_8$ and frozen at –196 °C. The vessel was charged with 4 atm of $N_2$ and warmed to r.t. The brick-red solution changed to olive green and was stirred for an additional 24 h. Filtration through Celite and removal of solvent gave a dark green, pentane-soluble powder. EI-MS *m*/*z* (%): 1049 ([M$^+$]: K($^{CyPh}$[NPN]V≡N)$_2$, 12), 505 ([M$^+$] – K($^{CyPh}$[NPN]V≡N), 100), 491 ($^{CyPh}$[NPN]V, 20).

### Reduction of 9 with 2.2 $KC_8$ under 1 atm $N_2$

Diethylether (50 mL) was transferred via syringe into a thick-walled reaction vessel charged with a magnetic stir bar, 0.252 g (0.413 mmol) of **9**, and 0.056 g (0.909 mmol) of $KC_8$ under an atmosphere of $N_2$. The vessel was sealed and the contents stirred for 24 h. Filtration through Celite and removal of solvent gave a brown, hexanes-soluble powder. Washing the powder with pentane produced an impure brown solid ($^{CyMes}$[NPN]V=NMes, **13**) and a brown solution, which, upon cooling to –37 °C, afforded brown needle crystals of MesN($SiMe_2CH_2$)$_2$PCy, **14**. Reductions of **8** and **10**–**12** were conducted in the same manner. **13**: EI-MS *m*/*z* (%): 708 ([M$^+$] $^{CyMes}$[NPN]V=NMes, 50), 575 ([M$^+$] – NMes, 100). **14**: $^1$H NMR ($C_6D_6$, 25 °C, 200 MHz) δ: 2.28, 2.32 (s, 6H total, *o*-Ph-C$H_3$), 2.40 (s, 3H, *p*-Ph-C$H_3$), 6.90, 7.25 (s, 2H total, *m*-Ph-*H*), 0.05, 0.58 (s, 12H total, Si-C$H_3$), 0.85, 1.39, 1.97 (m, 15H total, C$H_2$ and $C_6H_{11}$). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: –25.8 (s). Anal. calcd. for $C_{21}H_{38}NPSi_2$ (%): C 64.40, H 9.78, N 3.58; found: C 64.45, H 9.70, N 3.51. **Reduction of 8**: EI-MS *m*/*z* (%): 576 ([M$^+$] $^{PhPh}$[NPN]V=NPh, 20), 485 ([M$^+$] – NPh, 100). **Reduction of 10**: EI-MS *m*/*z* (%): 702 ([M$^+$] $^{PhMes}$[NPN]V=NMes, 35), 569 ([M$^+$] – NMes, 100). **Reduction of 11**: EI-MS *m*/*z* (%): 396 ([M$^+$] $^{CyMe}$[NPN]V=NMe, 8), 367 ([M$^+$] – NMe, 100). **Reduction of 12**: EI-MS *m*/*z* (%): 390 ([M$^+$] $^{PhMe}$[NPN]V=NMe, 12), 361 ([M$^+$] – NMe, 100).

### CyPh[NPN]$NbMe_3$ (15)

In the dark, a solution of 5.601 g (0.0106 mol) of **2** in 150 mL of $Et_2O$ maintained at –78 °C was added via cannula to a solution of 2.200 g (0.0106 mol) of $NbCl_2Me_3$ in 150 mL of $Et_2O$. The solution was stirred at –78 °C for 1 h, then warmed to –10 °C, producing an orange solution. Excess $Et_2O$ was removed in vacuo, and the resulting solid was dissolved in toluene and filtered through Celite. Toluene was removed in vacuo and the solid washed with pentane to afford **15** in 72% yield (4.42 g). The solid was highly light and thermally sensitive and was stored in a darkened vessel at –37 °C. Preparation of $^{PhPh}$[NPN]NbMe$_3$, **16**, and $^{CyMes}$[NPN]NbMe$_3$, **17**, was accomplished in the same manner. Reactions of **3**, **5**, and **6** did not afford the corresponding $^{R'R''}$[NPN]NbMe$_3$ species, as decomposition pathways prevented isolation of pure product. **15**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: 0.00, 0.34 (s, 12H, Si-(C*H*$_3$)), 0.75–1.42 (ov, m, 15H total, C*H*$_2$ and $C_6H_{11}$), 1.68 (s, 9H, Nb-(C*H*$_3$)$_3$), 6.96–7.12 (ov, m, 10H, N-Ph-*H*). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: 10.8 (s). **16**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: –0.08, 0.35 (s, 12H total, Si-(C*H*$_3$)), 1.20 (m, 4H total, C*H*$_2$), 1.63 (s, 9H, Nb-(C*H*$_3$)$_3$), 6.80–7.38, 7.60–7.85 (s, 12H total, N-Ph, P-Ph). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: 6.2 (s). **17**: $^1$H NMR ($C_6D_6$, 25 °C, 500 MHz) δ: 2.29 (s, 9H, Nb-(C*H*$_3$)$_3$), 2.10, 2.16 (s, 12H total, *o*-Ph-(C*H*$_3$)), 2.39 (s, 6H, *p*-Ph-C*H*$_3$), 0.21, 0.29 (s, 12H total, Si-(C*H*$_3$)), 0.91–2.08 (m, 15H total, C*H*$_2$ and $C_6H_{11}$), 6.82, 7.02 (s, 4H total, *m*-Ph-*H*). $^{31}$P{$^1$H} NMR ($C_6D_6$, 25 °C) δ: 11.2 (s).

### Attempted hydrogenations of 15–17

Hydrogenations of the three $^{R'R''}$[NPN]NbMe$_3$ complexes were attempted using the same methodology as that shown for **15** below. A 75 mL ethereal solution of 0.500 g (0.864 mmol) of **15** was prepared in a thick-walled reaction vessel and immediately cooled to –78 °C. $N_2$ was removed by successive freeze-pump-thaw cycles. The solution was then frozen at –196 °C, flushed with $H_2$, sealed, warmed to r.t., and stirred for 24 h. Solvent was removed in vacuo, yielding a dark brown solid. Extensive decomposition of **15** complicated analysis. In situ NMR studies (1 atm) confirmed that no hydride resonances were observable during the hydrogenation attempts.

## Results and discussion

One of the key advantages of the diamidophosphine ligands, referred to as [NPN], is their inherent ability to tune steric and electronic properties by varying the substituents on the amido and phosphine donors. In this report, $^{R'R''}$[NPN] refers to the ligand R′P($CH_2SiMe_2NR''$)$_2$. The ligand precursors are isolated as solvent adducts of the dilithium diamidophosphines both for ease of purification and to facilitate reaction with metal chlorides. The synthesis of $^{PhPh}$[NPN]Li$_2$(THF)$_2$, **1** (2), and $^{CyPh}$[NPN]Li$_2$(OEt$_2$), **2** (8), were reported previously. This report details the preparation of four new [NPN] precursors: $^{PhMes}$[NPN]Li$_2$(diox)$_2$, **3**, $^{CyMes}$[NPN]Li$_2$(THF), **4**, $^{PhMe}$[NPN]Li$_2$(diox)$_2$, **5**, and $^{CyMe}$[NPN]Li$_2$(diox), **6**. A general synthesis of these derivatives is shown in Scheme 1.

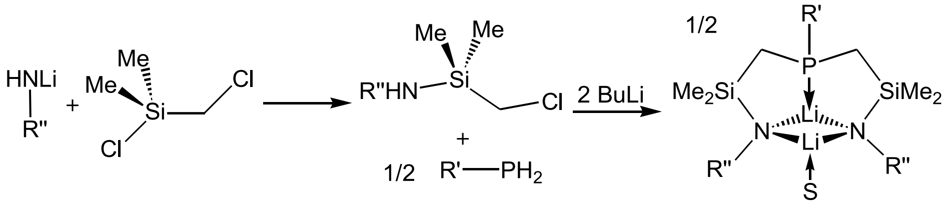
Synthesis of **4** and **5** proceeds by metathesis of MesNHLi with ClCH$_2$SiMe$_2$Cl at –78 °C to form a silylamine that reacts in situ with the desired primary phosphine, RPH$_2$, and 4 equiv (with respect to MesNHLi) of $^n$BuLi. When phenylphosphine is used in this methodology, the ligand precursor precipitates as a pale yellow solid, **3**, after addition of 2.5 equiv of dioxane to a hexanes solution of the product. Similarly, when cyclohexylphosphine is used in this methodology, white crystals (**4**) were isolated after addition of 1.5 equiv of tetrahydrofuran to a hexanes solution of the product. $^{PhMe}$[NPN]Li$_2$(diox)$_2$, **5**, and $^{CyMe}$[NPN]Li$_2$(diox), **6**, were prepared by an analogous procedure, except the requisite amine hydrochloride salt $MeNH_3^+Cl^-$ is used to prepare MeNHLi prior to metathesis. The ligand precursors were characterized by $^{31}$P{$^1$H}, $^1$H, and $^7$Li{$^1$H} NMR spectroscopy. Colorless platelet crystals of **4** were recrystallized from a saturated hexanes–toluene solution and analyzed by X-ray crystallography.

The molecular structure of **4** is shown as an ORTEP3 (17) drawing in Fig. 1. Relevant bond lengths and angles are listed in Table 3 and crystallographic data is located in Table 1. The X-ray data unambiguously show that **4** has a single coordinated THF molecule. The bond lengths from the amido nitrogen donors N1 and N2 to Li2 are approximately 0.2 Å shorter than the corresponding bond lengths from N1 and N2 to Li1, to which the THF molecule is coordinated. The P1—Li1 bond length is 2.589(4) Å, an average length for phosphorus—lithium bonds. Some disorder was evident. The crystalline lattice contained two different conformations of the ligand within the same unit cell. This manifested as overlapping opposite chair conformations of the cyclohexyl ring, as well as overlapping silyl methyl fragments.

Several interesting trends have been observed in the solution characterization of the six dilithio [NPN] precursors used in this report. The three ligand precursors with cyclohexyldonors (**2**, **4**, and **6**) are each monosolvent adducts, compared with **1**, **3**, and **5**, which have two coordinating solvent molecules. In each case, the solvent adduct isolated is the least soluble product. These same cyclohexylphosphine derivatives (**2**, **4**, and **6**) show no $^{31}$P–$^7$Li coupling in solution (r.t.) that could suggest their solution behaviour is different than that found for **4** in the solid state (Fig. 1). One possibility is that the phosphine donor does not bind to the lithium ions in solution. However, a low temperature $^{31}$P spectrum (–25 °C) of **2** shows a doublet due to $^7$Li coupling ($^1J_{PLi}$ = 17.4 Hz). It is likely that the lithium ions are undergoing intermolecular exchange in solution, fast enough at room temperature to lose coupling information. However, at lower temperatures, this process is slow, and coupling between $^7$Li and $^{31}$P is observed. In solution, the structure of the dilithio derivative is therefore likely the same as in the solid state with phosphine bound to lithium.

$^{PhPh}$[NPN] and $^{CyPh}$[NPN] ligand sets have already been applied to other group five metal-based systems. The complex $^{PhPh}$[NPN]TaMe$_3$ reacts with $H_2$ to form ($^{PhPh}$[NPN]Ta)$_2$(μ-H)$_4$ (1, 2). Under an atmosphere of dinitrogen, this complex loses 1 equiv of $H_2$ and binds dinitrogen to form ($^{PhPh}$[NPN]Ta)$_2$(μ-H)$_2$(μ-η$^1$:η$^2$-N$_2$). This complex has an intriguing side-on, end-on coordination mode that promotes reactivity with E-H species (E = B, Si, Al) (3, 4). Dinitrogen activation has also been observed by a related niobium system supported by a [P$_2$N$_2$] ligand set. Upon thermolysis, the complex ([P$_2$N$_2$]Nb)$_2$(μ-N$_2$) (where [P$_2$N$_2$] = PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh) decomposes into a bridging nitride species where one N atom from the activated $N_2$ inserts into the macrocycle backbone, forming the complex [P$_2$N$_2$]Nb(μ-N)Nb[PN$_3$] (where [PN$_3$] = PhPMe(CHSiMe$_2$NSiMe$_2$CH$_2$P-(Ph)CH$_2$SiMe$_2$NSiMe$_2$N)) (18). As well, the complexes $^{RPh}$[NPN]NbCl(DME), ($^{PhPh}$[NPN]NbCl)$_2$(μ-N$_2$), and $^{RPh}$[NPN]NbCl$_2$ (R = Cy, Ph; DME = dimethoxyethane) have been synthesized. The complex $^{CyPh}$[NPN]NbCl$_2$

**Scheme 1.**



**1:** R' = Ph, R" = Ph, S = 2 THF

**2:** R' = Cy, R" = Ph, S = $OEt_2$

**3:** R' = Ph, R" = Mes, S = 2 diox

**4:** R' = Cy, R" = Mes, S = THF

**5:** R' = Ph, R" = Me, S = 2 diox

**6:** R' = Cy, R" = Me, S = diox

**Fig. 1.** ORTEP 3 plot for **4** (50% probability, THF carbons omitted for clarity).

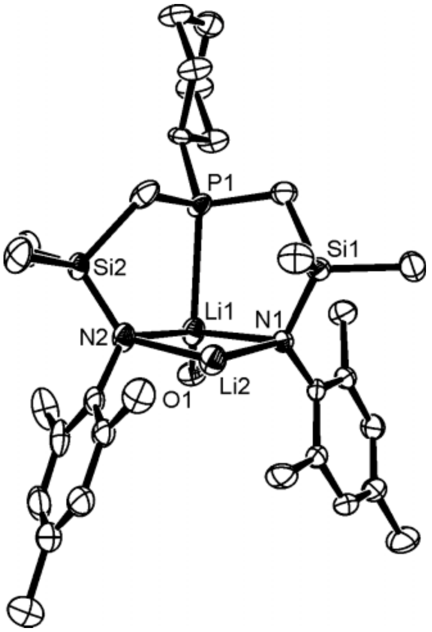


**Table 3.** Selected bond distances (Å) and angles (°) for $^{\mathrm{CyMes}}$[NPN]$Li_2$(THF), **4**.

| | |
|---|---|
| **Bond distances (Å)** | |
| P(1)—Li(1) | 2.589(4) |
| N(1)—Li(1) | 2.106(4) |
| N(1)—Li(2) | 1.943(4) |
| N(2)—Li(1) | 2.133(4) |
| N(2)—Li(2) | 1.964(4) |
| O(1)—Li(1) | 1.923(4) |
| **Bond angles (°)** | |
| C(7)-N(1)-Li(1) | 103.74(15) |
| C(7)-N(1)-Li(2) | 123.97(17) |
| C(22)-N(2)-Li(2) | 94.27(16) |
| C(22)-N(2)-Li(1) | 119.11(17) |
| Li(2)-N(2)-Li(1) | 73.74(15) |
| Li(2)-N(1)-Li(1) | 74.77(15) |
| O(1)-Li(1)-P(1) | 121.74(16) |

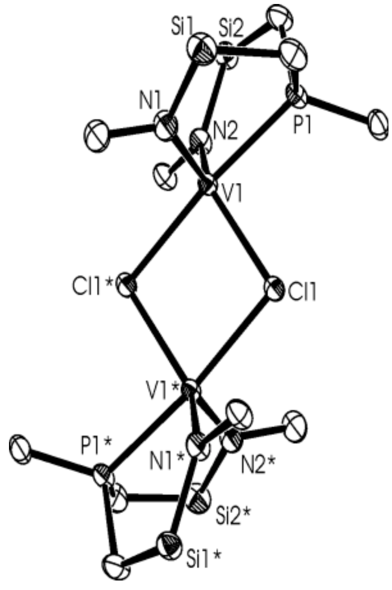
decomposes in solution to form an imide, $^{\mathrm{CyPh}}$[NPN]NbCl(=NPh), a cyclized [NP] ligand, $CyP(CH_2SiMe_2)_2NPh$, and a niobium(III) product by an intermolecular N—Si bond scission (8). The goal of this work is to examine how ligand modifications would affect other group 5 precursors.

Application of these ligand sets to vanadium(III) could afford species of the form [NPN]VCl from which a number of reactivities can be explored. Behavior of these systems might mimic that seen for niobium and generate a dinitrogen complex directly, analogous to ($^{\mathrm{PhPh}}$[NPN]NbCl)(μ-$N_2$) chemistry. Alternatively, if the [NPN]VCl system were reduced under a dinitrogen atmosphere it would give a complex isoelectronic with Mo($N^t$BuAr)$_3$, which coordinates and splits molecular nitrogen to form the nitride ($N^t$BuAr)$_3$Mo≡N (19, 20). The cleavage of molecular nitrogen was also observed when a bisamidoamine vanadium chloride complex was reduced (21).

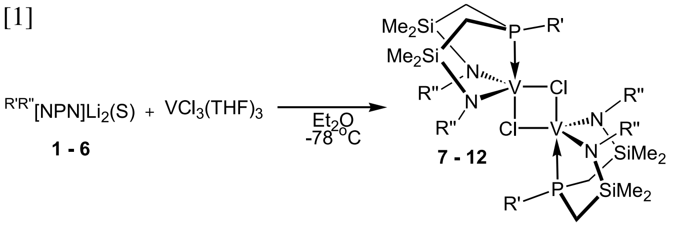
Treatment of a cooled solution of $VCl_3(THF)_3$ in THF with an $Et_2O$ solution of $^{\mathrm{CyPh}}$[NPN]$Li_2$($OEt_2$) gave a brick-red paramagnetic solid, $^{\mathrm{CyPh}}$[NPN]VCl, **7**. Mass spectrometry and elemental analysis confirmed the empirical formula. Recrystallization of **7** from a layered benzene–HMDS solution at –35 °C gave red block crystals of ($^{\mathrm{CyPh}}$[NPN]VCl)$_2$. X-ray analysis of the crystals, isolated in 78% yield, showed that the compound exists as a chloride-bridged dimer. The molecular structure of **7** is shown as an ORTEP drawing in Fig. 2. Relevant bond lengths and angles and crystallographic data are listed in Tables 2 and 4, respectively. The V(1)—Cl(1) and V(1*)—Cl(1) bond lengths of 2.3632(4) and 2.4913(4) Å, respectively, are average for a loosely bound chloride dimer (22); the compound appears as the monomer in mass spectrometry studies. The vanadium amide bond lengths of 1.935(1) and 1.934(1) Å agree with other amido vanadium chloride systems (23). While the V(1)—P(1) bond length of 2.4323(5) Å is not unusual for vanadium phosphine systems (23), it is short for related vanadium chloride dimers (~2.6–2.7 Å) (24–27). The overall complex is distorted trigonal bipyramidal with chlorine and phosphine ligands occupying the apical positions.

Similar reactions of ligand precursors **1**, **3**, **4**, **5**, and **6** with $VCl_3(THF)_3$ produced the vanadium chlorides $^{R'R''}$[NPN]VCl (R″ = Ph, Cy; R″ = Ph, Mes, Me; **8**–**12**). Characterization by mass spectrometry and elemental analysis confirmed the empirical formula in each case. A general synthesis is shown in eq. [1].

**Fig. 2.** ORTEP 3 plot for **7** (50% probability; silyl methyl and R′ and R″ groups, save the attached carbons, have been omitted for clarity).



[1]



**1 - 6** **7 - 12**

**Table 4.** Selected bond distances (Å) and angles (°) for ($^{CyPh}$[NPN]VCl)$_2$, **7**.

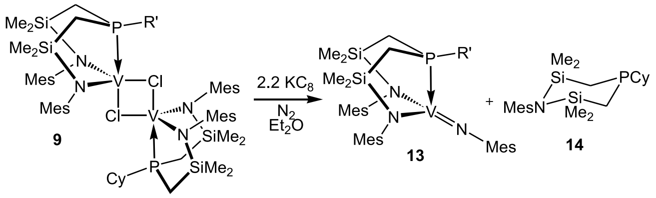
| **Bond distances (Å)** | |
|---|---|
| V(1)—Cl(1) | 2.3632(4) |
| V(1)—Cl(1*) | 2.4913(4) |
| V(1)—P(1) | 2.4323(5) |
| V(1)—N(2) | 1.934(1) |
| V(1)—N(1) | 1.935(1) |
| **Bond angles (°)** | |
| Cl(1)-V(1)-Cl(1*) | 84.68(2) |
| Cl(1)-V(1)-N(1) | 115.77(4) |
| Cl(1)-V(1)-P(1) | 88.90(2) |
| Cl(1)-V(1)-N(2) | 127.32(4) |
| N(1)-V(1)-N(2) | 116.17(6) |
| P(1)-V(1)-N(1) | 86.46(4) |
| P(1)-V(1)-N(2) | 86.00(4) |

Reductions of **7–12** with potassium graphite ($KC_8$) were conducted under four conditions: 1 atm $N_2$ and 2.2 equiv of $KC_8$, 4 atm $N_2$ and 2.2 equiv of $KC_8$, 1 atm $N_2$ and 3.3 equiv of $KC_8$, 4 atm $N_2$ and 3.3 equiv of $KC_8$. Reduction of **7** at 4 atm of $N_2$ with 2.2 equiv of $KC_8$ at –78 °C gave a strongly purple colored solution upon warming to r.t. Removal of KCl followed by recrystallization from a saturated pentane solution gave a deep purple paste, highly soluble in common organic solvents. Mass spectral analysis of the product indicated the formation of a $^{CyPh}$[NPN]V≡N species with a peak at *m/z* 505 ($C_{24}H_{37}N_3Si_2PV$), but repeated attempts to grow diffractable crystals failed. A paramagnetic impurity prevented purification and full characterization of the product. The observation of a mononuclear species by mass spectrometry does not, of course, prove its formulation. The species could have been generated in the experiment from a dinuclear bisnitride complex; however, it is unlikely to be generated from a compound with an intact $N_2$ moiety (18).

Reduction of **7** at 4 atm of $N_2$ with 3.3 equiv of $KC_8$ at –78 °C gave a deep olive green solution upon warming to r.t. From the solution, a dark green solid was isolated and characterized by mass spectrometry. A small peak at *m/z* 1050 ($C_{48}H_{74}KN_6P_2Si_4V_2$), corresponding to K($^{CyPh}$[NPN]V≡N)$_2$, as well as a substantial $^{CyPh}$[NPN]V≡N peak (*m/z* 505, 100%), suggested dinitrogen incorporation during the reduction process. Unfortunately, the reduced products could not be purified. Attempts to improve the synthesis of the vanadium nitride by changing solvent, reaction time, $N_2$ pressure, reducing agent, or temperature were unsuccessful. Similarly, reductions of other vanadium chlorides (**8–12**) were unproductive. In several cases, there was no evidence of nitride formation.

The reduction of ($^{CyMes}$[NPN]VCl)$_2$, **9**, illustrated the problems associated with reduction of the vanadium chlorides. Upon workup of the reaction of **9** with 2.2 equiv of $KC_8$, a peak was observed in the mass spectrum at *m/z* 709, which corresponds to $^{CyMes}$[NPN]V=NMes, as supported by theoretical isotope pattern calculations. The vanadium imide moiety $^{CyMes}$[NPN]V=NMes is the likely product of ring-closing of the [NPN] ligand on itself. Scissioning of one of the Si—N bonds and one of the N—V bonds in the ([NPN]VCl)$_2$ species during reduction would result in the vanadium imide species **13** and the elimination of a six-membered heteroatomic ring **14**, as illustrated in eq. [2]. Crystals of **14** formed out of a toluene–hexanes solution, and the structure was verified by $^1$H NMR. Peaks corresponding to imide formation were observed in the mass spectra of each of the reductions conducted, no matter which substrate was reduced. As mentioned, decomposition of [NPN] metal complexes to form imides has complicated a previous study as well: the imide $^{CyPh}$[NPN]NbCl(=NPh) was generated from the decomposition of $^{CyPh}$[NPN]$NbCl_2$ (8).

[2]

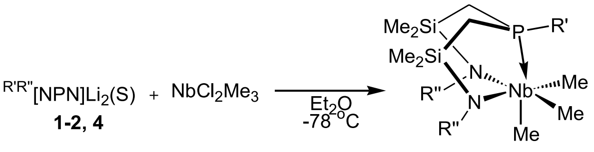


**9** **13** **14**

The [NPN] ligand may provide access to attractive Nb(V) complexes since the Ta(V) complex $^{PhPh}$[NPN]$TaMe_3$ reacts with $H_2$ to form ($^{PhPh}$[NPN]Ta)$_2$(μ-H)$_4$, a precursor to the dinitrogen complex ($^{PhPh}$[NPN]Ta)$_2$(μ-H)$_2$(μ-η$^1$:η$^2$-$N_2$) (2). We examined the formation of $^{R'R''}$[NPN]$NbMe_3$ and its reactivity with dihydrogen.

Production of $^{CyPh}$[NPN]$NbMe_3$ (**15**) was accomplished via addition of a –78 °C solution of ligand to a cooled solution of $NbCl_2Me_3$, freshly sublimed before use. After solvent removal at –10 °C, the resultant brown solid was extracted with pentane to generate an orange solid that was characterized by $^1H$ and $^{31}P\{^1H\}$ NMR and mass spectrometry. The product was extremely photo- and thermo-sensitive and was stored in an opaque vessel at –37 °C. Thermal instability precluded the use of elemental analysis and $^{13}C\{^1H\}$ NMR for characterization. A general reaction pathway is shown in eq. [3].

[3]



15-17

Reactions of $NbCl_2Me_3$ with ligand precursors **1**, **3**, **4**, **5**, and **6** were not as successful. The products from these reactions were more thermally unstable and frequently decomposed prior to spectroscopic analysis. Only $^{PhPh}$[NPN]$NbMe_3$ (**16**) and $^{CyMes}$[NPN]$NbMe_3$ (**17**) were stable enough to characterize spectroscopically.

Hydrogenation of complexes **15**–**17** was attempted at 4 atm pressure. Following the addition of $H_2$, the reaction mixtures turned black and a precipitate formed. Analysis of the reaction mixture by NMR showed extensive decomposition. No hydride resonances were observed at the expected chemical shift for a niobium hydride. Attempts to vary reaction conditions to isolate the putative polyhydride species, by changing the concentration of reagents, temperature, exposure to light, pressure of $H_2$, solvent, or time of reaction, were unsuccessful. It is suspected that the trimethyl starting materials are too unstable to withstand the hydrogenation process.

## Conclusions

While a number of reports have shown the applicability of Ta(V), Nb(III), and V(III) systems to dinitrogen activation, in this work we have shown that small changes to the electronics and sterics of these systems can prevent such reaction pathways. Six variants of the [NPN] diamidophosphine ligand were used to prepare ($^{R'R''}$[NPN]VCl)$_2$ complexes, to investigate their ability to coordinate and cleave dinitrogen upon reduction. Unfortunately, reduction of these complexes under a variety of conditions was complicated by ligand degradation to form a V(IV) imide. While some nitride-containing material was formed, it was not isolable. Similarly, the complexes $^{R'R''}$[NPN]$NbMe_3$ were prepared, with the goal that these highly unstable materials could be hydrogenated in an analogous manner to the formation of $([NPN]Ta)_2(\mu\text{-}H)_2(\mu\text{-}\eta^1{:}\eta^2\text{-}N_2)$; however, their thermal and photochemical decomposition occurred prior to hydrogenation. What becomes evident from this work is just how changes in ligand design or metal centres can lead to quite different and unpredictable reaction behaviour.

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