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Supporting Information

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"An Isolable and Monomeric Phosphorus Radical that is Resonance-Stabilized by the Vanadium(IV/V) Redox Couple"

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Contents **Page**

Synthetic Details

General

All manipulations were performed in a Vacuum Atmospheres model MO-40M glove box under an atmosphere of purified dinitrogen. Anhydrous-grade, oxygen-free tetrahydrofuran (THF) was purchased from Aldrich and further dried by passing through a column of molecular sieves and stirring with sodium for at least 12 hours prior to filtration through Celite to remove sodium. Hexamethyldisiloxane was distilled from sodium benzophenone and stored over molecular sieves. All other solvents were obtained anhydrous and oxygen-free by bubble degassing (N_2) and purification through columns of alumina and Q5.[1] Diethyl ether (Et_2O) was additionally dried by stirring over sodium for 12 h, followed by filtration through Celite. Deuterated solvents were purchased from Cambridge Isotope Labs. Benzene-d_6 and toluene-d_8 were degassed and stored over 4 Å molecular sieves for at least 2 days prior to use. THF-d_8 was stirred over sodium and subsequently vacuum transferred. Celite 435 (EM Science), molecular sieves (Aldrich), and alumina were dried by heating at 200 ºC under dynamic vacuum for at least 24 hours prior to use. Sodium azide (Aldrich) was dried under vacuum and washed thoroughly with anhydrous THF. Ph_2S_2 and Ph_2Se_2 were dried under vacuum and recrystallized from anhydrous Et_2O. *p*-Tetrachlorobenzoquinone was purchased from Aldrich and sublimed *in vacuo* prior to use. $VCl_3(THF)_3$,[2] $LiN(Np)Ar{\cdot}Et_2O$ (Np = neopentyl, Ar = 3,5-$C_6H_3Me_2$),[3] and $Ti(N[t\text{Bu}]Ar)_3$[4] were prepared according to literature procedures. Anhydrous $SnCl_2$ was purchased from Strem and used without further purification. All other reagents were purchased from commercial sources and used without further purification. All glassware was oven-dried at >170 ºC prior to use. NMR spectra were obtained on Varian Mercury 300 or Varian Inova 500 instruments equipped with Oxford Instruments superconducting magnets and referenced to residual C_6D_5H (7.16 ppm), C_4D_7HO (1.73 ppm) or $CD_3C_6D_4H$ (7.00 ppm). ^{77}Se NMR spectra were referenced to Me_2Se (0 ppm) by comparison to external Ph_2Se_2 (460 ppm, $CDCl_3$). ^{51}V and ^{31}P NMR spectra were referenced externally to neat $OVCl_3$ and 85% H_3PO_4, respectively. Conversion yields for **1**-SPh, **1**-SePh, and **4** were taken using 8-scan, ^{1}H NMR spectra with a delay time of 128 s; the observed integral ratios did not change upon lengthening the delay time to 256 s. Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana.

$V(N[Np]Ar)_3$ (2): Pink $VCl_3(THF)_3$ powder (13.334 g, 35.689 mmol) was slowly added over the course of 1 min to a chilled (ca. –50 ºC), stirring solution of $LiN(Np)Ar{\cdot}Et_2O$ (29.488 g, 108.66 mmol, 3.04 equiv) in 100 mL Et_2O. The color of the resulting solution turned first pink, then brown, and finally dark green. The reaction mixture was allowed to stir while warming to 23 ºC for 5 h, after which time it was concentrated to dryness under dynamic vacuum. The products were dissolved in pentane (ca. 100 mL) and the solution was filtered through Celite to remove LiCl. The filtrate was concentrated *in vacuo* and solids were subsequently crystallized from this solution at –35 ºC in two crops. The crystallized solids were washed with cold pentane (–35 °C, 20 mL) and subsequently dried under vacuum to yield a dark green powder (15.352 g, 24.687 mmol, 69%). M.p. 151-152.5 °C. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 7.4 (v. br), 2.5 (br, $\Delta\nu_{1/2}$ = 290 Hz), 1.5 (br, $\Delta\nu_{1/2}$ = 33 Hz) ppm. Anal. calcd: C, 75.33; H, 9.73; N, 6.76; found: C, 74.74; H, 9.19; N, 6.96.

Magnetic susceptibility determination on **2**: A solution of hexamethyldisiloxane (2 drops) in C_6D_6 (0.7 mL) was prepared. A few drops of this solution were placed in a capillary tube, which was then flame-sealed. The remaining solution (0.478 g) was added to **2** (0.014 g). The ^{1}H NMR spectrum of this solution along with the coaxial capillary showed resonances attributable to hexamethyldisiloxane at 0.121 and –0.391 ppm, corresponding to a magnetic susceptibility of 2.70 μ_B after application of diamagnetic corrections.

ClV(N[Np]Ar)$_3$ (2-Cl): An Et_2O solution of **2** (75 mg, 0.121 mmol) was added to dry $SnCl_2$ (12 mg, 0.063 mmol, 0.51 equiv). As the reaction mixture stirred for 30 min, the formation of tin metal was observed, and the color of the solution changed from dark green to brown. The reaction mixture was filtered through Celite, leaving behind a gray solid (Sn metal). The filtrate was concentrated *in vacuo* to 1 mL and layered with pentane. This solution was chilled to –35 ºC and the black microcrystals of **2**-Cl were precipitated in several crops, washed with cold pentane and dried *in vacuo* (45 mg, 0.068 mmol, 57%). M.p. 209-209.5 ºC. X-Band EPR (toluene, 20 ºC) g_{iso} = 1.973, $A_{iso}(^{51}V)$ = 67.9 G. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): 0.8 (br, $\Delta\nu_{1/2}$ = 360 Hz) ppm. Anal. calcd: C, 71.30; H, 9.21; N, 6.40; Cl, 5.33; found: C, 70.81; H, 8.63; N, 6.53; Cl, 5.48.

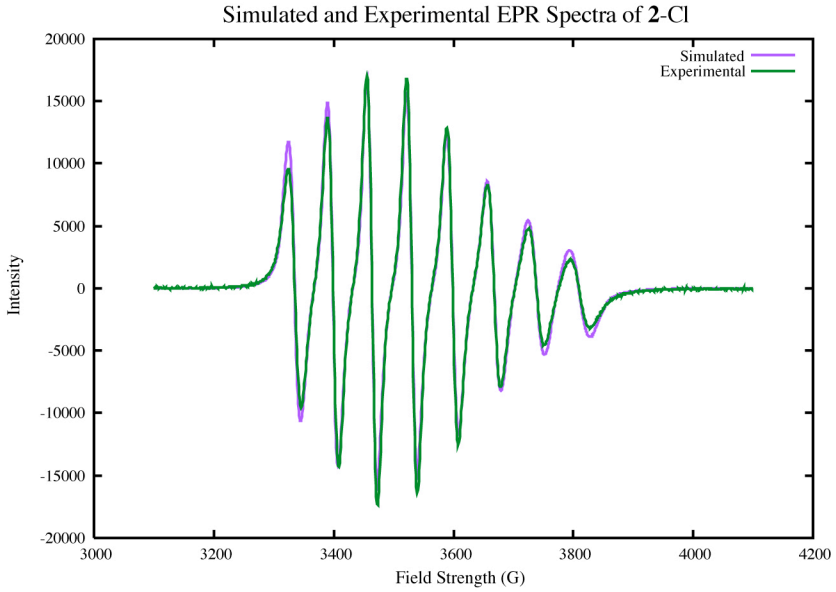

Figure S1. Experimental and simulated EPR spectra of **2**-Cl. Simulation was performed with Bruker Simfonia.

Magnetic susceptibility determination on **2**-Cl: A solution of hexamethyldisiloxane (2 drops) in C_6D_6 (0.7 mL) was prepared. A few drops of this solution were placed in a capillary tube, which was then flame-sealed. The remaining solution (0.643 g) was added to dry **2**-Cl (0.016 g). The ^{1}H NMR spectrum of this solution along with the coaxial capillary showed resonances attributable to hexamethyldisiloxane at 0.121 and 0.009 ppm, corresponding to a magnetic susceptibility of 1.64 μ_B after application of diamagnetic corrections.

NaNV(N[Np]Ar)$_3$ (Na[3]): A thawing suspension of NaN_3 (1.310 g, 20.15 mmol, 3.02 equiv) in THF (20 mL) was added to a stirring, thawing solution of **2** (4.150 g, 6.674 mmol) in THF (30

mL) and stirred for 18 h in a round-bottom flask fitted with a septum pierced with a needle. The reaction mixture was then filtered through Celite and the solvent was removed from the filtrate under dynamic vacuum. Et_2O (20 mL) was added and removed *in vacuo*, followed by the addition of pentane (20 mL) and its removal *in vacuo,* to assist in the removal of residual THF. The yellow solids thus obtained were then collected atop a sintered glass frit, washed with pentane (40 mL), and dried under dynamic vacuum to yield Na[**3**] as a yellow powder (3.391 g, 5.147 mmol, 77% yield). ^{1}H NMR (300 MHz, THF-d_8, 20 °C): δ = 6.38 (s, 6H, *o*-Ar), 6.11 (s, 3H, *p*-Ar), 4.29 (s, 6H, N-CH_2), 1.95 (s, 18H, Ar-Me), 0.76 (s, 27H, *t*Bu) ppm. ^{13}C NMR (126 MHz, THF-d_8, 20 °C): δ = 161.6 (*ipso*-Ar), 137.1, 120.9, 120.5, 74.8 (N-*C*H_2), 36.6 (*C*$(CH_3)_3$), 30.1 (C(*C*$H_3)_3$), 21.9 (Ar-*C*H_3) ppm. ^{51}V NMR (132 MHz, THF-d_8, 20 °C): δ = –190.5 ($\Delta\nu_{1/2}$ = 120 Hz) ppm. Anal. calcd: C, 71.10; H, 9.18; N, 8.50; found: C, 70.12; H, 9.17; N, 8.30.

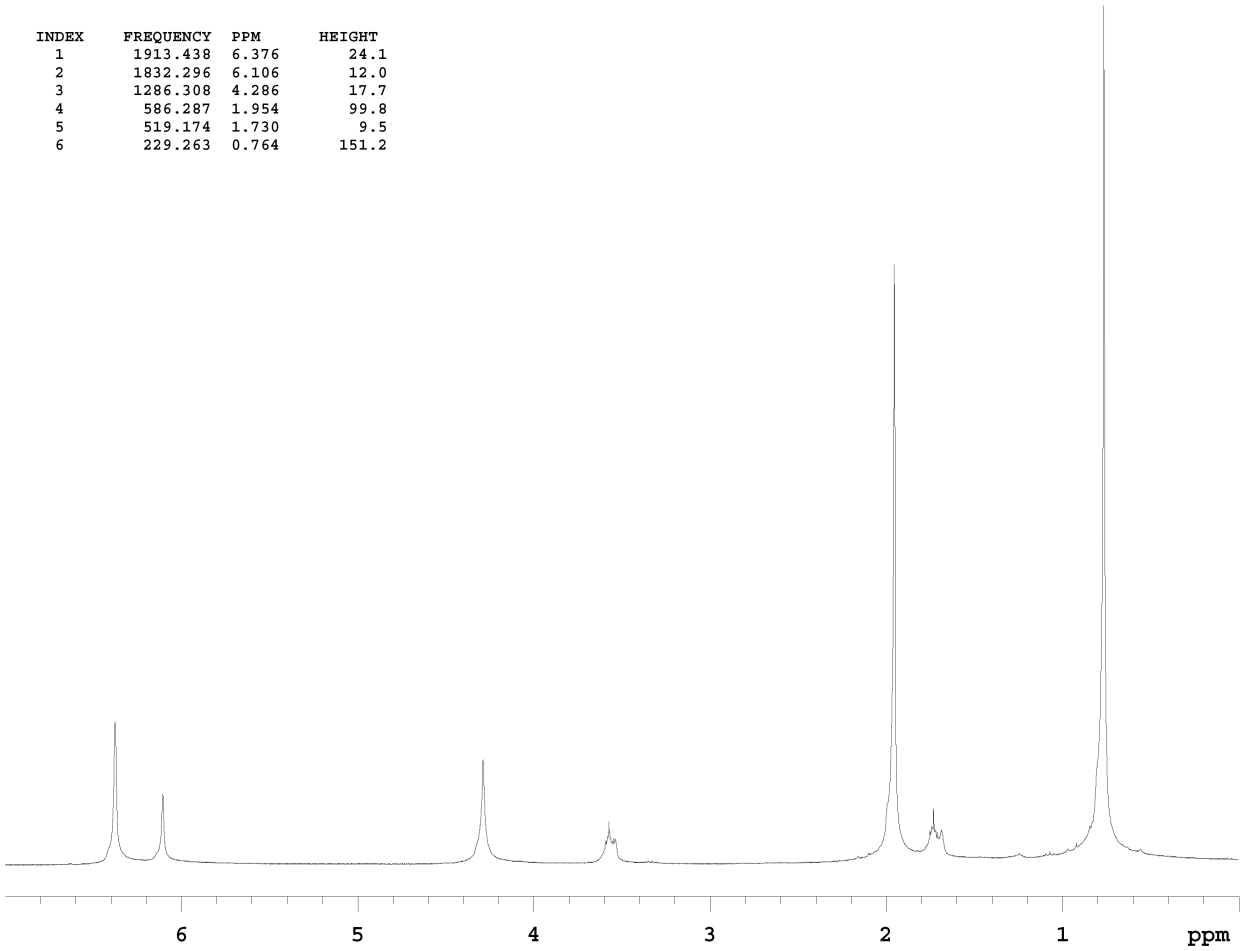

Figure S2. ^{1}H NMR spectrum of Na[**3**] in THF-d_8 at 20 ºC.

ClP[NV(N[Np]Ar)$_3$]$_2$ (1-Cl): THF solutions of Na[**3**] (3.128 g, 4.748 mmol, 2.04 equiv; 20 mL THF) and PCl_3 (0.319 g, 2.32 mmol; 5 mL THF) were frozen in a liquid nitrogen cooled cold well. The thawing PCl_3 solution was then slowly added to the thawing, stirring solution of Na[**3**] to give a dark red-brown reaction mixture. The reaction mixture was allowed to stir for 5 h, after which time the solvent was removed *in vacuo*. Pentane (ca. 20 mL) was added to the remaining solids and subsequently removed from the product to assist in the removal of residual THF. The

solids so obtained were then dissolved in toluene (40 mL), and this solution was filtered through Celite to remove NaCl. The filtrate was dried under dynamic vacuum and the crude solids were isolated (2.920 g, 93% assuming pure **1**-Cl). The EPR spectrum of this material showed the presence of a paramagnetic impurity, which was identified as **2**-Cl. The crude solids were extracted into pentane (20 mL) to leave behind insoluble **2**-Cl. The filtrate was chilled to –35 ºC and **1**-Cl precipitated as a red-brown solid which was isolated in two crops (1.500 g, 1.121 mmol, 48%); comparison of the EPR spectrum of this material to that of pure **2**-Cl indicated that it contained only ca. 1% of a **2**-Cl impurity. M.p. 150-154 °C. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 6.59 (s, 6H, *p*-Ar), 6.58 (s, 12H, *o*-Ar), 4.85 (d, *J* = 13 Hz, 6H, N-C*H*$_2$), 4.78 (d, *J* = 13 Hz, 6H, N-C*H*$_2$), 2.17 (s, 36H, Ar-Me), 1.14 (s, 54H, *t*Bu) ppm. ^{13}C NMR (126 MHz, C_6D_6, 20 °C): δ = 157.2 (*ipso*-Ar), 137.9, 126.5, 122.1, 77.8 (N-*C*H$_2$), 36.8 (*C*(CH$_3$)$_3$), 30.1 (C(*C*H$_3$)$_3$), 22.0 (Ar-*C*H$_3$) ppm. ^{31}P NMR (121 MHz, C_6D_6, 20 °C): δ = 184.0 (br, $\Delta\nu_{1/2}$ = 247 Hz) ppm. ^{51}V NMR (132 MHz, C_6D_6, 20 °C): δ = 118.4 ppm ($\Delta\nu_{1/2}$ = 708 Hz). Anal. calcd: C, 70.01; H, 9.04; N, 8.37; found: C, 69.37; H, 8.52; N, 8.53.

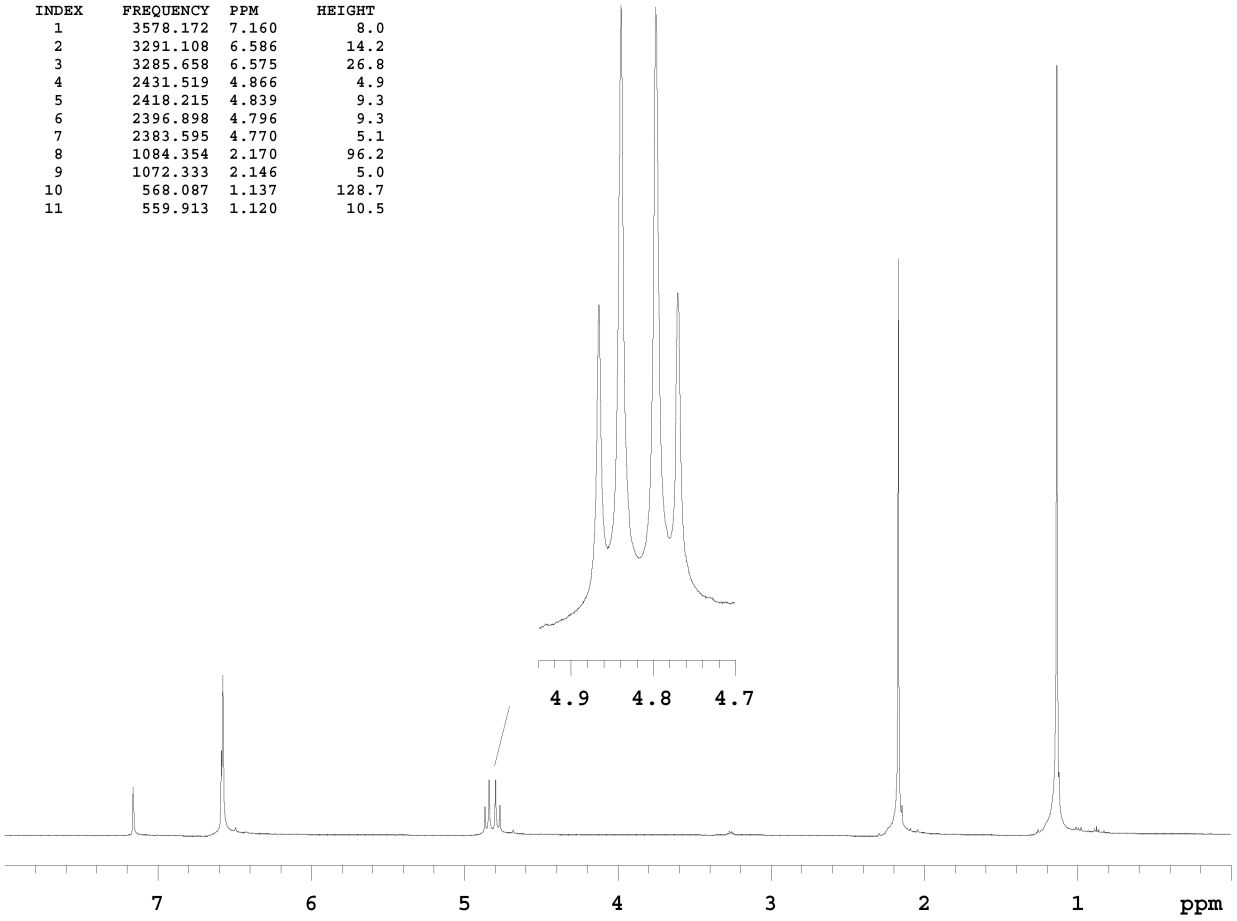

Figure S3. ^{1}H NMR spectrum of **1**-Cl in benzene-d_6 at 20 ºC.

P[NV(N[Np]Ar)$_3$]$_2$ (1): A thawing suspension of KC_8 (0.117 g, 0.865 mmol, 1.00 equiv) in THF (5 mL) was added dropwise to a stirring, thawing solution of **1**-Cl (1.160 g, 0.8669 mmol) in THF (10 mL). An aliquot taken after 2.5 h indicated incomplete conversion to **1**, so a suspension

of KC_8 (0.006 g, 0.04 mmol, 0.05 equiv) in THF (2 mL) was added to the reaction mixture. After the reaction mixture had stirred for a total of 4 h, the solution was concentrated to dryness under dynamic vacuum. Pentane (10 mL) was added to the remaining solids and subsequently removed *in vacuo* to assist in the removal of residual THF. The solids so obtained were dissolved in pentane (20 mL), and the resulting solution was filtered through Celite to remove potassium chloride and graphite. The filtrate was concentrated *in vacuo* and stored at –35 ºC for several days to yield **1** as dark brown crystals (0.874 g, 0.671 mmol, 77%, 3 crops). M.p. 157-159.5 °C. ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ = 2.8 (br, $\Delta\nu_{1/2}$ = 280 Hz), 1.3 (br, $\Delta\nu_{1/2}$ = 240 Hz) ppm. Anal. calcd: C, 71.91; H, 9.28; N, 8.60; found: C, 71.84; H, 9.01; N, 8.89.

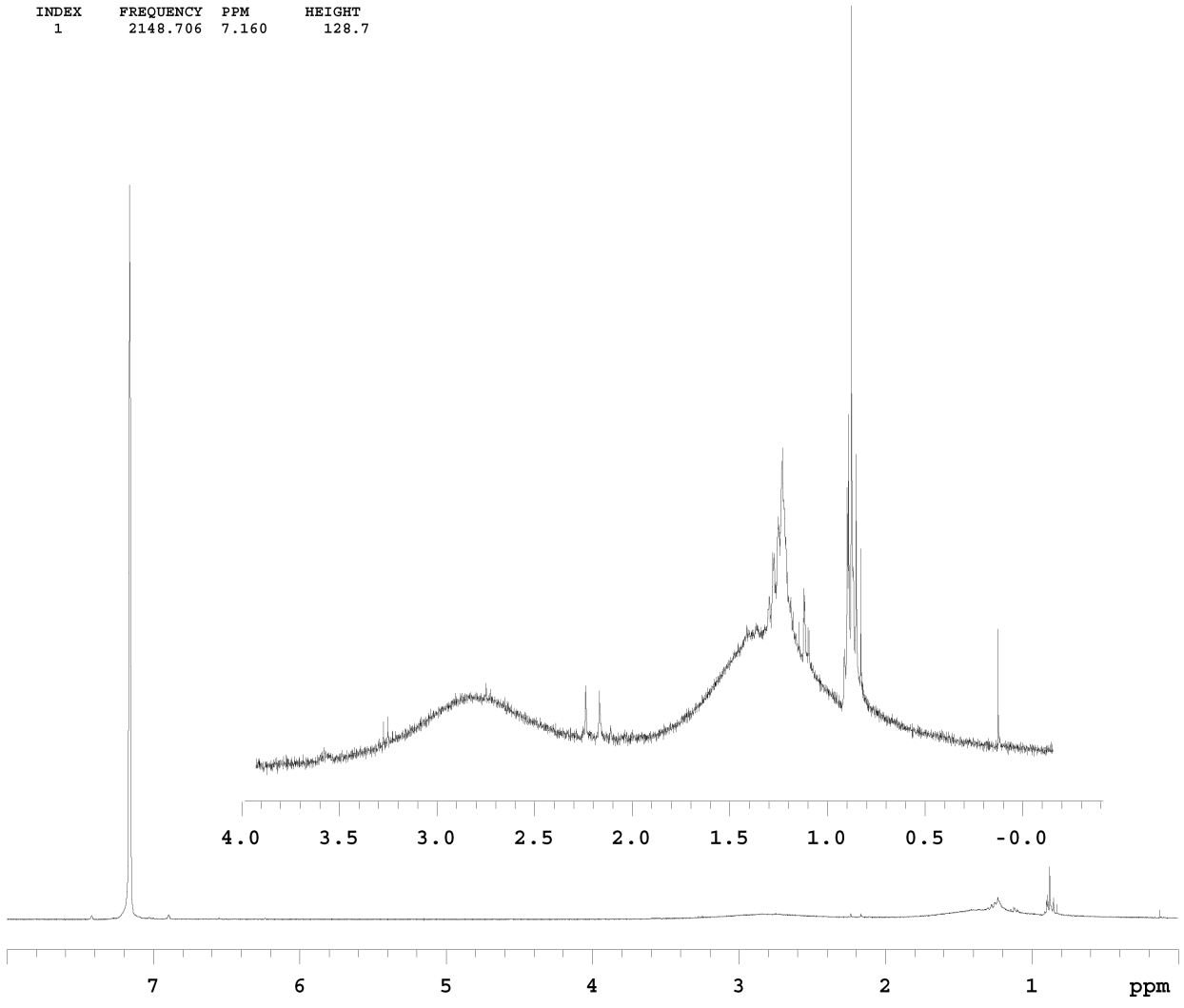

Figure S4. ^{1}H NMR spectrum of **1** in benzene-d_6 at 20 ºC. Trace solvents are present.

Magnetic susceptibility determination on **1**: A solution of hexamethyldisiloxane (1 drop) in C_6D_6 (10 drops) was prepared. A few drops of this solution were placed in a capillary tube, which was then flame-sealed. The ^{1}H NMR spectrum of a solution of **1** (0.034 g) in hexamethyldisiloxane

(2 drops) and C_6D_6 (0.7 mL, 0.678 g total) along with the coaxial capillary showed resonances attributable to hexamethyldisiloxane at 0.121 and 0.061 ppm, corresponding to a magnetic susceptibility of 1.67 μ_B after application of diamagnetic corrections.

Alternate Synthesis of **1**: An Et_2O solution (1.5 mL) of Ti(N[*t*Bu]Ar)$_3$ (13 mg, 0.023 mmol, 1.0 equiv) was added dropwise to a stirring Et_2O solution (1.5 mL) of **1**-Cl (31 mg, 0.023 mmol). The reaction mixture was allowed to stir for 1.5 h, after which time it was dried under dynamic vacuum and then dissolved in benzene-d_6. The ^{1}H NMR spectrum of an aliquot of the reaction mixture indicated that ClTi(N[*t*Bu]Ar)$_3$[5] was the major diamagnetic reaction product, and the EPR spectrum indicated the presence of **1**.

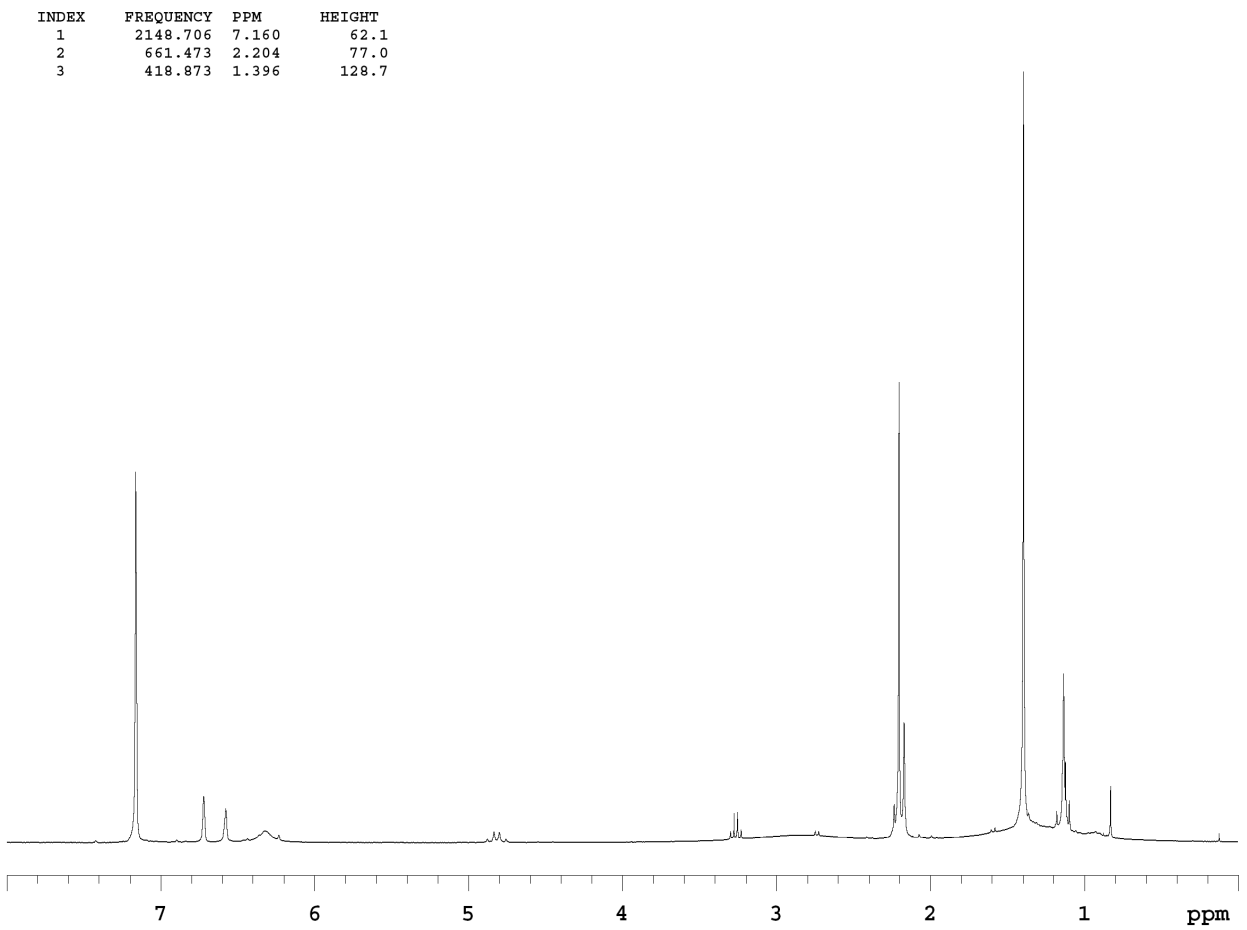

Figure S5. ^{1}H NMR spectrum of **1** and ClTi(N[*t*Bu]Ar)$_3$ in benzene-d_6 at 20 ºC. The presence of **1** can be seen in the baseline of the spectrum, and a small amount of residual **1**-Cl is present.

PhS-P[NV(N[Np]Ar)$_3$]$_2$ (1-SPh): An Et_2O solution (4 mL) of **1** (100 mg, 0.0768 mmol) was added to dry Ph_2S_2 (9 mg, 0.0412 mmol, 0.54 equiv). After stirring for 1 h, the reaction mixture was dried under dynamic vacuum to a dark red solid (0.108 g, .0766 mmol, 99.6%). Crystals of **1**-SPh can be grown from hexamethyldisiloxane at –35 ºC. M.p. 170-172 °C. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 7.61 (d, *J* = 8 Hz, 2H, *o*-Ph), 7.07 (m, 3H, *m,p*-Ph), 6.66 (s, 12H, *o*-Ar), 6.58 (s, 6H, *p*-Ar), 4.79 (d, *J* = 14 Hz, 6H, N-CH_2), 4.75 (d, *J* = 14 Hz, 6H, N-CH_2), 2.20 (s, 36H, Ar-Me), 1.08 (s, 54H, *t*Bu) ppm. ^{13}C NMR (126 MHz, C_6D_6, 20 °C): δ = 156.9 (*ipso*-Ar),

137.9, 136.8 (d, J_{CP} = 18 Hz, *ipso*-Ph), 131.4 (d, J_{CP} = 9 Hz, *o*-Ph), 129.5, 126.5, 126.0, 121.8, 76.4 (N-CH_2), 36.7 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$), 22.1 (Ar-CH_3) ppm. ^{31}P NMR (121 MHz, C_6D_6, 20 °C): δ = 197.5 (br, $\Delta\nu_{1/2}$ = 210 Hz) ppm. ^{51}V NMR (132 MHz, C_6D_6, 20 °C): δ = 97.8 ($\Delta\nu_{1/2}$ = 750 Hz) ppm. Anal. calcd: C, 71.46; H, 8.92; N, 7.94; found: C, 71.45; H, 8.99; N, 8.20.

INDEX	FREQUENCY	PPM	HEIGHT
1	3804.650	7.613	2.9
2	3797.116	7.598	3.2
3	3578.172	7.160	13.2
4	3570.158	7.144	2.6
5	3562.144	7.128	3.6
6	3329.896	6.663	29.0
7	3285.658	6.575	16.6
8	2402.348	4.807	3.6
9	2388.884	4.780	12.3
10	2381.190	4.765	11.9
11	2367.567	4.738	3.5
12	1635.401	3.272	2.5
13	1628.509	3.259	2.6
14	1114.647	2.230	2.5
15	1099.420	2.200	104.6
16	1082.430	2.166	2.9
17	565.523	1.132	3.3
18	558.631	1.118	6.5
19	551.258	1.103	6.5
20	540.839	1.082	128.7

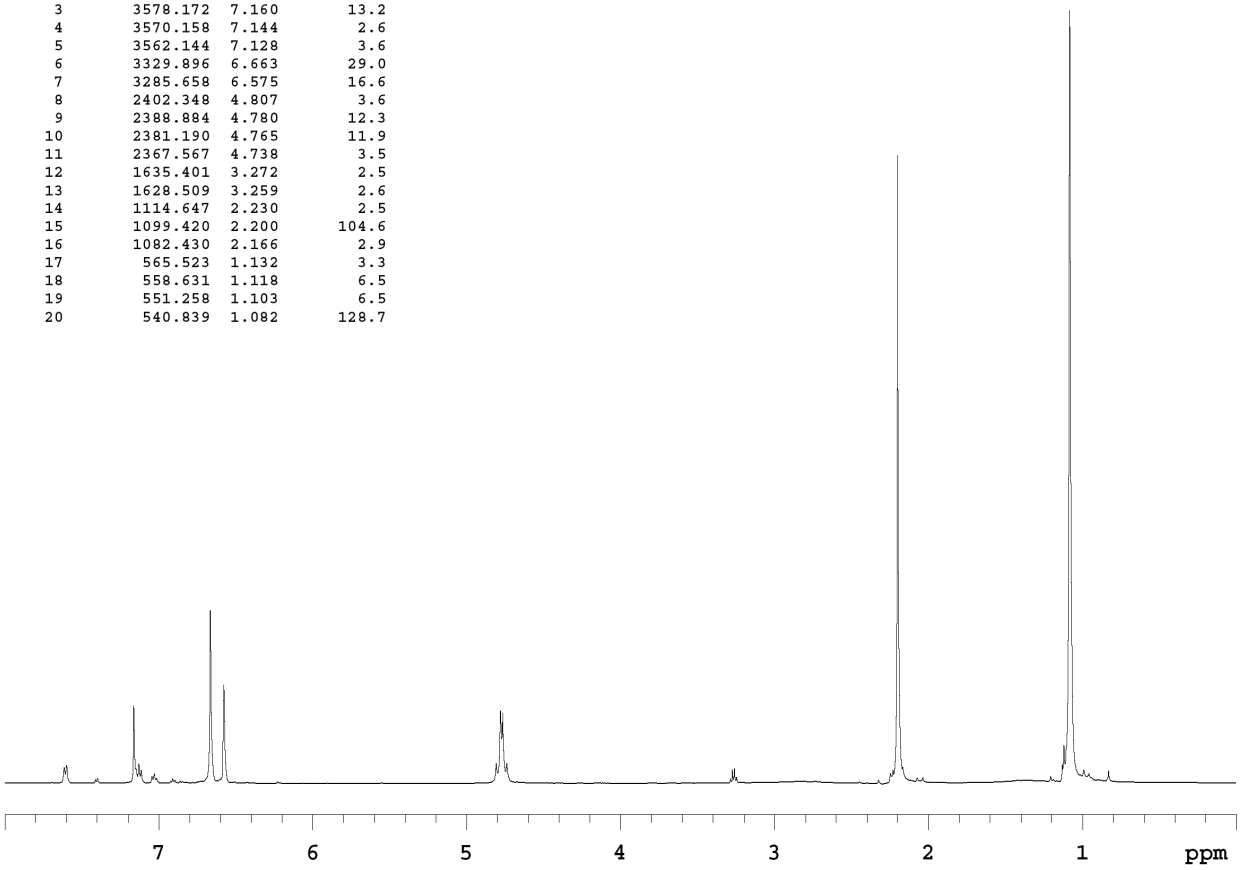

Figure S6. ^{1}H NMR spectrum of crude **1**-SPh in benzene-d_6 at 20 ºC.

Conversion of **1** to **1**-SPh: From a stock solution of Ph_2S_2 (0.050 g, 0.23 mmol) in THF (1.379 g), an aliquot (0.089 g, 0.014 mmol) was set aside. From a stock solution of **1** (0.107 g, 0.0821 mmol) in THF (4.523 g), an aliquot (1.572 g, 0.02789 mmol, 2.0 equiv) was added dropwise to the stirring Ph_2S_2 aliquot. The reaction mixture was allowed to stir for 1 h, after which THF was removed *in vacuo*. From a stock solution of ferrocene (0.045 g, 0.24 mmol) in THF (2.495 g), an aliquot (0.308 g, 0.0293 mmol) was added to the crude solids, and THF was again removed *in vacuo*. ^{1}H NMR (500 MHz, C_6D_6, 20 °C) indicated 97.1% conversion of **1** to **1**-SPh by comparison of the integrals of the aryl methyl resonance of **1**-SPh and the internal ferrocene standard resonance.

PhSe-P[NV(N[Np]Ar)$_3$]$_2$ (1-SePh): An Et_2O solution (4 mL) of **1** (105 mg, 0.0806 mmol) was added to dry Ph_2Se_2 (13 mg, 0.0416 mmol, 0.52 equiv). After stirring for 1 h, the reaction mixture was dried under vacuum to a dark red solid (0.117 g, 0.0802 mmol, 99.5%). Crystals of **1**-SePh can be grown from hexamethyldisiloxane at –35 ºC. M.p. 153-155 °C. ^{1}H NMR (500

MHz, C_6D_6, 20 °C): δ = 7.77 (d, 2H, J = 8 Hz, *o*-Ph), 7.08 (m, 3H, *m,p*-Ph), 6.66 (s, 12H, *o*-Ar), 6.58 (s, 6H, *p*-Ar), 4.77 (s, 12H, N-CH_2), 2.20 (s, 36H, Ar-Me), 1.08 (s, 54H, *t*Bu) ppm. ^{13}C NMR (126 MHz, C_6D_6, 20 °C): δ = 156.9 (*ipso*-Ar), 137.8, 133.7 (d, J_{CP} = 7 Hz, *o*-Ph), 132.7 (d, J_{CP} = 17 Hz, *ipso*-Ph), 129.7, 126.9, 126.0, 121.9, 76.1 (N-CH$_2$), 36.7 (C(CH$_3$)$_3$), 30.3 (C(CH$_3$)$_3$), 22.1 (Ar-CH$_3$) ppm. ^{31}P NMR (121 MHz, C_6D_6, 20 °C): δ = 204.7 (br, $\Delta\nu_{1/2}$ = 140 Hz) ppm. ^{51}V NMR (132 MHz, C_6D_6, 20 °C): δ = 113.7 ppm ($\Delta\nu_{1/2}$ = 980 Hz). ^{77}Se NMR (95 MHz, C_6D_6, 20 °C): δ = 562.0 (d, J_{SeP} = 327 Hz). Anal. calcd: C, 69.16; H, 8.64; N, 7.68; found: C, 69.82; H, 8.84; N, 7.84.

INDEX	FREQUENCY	PPM	HEIGHT
1	3886.714	7.777	2.8
2	3879.180	7.762	3.0
3	3578.172	7.160	3.4
4	3572.722	7.149	2.2
5	3565.029	7.134	3.4
6	3557.496	7.119	2.3
7	3329.575	6.663	28.1
8	3289.505	6.582	15.6
9	2382.954	4.768	24.4
10	1635.241	3.272	2.4
11	1628.188	3.258	2.5
12	1101.504	2.204	107.3
13	565.683	1.132	3.6
14	563.119	1.127	3.3
15	558.791	1.118	6.3
16	551.578	1.104	5.2
17	540.038	1.081	128.7

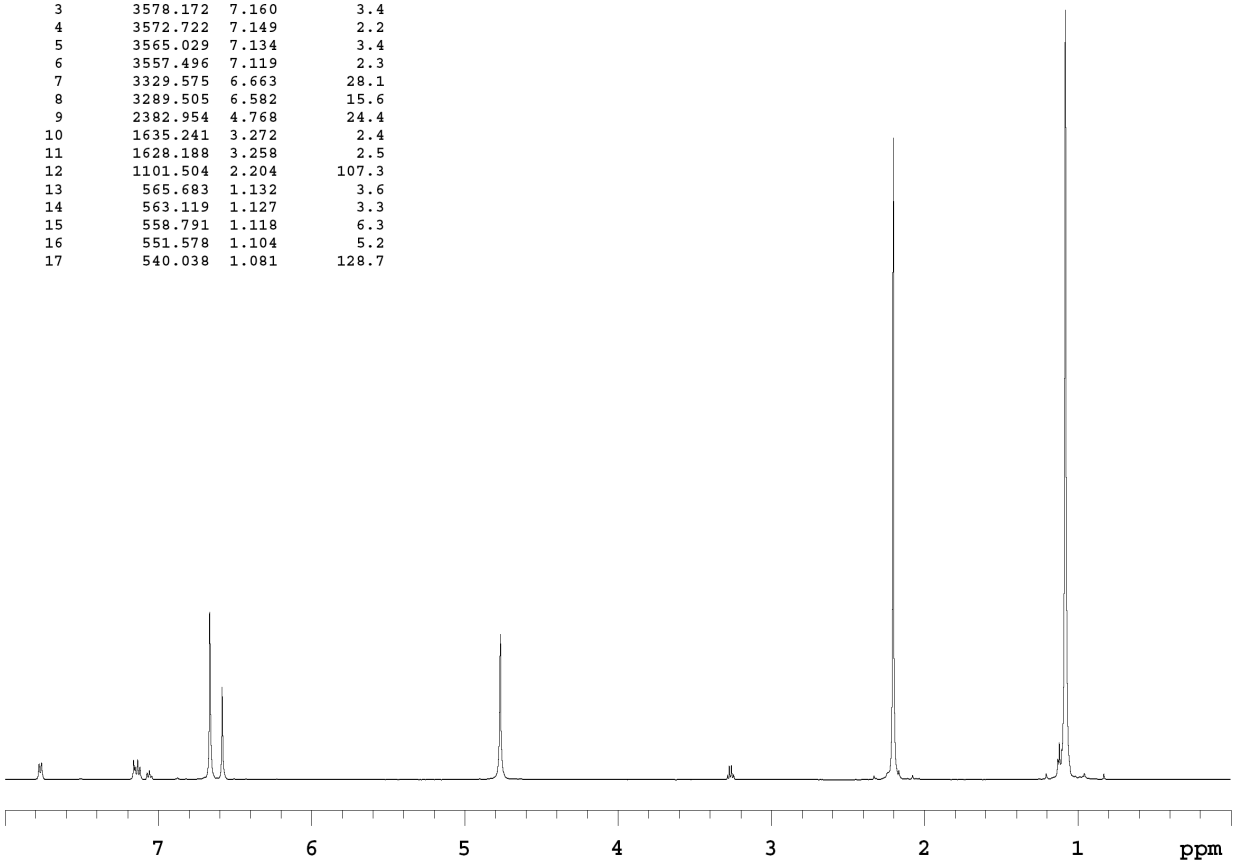

Figure S7. ^{1}H NMR spectrum of crude **1**-SePh in benzene-d_6 at 20 ºC.

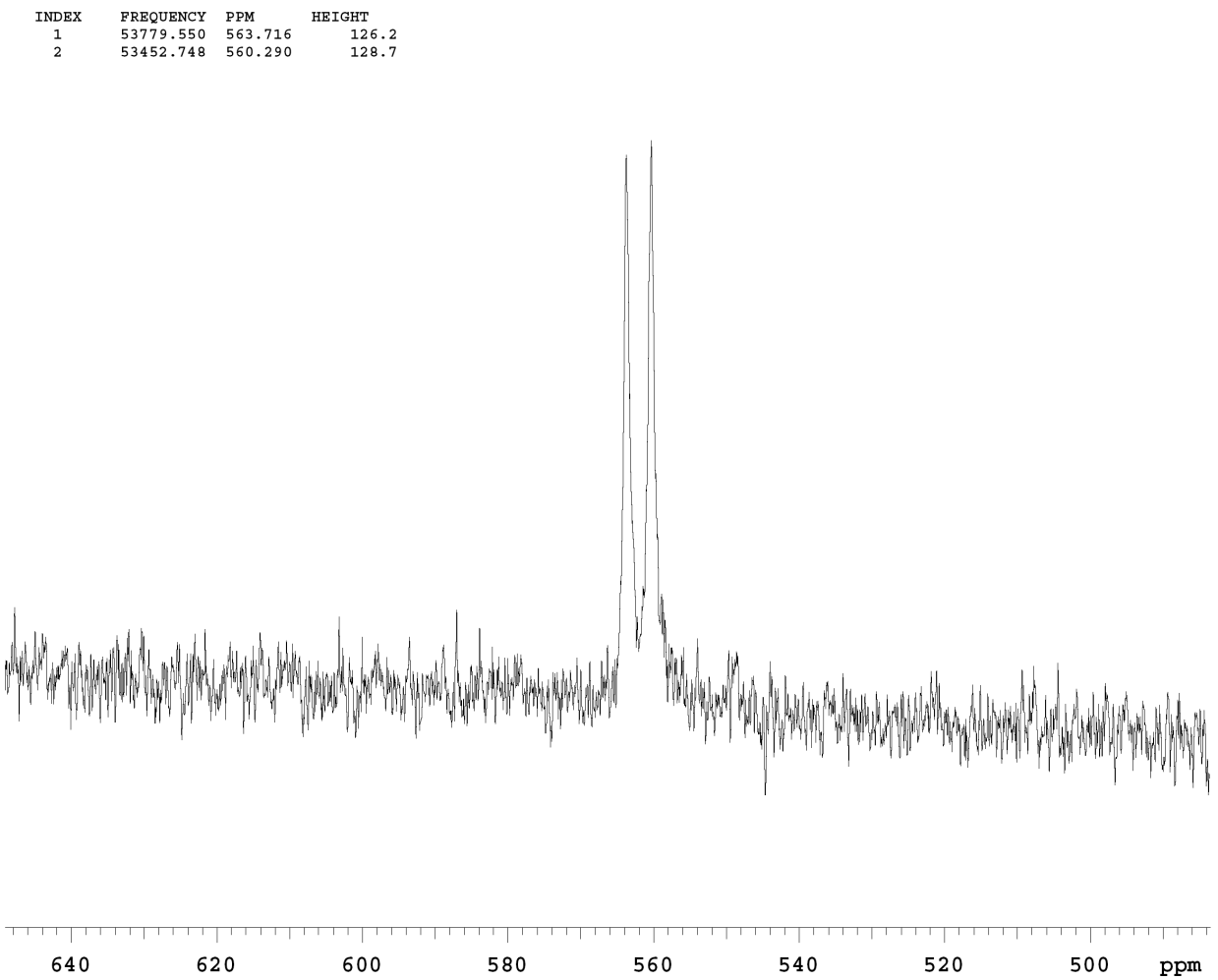

Figure S8. ^{77}Se NMR spectrum of **1**-SePh in benzene-d_6 at 20 ºC, with 10 Hz line broadening.

Conversion of **1** to **1**-SePh: From a stock solution of Ph_2Se_2 (0.046 g, 0.23 mmol) in THF (2.484 g), an aliquot (0.208 g, 0.012 mmol) was set aside. From a stock solution of **1** (0.107 g, 0.0821 mmol) in THF (4.523 g), an aliquot (1.340 g, 0.02377 mmol, 2.0 equiv) was added dropwise to the stirring Ph_2Se_2 aliquot. The reaction mixture was allowed to stir for 1 h, after which time the THF was removed *in vacuo*. From a stock solution of ferrocene (0.045 g, 0.24 mmol) in THF (2.495 g), an aliquot (0.221 g, 0.0210 mmol) was added to the crude solids, and THF was again removed *in vacuo*. ^{1}H NMR (500 MHz, C_6D_6, 20 °C) indicated 97.6% conversion of **1** to **1**-SePh by comparison of the integrals of the aryl methyl resonance of **1**-SePh and the internal ferrocene standard resonance.

{[(Ar[Np]N)$_3$VN]$_2$P}$_2$(μ-OC$_6$Cl$_4$O) (4): A THF solution (4 mL) of **1** (98 mg, 0.0752 mmol) was added to dry tetrachlorobenzoquinone (10 mg, 0.0407 mmol, 0.54 equiv). After stirring for 1 h, the reaction mixture was dried under dynamic vacuum to a red-black solid (0.117 g, 0.0802 mmol, 99.5%). Crystals of **4** can be grown from Et_2O at –35 ºC. M.p. 195-197°C. ^{1}H NMR (500 MHz, C_6D_6, 20 °C): δ = 6.80 (br s, 24H, *o*-Ar, 6.65 (s, 12H, *p*-Ar), 4.67 (br s, 24H, N-CH_2), 2.31 (s, 72H, Ar-Me), 1.07 (s, 108H, *t*Bu) ppm. ^{13}C NMR (126 MHz, C_6D_6, 20 °C): δ = 157.7 (*ipso*-

Ar), 146.0, 137.9, 127.0, 126.0, 121.9 (br, *o*-Ar), 75.4 (br, N-*C*H_2), 36.7 (*C*$(CH_3)_3$), 30.5 (C(*C*$H_3)_3$), 22.1 (Ar-*C*H_3) ppm. ^{31}P NMR (121 MHz, C_6D_6, 20 °C): δ = 189.6 (br, $\Delta\nu_{1/2}$ = 210 Hz) ppm. ^{51}V NMR (132 MHz, C_6D_6, 20 °C): δ = –46.5 ($\Delta\nu_{1/2}$ = 3750 Hz) ppm. Anal. calcd: C, 68.24; H, 8.48; N, 7.86; found: C, 68.33; H, 8.62; N, 8.18.

INDEX	FREQUENCY	PPM	HEIGHT
1	3578.172	7.160	5.7
2	3398.176	6.800	3.5
3	3322.042	6.647	27.4
4	2330.702	4.664	4.0
5	1156.320	2.314	128.7
6	1115.448	2.232	3.4
7	634.925	1.270	3.6
8	628.353	1.257	4.2
9	621.461	1.244	3.6
10	603.670	1.208	3.9
11	597.258	1.195	3.9
12	535.390	1.071	72.2
13	485.062	0.971	4.0
14	444.510	0.889	6.1
15	437.779	0.876	9.0
16	430.726	0.862	5.3

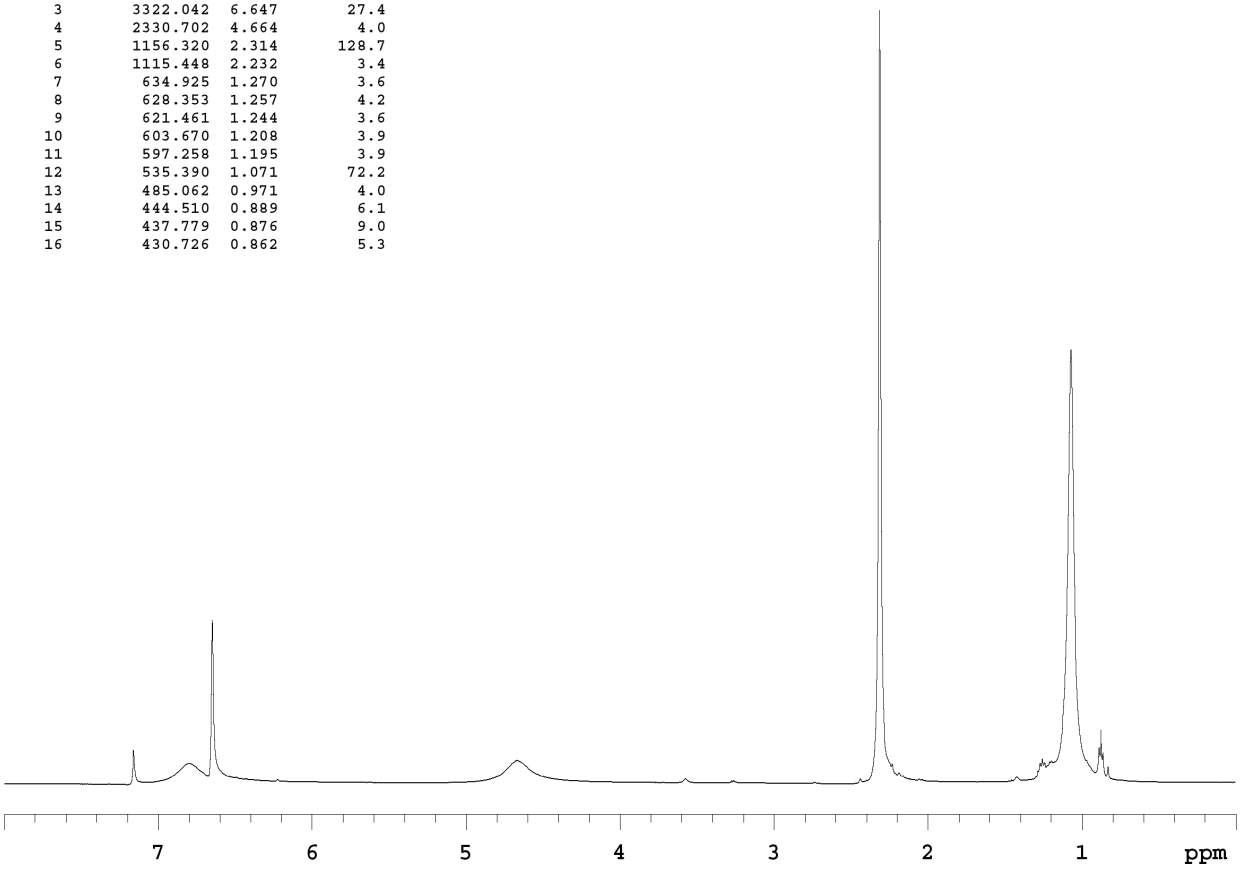

Figure S9. ^{1}H NMR spectrum of crude **4** in benzene-d_6 at 20 ºC.

Conversion of **1** to **4**: From a stock solution of *p*-tetrachlorobenzoquinone (0.040 g, 0.16 mmol) in THF (2.533 g), an aliquot (0.178 g, 0.011 mmol) was set aside. From a stock solution of **1** (0.107 g, 0.0821 mmol) in THF (4.523 g), an aliquot (1.265 g, 0.02244 mmol, 2.0 equiv) was added dropwise to the stirring Ph_2S_2 aliquot. The reaction mixture was allowed to stir for 1 h, after which THF was removed *in vacuo*. From a stock solution of ferrocene (0.045 g, 0.24 mmol) in THF (2.495 g), an aliquot (0.226 g, 0.0215 mmol) was added to the crude solids, and THF was again removed *in vacuo*. ^{1}H NMR (500 MHz, C_6D_6, 20 °C) indicated 99.5% conversion of **1** to **4** by comparison of the integrals of the aryl methyl resonance of **4** and the internal ferrocene standard resonance.

Reaction of 1-Cl with LiHBEt$_3$: A toluene-d_8 solution (0.6 mL) of **1**-Cl (0.027 g, 0.020 mmol) was placed in a sealable (J. Young) NMR tube and frozen in a liquid nitrogen cooled cold well. A few drops of toluene-d_8 were added to this tube, and this layer was also frozen. Finally, a solution of 1.0 M $LiHBEt_3$ (20 μL, 0.020 mmol, 1.0 equiv) in THF was added to the NMR tube

via a syringe, and the contents of the tube were frozen. The NMR tube was placed under vacuum and sealed, then kept at –95 °C in an acetone/liquid N_2 bath for 30 minutes. After this time, the tube was placed in an NMR spectrometer at –20 °C. The ^{1}H NMR spectrum showed resonances corresponding to **1**-Cl. Upon warming the tube to –12 °C, the ^{1}H NMR spectra indicated partial consumption of **1**-Cl along with generation of H_2 (δ = 4.49 ppm) and **1**. A stack plot showing 10 consecutive spectra taken 35 s apart at –12 °C is shown in Figure S10.

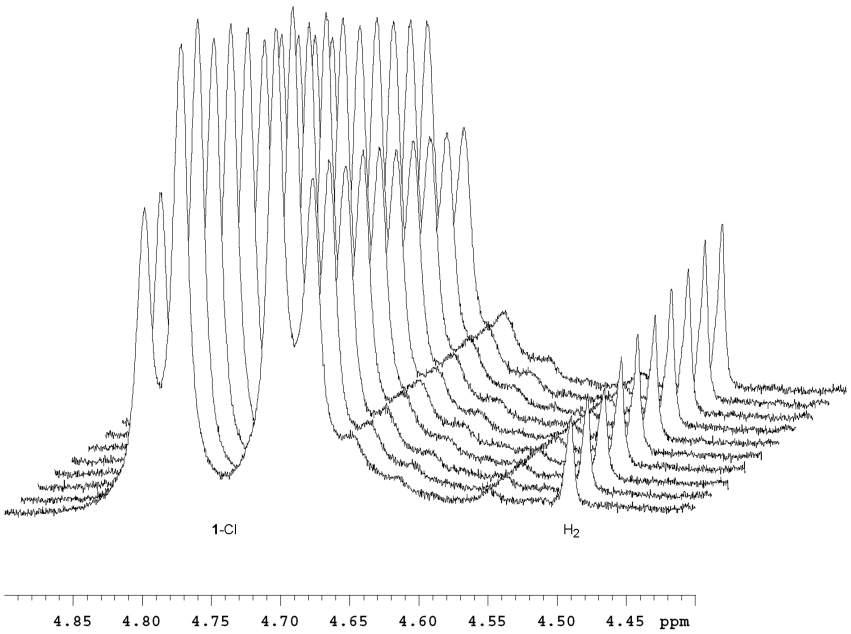

Figure S10. Generation of H_2 and consumption of **1**-Cl as assayed by low-temperature ^{1}H NMR spectroscopy.

Attempted reaction of 1 with P_4: A benzene-d_6 solution (1.5 mL) of P_4 (0.004 g, 0.03 mmol, 1.2 equiv) was added to dry, stirring **1** (0.034 g, 0.026 mmol). ^{1}H NMR spectra of aliquots of the reaction mixture taken after 3 h and after 2 d indicated no reaction. The corresponding ^{31}P NMR spectra showed only a singlet at –520 ppm, attributable to P_4.

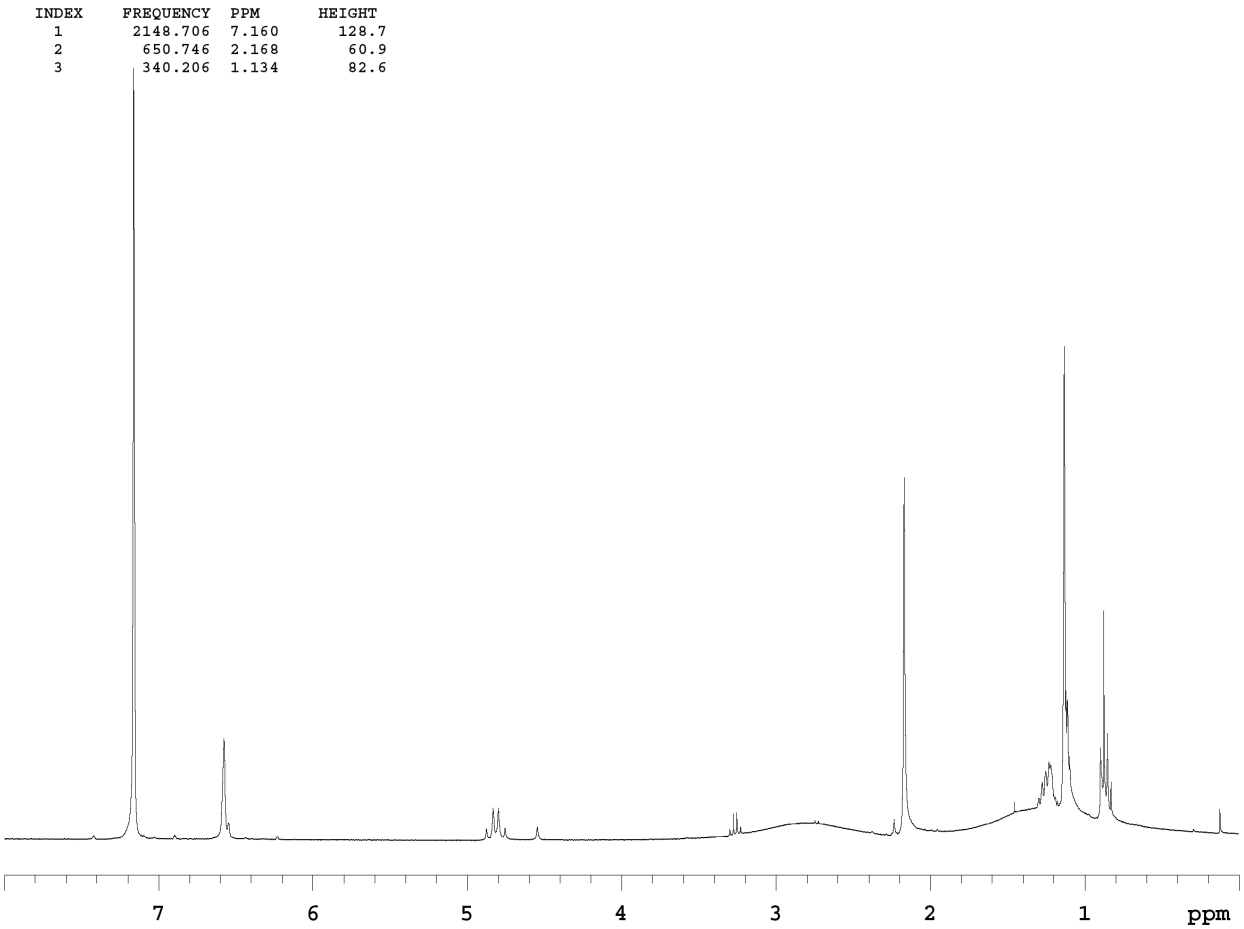

Figure S11. ^{1}H NMR spectrum of the attempted reaction between **1** and P_4 in benzene-d_6 at 20 ºC, taken after 3 h. The most prominent diamagnetic resonances are attributed to a small amount of **1**-Cl present in this sample of **1** as an impurity.

Attempted reaction of 1 with Gomberg's dimer: An Et_2O solution (2 mL) of **1** (0.024 g, 0.018 mmol) was added dropwise to a stirring Et_2O solution (2 mL) of Gomberg's dimer (0.009 g, 0.019 mmol, 1 equiv). After 1 h the reaction was concentrated to dryness under dynamic vacuum and then dissolved in benzene-d_6. Analysis by ^{1}H NMR spectroscopy indicated that no appreciable reaction had occurred.

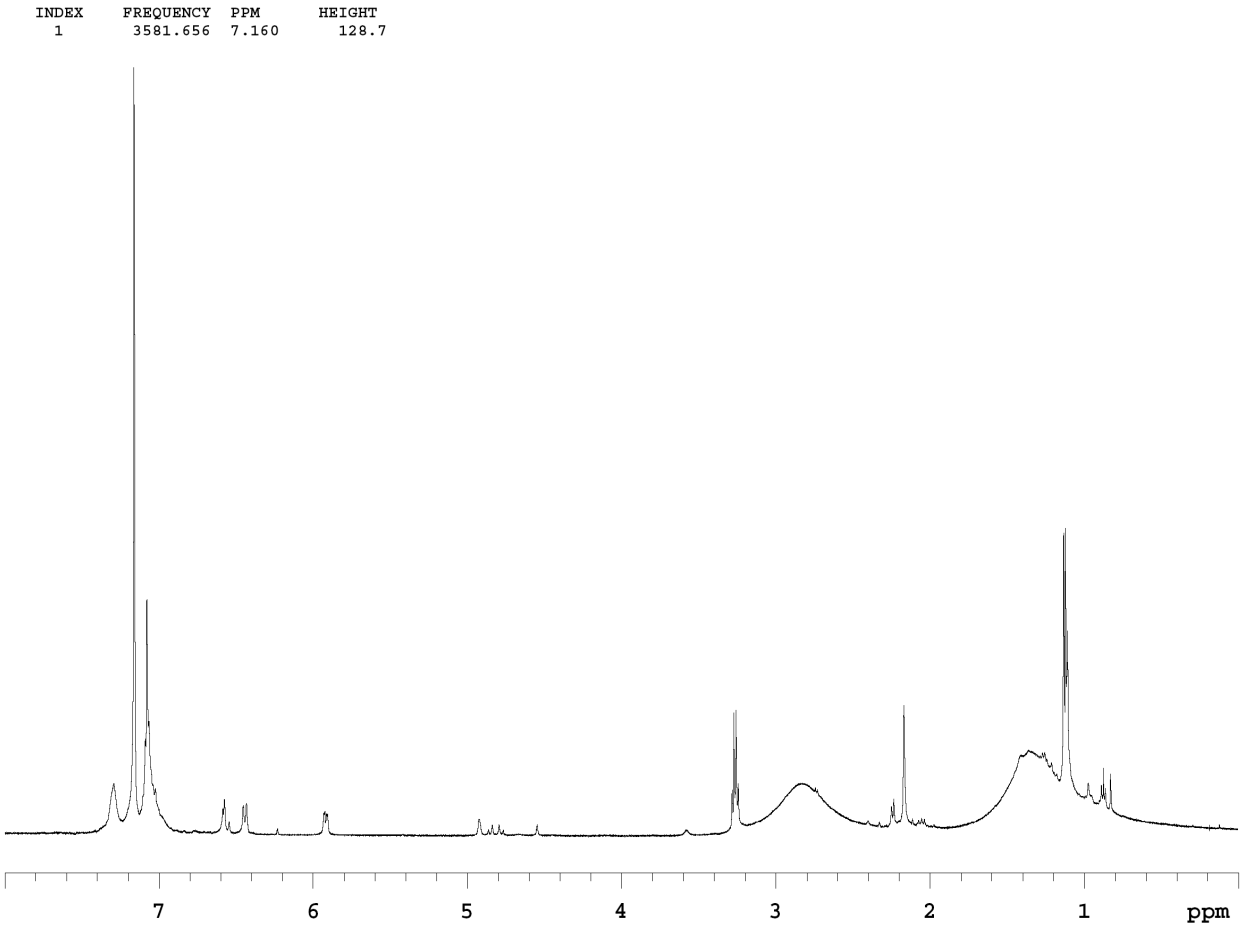

Figure S12. ^{1}H NMR spectrum of the attempted reaction between **1** and Gomberg's dimer in benzene-d_6 at 20 ºC, taken after 1 h.

Attempted reaction of 1 with *n*Bu$_3$SnH: A thawing Et_2O solution (2 mL) of **1** (0.045 g, 0.0345 mmol) was added dropwise to a stirring, thawing solution of *n*Bu$_3$SnH (12 mg, 0.0412 mmol, 1.2 equiv). After 75 min the reaction mixture was concentrated to dryness and then dissolved in benzene-d_6. Analysis by ^{1}H NMR spectroscopy indicated that no appreciable reaction had occurred.

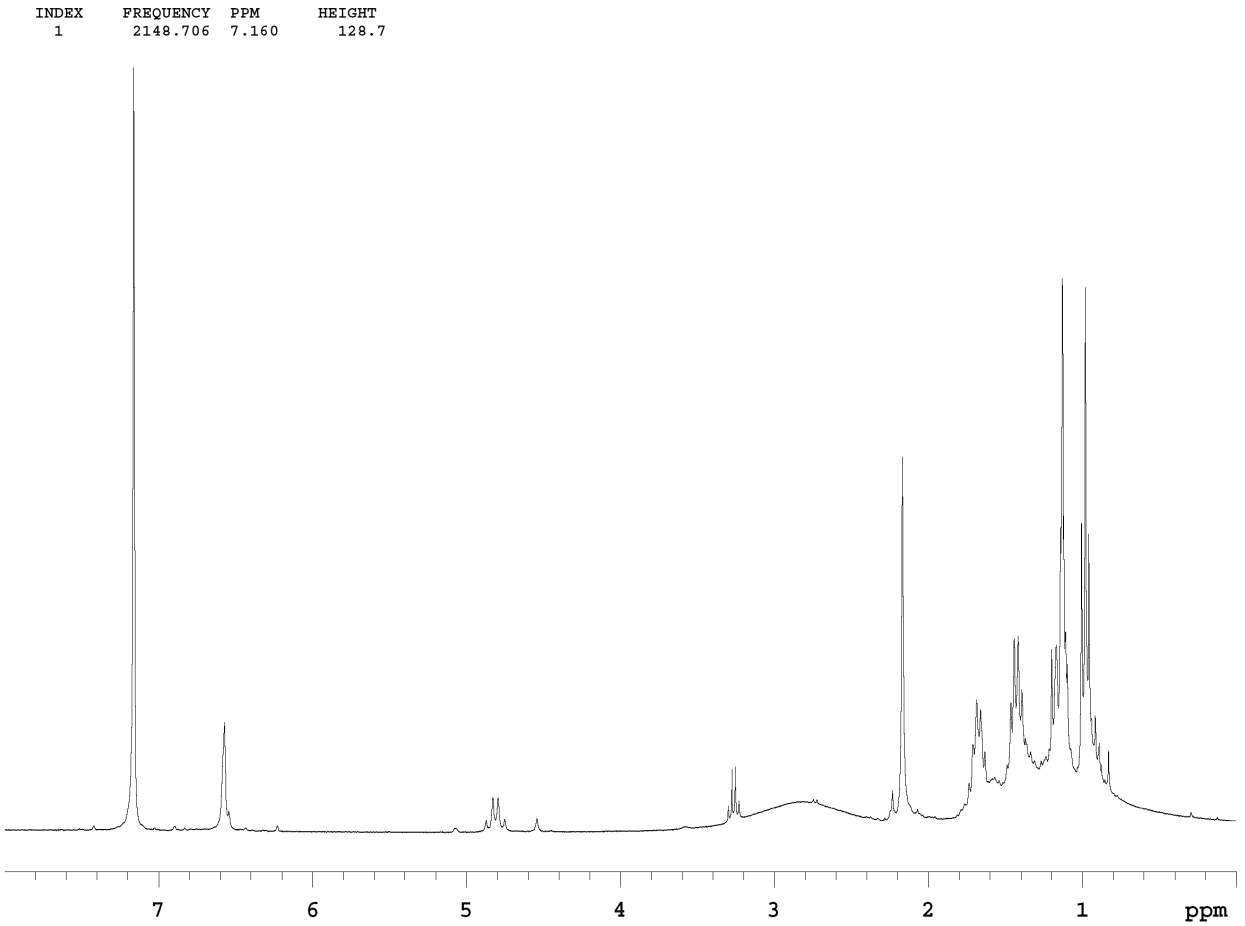

Figure S13. ^{1}H NMR spectrum of the attempted reaction between **1** and *n*Bu$_3$SnH in benzene-d_6 at 20 ºC, taken after 75 min. A small amount of **1**-Cl is present as an impurity.

Attempted reaction of 1 with *n*Bu_2SnH_2: A thawing Et_2O solution (2 mL) of **1** (0.046 g, 0.0353 mmol) was added dropwise to a stirring, thawing solution of *n*Bu_2SnH_2 (9 mg, 0.0383 mmol, 1.1 equiv). After 5 h the reaction mixture was concentrated to dryness under dynamic vacuum and then dissolved in benzene-d_6. Analysis by ^{1}H NMR spectroscopy indicated that no appreciable reaction had occurred.

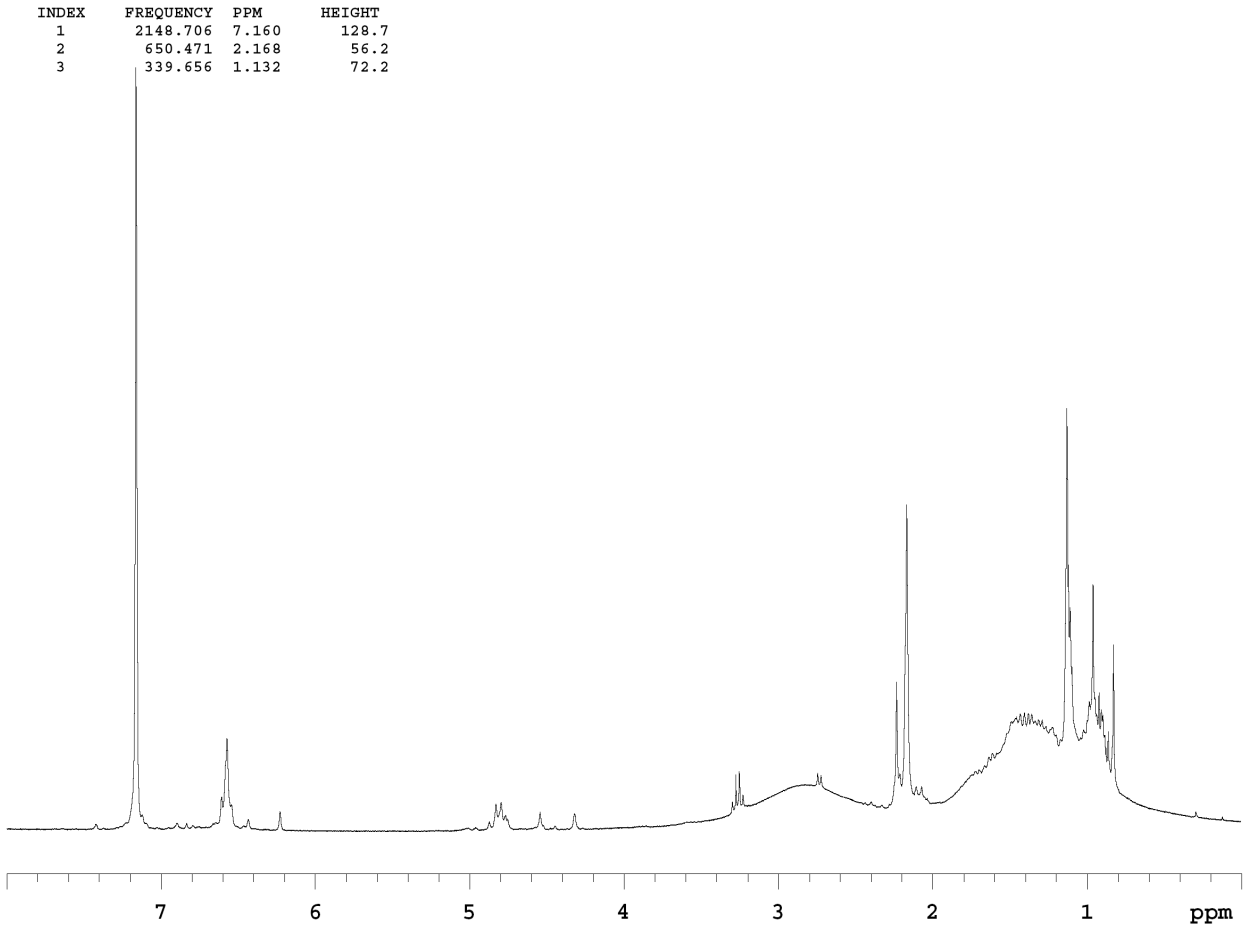

Figure S15. ^{1}H NMR spectrum of the attempted reaction between **1** and *n*Bu_2SnH_2 in benzene-d_6 at 20 ºC, taken after 5 h.

Attempted reaction of 1 with $Cp(CO)_3MoH$: A thawing Et_2O solution (4 mL) of **1** (75 mg, 0.0576 mmol) was added dropwise to a stirring, thawing Et_2O solution (1 mL) of $Cp(CO)_3MoH$ (14 mg, 0.0569 mmol, 1.0 equiv). After 3.5 h the reaction mixture was concentrated to dryness under dynamic vacuum and then dissolved in benzene-d_6. Analysis by ^1H NMR spectroscopy indicated only partial decomposition of **1**.

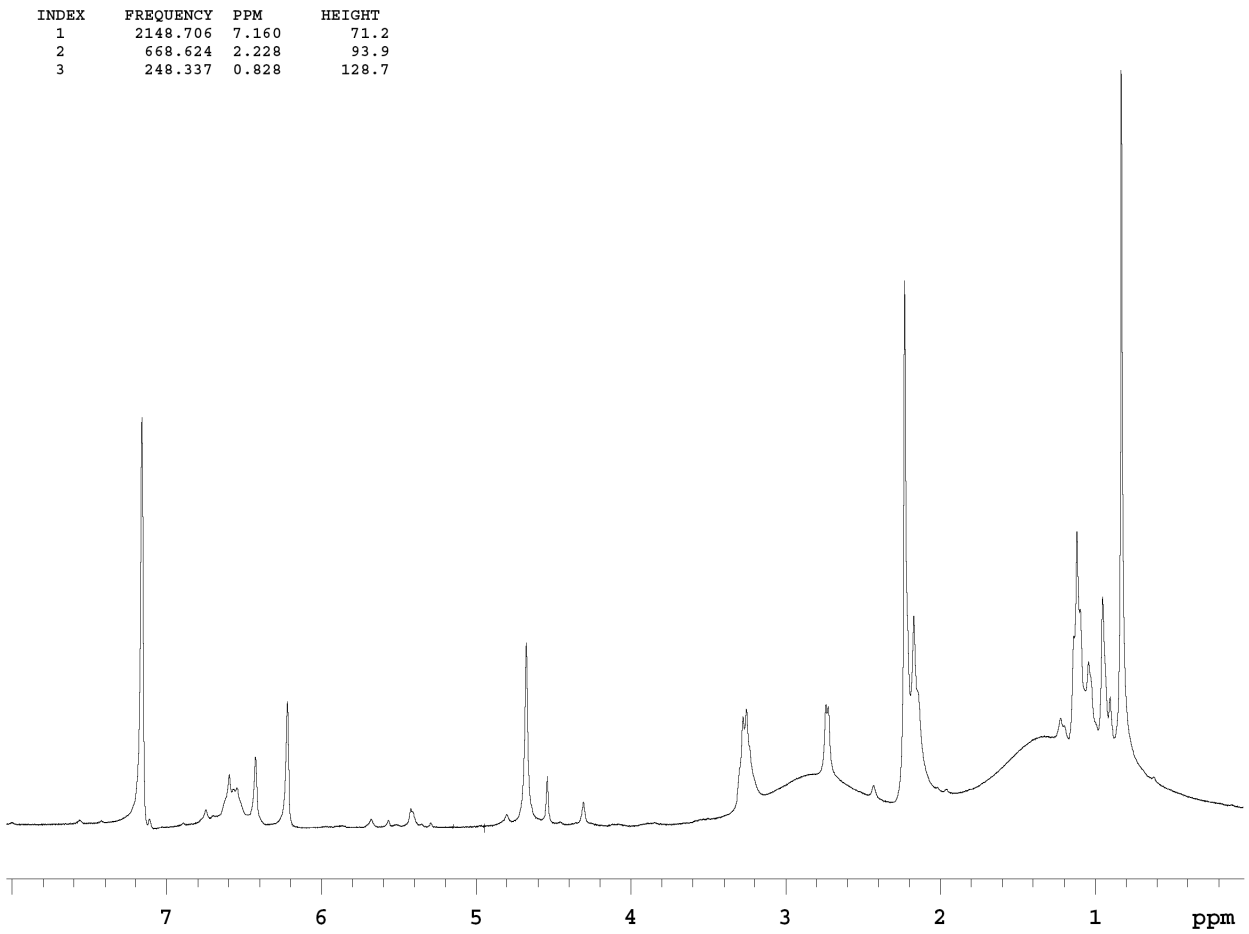

Figure S16. ^1H NMR spectrum of the attempted reaction between **1** and $Cp(CO)_3MoH$ in benzene-d_6 at 20 ºC, taken after 3.5 h. The most prominent diamagnetic resonances are attributed to free amine, HN(Np)Ar.

X-Ray Diffraction Studies on 1 and 1-SePh

Diffraction quality crystals were grown from Et_2O (**1**) or $(Me_3Si)_2O$ (**1**-SePh) solutions that were chilled to –35 ºC for several days. Crystals were mounted with oil on either a glass fiber or in a nylon loop. Low-temperature data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) performing ϕ- and ω-scans. A semi-empirical absorption correction was applied to the diffraction data using SADABS.[6] All structures were solved by direct or Patterson methods using SHELXS[7] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[8] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Further details of the data collection and refinement are described below, provided in tabular form in Table S1, and with greater details available in cif format from the CCDC under deposition numbers 617350 and 617351.[9]

Compound **1** crystallizes in the monoclinic space group *C*2/*c* with one half molecule in the asymmetric unit, the second half is generated by the crystallographic twofold, which runs through the phosphorus atom in the N-P-N plane, thus relating the two P-bound nitrogen atoms by symmetry. Upon refinement, high residual electron density was observed throughout the structure. The density showed evidence of a whole molecule disorder,[10, 11] and when refined as such the occupancy of the main component refined to ~95%. Because of this high occupancy of the main component, the minor component was removed from the final refinement. However, the phosphorus atom of the remaining component was also disordered and slightly removed from the special position. Roughly 70% of the P-atom occupancy falls just off of the special position, while the remaining 30% is split between two symmetry-related positions further removed from this position. The occupancies of the phosphorus atoms were refined independently, while restraining the sum of these occupancies to be unity. In addition, similarity restraints on 1-2 and 1-3 distances along the NPN-bridge were applied, and the anisotropic displacement parameters of the two independent P atom positions were constrained to be identical. Data on a second crystal of **1** revealed the same disorders.

Compound **1**-SePh crystallizes in the triclinic space group $P\bar{1}$ with one molecule of **1**-Se and 2.5 molecules of $(Me_3Si)_2O$ in the asymmetric unit The half molecule of solvent resides on, and violates the symmetry of, the inversion center. The remaining two solvent molecules were modeled over two positions each, with the sum of their occupancies constrained to unity while their ratios were allowed to refine freely. In addition, similarity restraints on 1-2 and 1-3 distances and rigid bond restraints to the thermal parameters were applied to the solvent molecules. As a result of these disorders some of the thermal ellipsoids of solvent remain quite large. Also, the P-SePh unit of **1**-SePh shows disorder over two positions that are related by inversion about the pyramidal phosphorus center. Similarity restraints on 1-2 and 1-3 distances along the P-SePh moiety were applied and the sum of the occupancies of the two components was constrained to unity, while the relative occupancies were allowed to refine freely to ~84:16. IUCr's *checkCIF* (http://journals.iucr.org/services/cif/checkcif.html) reports an inter-molecular contact between two disordered solvent molecules (C43A – C43A), and also between two of the phenyl carbons (C5A-C5A); as both of these atoms are part of the minor component to the disorders described above, they are not likely to coexist in adjacent cells and we need not be concerned.

We would like to acknowledge the assistance of Prof. Dr. Anthony Spek, Utrecht University (Netherlands), for his validation of the structure of radical **1**.

Table S1: Crystallographic Data

	1	**1**-SePh · $(Me_3Si)_2O)_{2.5}$
CCDC Deposition Number	617350	617351
Formula	$C_{78}H_{120}N_8PV_2$	$C_{99}H_{170}N_8O_{2.5}PSeSi_5V_2$
Color	Black	Red-black
Morphology	Plate	Shard
Size, mm	$0.50 \times 0.50 \times 0.05$	$0.15 \times 0.10 \times 0.05$
Crystal System	Monoclinic	Triclinic
Space Group	*C2/c*	$P\bar{1}$
Temperature, K	100(2)	100(2)
a, Å	32.491(2)	17.1892(8)
b, Å	12.1610(7)	18.6837(9)
c, Å	19.6848(13)	20.8321(10)
α, deg	90	97.5270(10)
β, deg	98.388(2)	108.4650(10)
γ, deg	90	113.2450(10)
V, Å^3	7694.8(8)	5573.6(5)
Z	4	2
D_χ, g cm^{-3}	1.124	1.111
μ, (Mo *Kα*), mm^{-1}	0.309	0.608
No. Reflections	74138	121639
No. Ind. Ref. (No. $I > 2\ \sigma(I)$)	10770 (8620)	29967 (18906)
$2\theta_{max}/2\theta_{min}$	29.57 / 2.03	29.13 / 1.87
R_{int}	0.0503	0.0667
F(000)	2820	2010
Goodness of Fit	1.064	1.019
R(F))[a]	0.0774	0.0570
$wR(F^2)$[a]	0.2276	0.1660
Largest difference peak / hole (e/Å^3)	1.839 / –0.378	1.288 / –0.767

[a] Quantity minimized = $wR(F^2) = \sum[w(F_o^2-F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o-F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = 2F_c^2 + \mathrm{Max}(F_o, 0)]/3$

Computational Details

General

All calculations were carried out using ADF 2004.01 from Scientific Computing and Modeling (http://www.scm.com). [12, 13] In all cases the LDA functional employed was that of Vosko, Wilk, and Nusair (VWN)[14] while the GGA part was handled using the functionals of Becke and Perdew (BP86).[15-17] In addition, all calculations were carried out using the Zero Order Regular Approximation (ZORA) for relativistic effects.[18-20] In all cases the basis sets were triple-zeta with two polarization functions (TZ2P) as supplied with ADF. Frozen core approximations were not made, *i.e.* all electrons were accounted for in the model. Crystal coordinates for **1** were used as a guide for the initial geometry and symmetry constraints were applied when appropriate (C_2 for **1m**, C_{3v} for PH_3, and C_{2v} for PH_2).

Major orbital contributions to the SOMO are shown in Table S3, and this orbital was visualized using the DGRID software package[21] in conjunction with VMD.[22] This orbital is depicted graphically in the main text. Atoms holding major contributions of the spin density are listed in Table S4, along with the values of these spin densities.

To estimate the P-H bond strength in **1m**-H, we considered the following isodesmic reaction:[23] **1m**-H + PH_2 → **1m** + PH_3. The electronic energies of **1m**, **1m**-H, ·PH_2 and PH_3 are presented in Table S2 and are with reference to fully optimized geometries.[24, 25]

All calculations were carried out on a four- or an eight-processor Quantum Cube workstation from Parallel Quantum Solutions (http://www.pqs-chem.com).

Table S2. Energies (kcal/mol) related to the **1m**-H homolytic P-H bond strength calculation

	1m-H	·PH_2	**1m**	PH_3
Electronic Energy	-14716.80	-246.02	-14631.94	-354.77

Table S3. Orbital contributions to the SOMO of **1m**.

Atom	Orbital	% Composition
P	p_y	31.30
$V_A + V_B$	d_{xy}	39.49
	d_{x2-y2}	8.33

Table S4. Spin densities on P and V in **1m**.

Atom	Spin Density
P	0.377430
V_A	0.375225
V_B	0.375225

Optimized Geometry in Cartesian Coordinates (Å) of Calculated Molecules:

1m (C_2 symmetry)

N	1.334123	0.012034	0.202214
V	3.027062	0.213484	0.004913
N	3.823374	0.517602	1.688624
C	3.204918	1.572556	2.504298
H	3.004294	1.209335	3.524901
H	3.853140	2.460954	2.571262
H	2.252624	1.882058	2.058558
C	5.104897	0.097463	2.138710
C	5.323230	-1.223371	2.562248
C	6.595079	-1.634199	2.970962
C	7.664426	-0.733969	2.969869
C	7.449011	0.587524	2.567037
C	6.182339	1.003129	2.160290
H	4.485504	-1.919914	2.560656
H	6.751023	-2.663295	3.293538
H	8.657303	-1.056425	3.282263
H	8.274506	1.299562	2.553647
H	6.025212	2.027291	1.820798
N	3.171080	1.844204	-0.943843
C	2.080084	2.490717	-1.677117
H	1.131112	2.007016	-1.423895
H	2.232323	2.410398	-2.767104
H	2.010268	3.562382	-1.430804
C	4.370686	2.601946	-0.816295
C	4.374327	3.851990	-0.161646
C	5.566148	4.550134	0.028856
C	6.778775	4.023241	-0.430700
C	6.781971	2.798425	-1.098109
C	5.589324	2.099340	-1.298980
H	5.593613	1.153357	-1.837946
H	7.714370	2.375906	-1.471195
H	7.709584	4.566578	-0.272376
H	5.551064	5.508578	0.547751
H	3.437894	4.260806	0.217281
N	3.596570	-1.319586	-0.941869
C	2.697888	-2.446189	-1.252797
H	2.851914	-2.803673	-2.282530
H	1.655624	-2.138322	-1.132507
H	2.893109	-3.294241	-0.574513
C	4.849801	-1.374100	-1.627822
C	4.904541	-1.284251	-3.033285
C	6.129229	-1.308950	-3.697104
C	7.322976	-1.430160	-2.975838
C	7.276090	-1.532798	-1.585604
C	6.050078	-1.509626	-0.916096
H	6.014316	-1.596064	0.167970
H	8.195731	-1.635533	-1.010467
H	8.280169	-1.445220	-3.496251
H	6.155953	-1.222365	-4.783067
H	3.978079	-1.166280	-3.595649
P	0.000000	0.000000	1.162865
N	-1.334123	-0.012034	0.202214

V	-3.027062	-0.213484	0.004913
N	-3.823374	-0.517602	1.688624
C	-3.204918	-1.572556	2.504298
H	-3.004294	-1.209335	3.524901
H	-3.853140	-2.460954	2.571262
H	-2.252624	-1.882058	2.058558
C	-5.104897	-0.097463	2.138710
C	-5.323230	1.223371	2.562248
C	-6.595079	1.634199	2.970962
C	-7.664426	0.733969	2.969869
C	-7.449011	-0.587524	2.567037
C	-6.182339	-1.003129	2.160290
H	-4.485504	1.919914	2.560656
H	-6.751023	2.663295	3.293538
H	-8.657303	1.056425	3.282263
H	-8.274506	-1.299562	2.553647
H	-6.025212	-2.027291	1.820798
N	-3.171080	-1.844204	-0.943843
C	-2.080084	-2.490717	-1.677117
H	-1.131112	-2.007016	-1.423895
H	-2.232323	-2.410398	-2.767104
H	-2.010268	-3.562382	-1.430804
C	-4.370686	-2.601946	-0.816295
C	-4.374327	-3.851990	-0.161646
C	-5.566148	-4.550134	0.028856
C	-6.778775	-4.023241	-0.430700
C	-6.781971	-2.798425	-1.098109
C	-5.589324	-2.099340	-1.298980
H	-5.593613	-1.153357	-1.837946
H	-7.714370	-2.375906	-1.471195
H	-7.709584	-4.566578	-0.272376
H	-5.551064	-5.508578	0.547751
H	-3.437894	-4.260806	0.217281
N	-3.596570	1.319586	-0.941869
C	-2.697888	2.446189	-1.252797
H	-2.851914	2.803673	-2.282530
H	-1.655624	2.138322	-1.132507
H	-2.893109	3.294241	-0.574513
C	-4.849801	1.374100	-1.627822
C	-4.904541	1.284251	-3.033285
C	-6.129229	1.308950	-3.697104
C	-7.322976	1.430160	-2.975838
C	-7.276090	1.532798	-1.585604

1m-H (no symmetry constraints)

P	0.047561	0.041513	-0.026149
N	0.030328	0.037188	1.669029
V	0.847650	-0.027327	3.135440
N	2.698693	0.119955	2.823400
C	3.245679	-0.804021	1.825275
H	3.871262	-1.580948	2.297190
H	2.429221	-1.307730	1.289624
H	3.859557	-0.267474	1.083247
C	3.678526	0.819437	3.576480

C	3.803401	2.217033	3.479749
C	4.764920	2.899020	4.231970
C	5.619940	2.195812	5.086153
C	5.512346	0.803999	5.180202
C	4.554619	0.121268	4.431048
H	4.453460	-0.960452	4.525268
H	6.165350	0.246958	5.847167
H	6.368650	2.727693	5.674453
H	4.847090	3.978651	4.146883
H	3.134962	2.755475	2.809281
N	0.561743	-1.767237	3.830029
C	-0.504792	-2.680838	3.395775
H	-1.201606	-2.885620	4.225274
H	-0.097218	-3.645281	3.056029
H	-1.061356	-2.222858	2.574510
C	1.525258	-2.331808	4.717455
C	1.719433	-1.789394	5.996023
C	2.706232	-2.296546	6.843546
C	3.506184	-3.365663	6.441146
C	3.304468	-3.929072	5.176101
C	2.326168	-3.422567	4.321552
H	2.190788	-3.857482	3.331446
H	3.923407	-4.767807	4.849196
H	4.274361	-3.760444	7.103918
H	2.842829	-1.848434	7.830165
H	1.084724	-0.966638	6.322980
N	0.078491	1.370938	4.143418
C	-0.892707	2.333017	3.602805
H	-0.459567	3.348589	3.585075
H	-1.804113	2.374263	4.222480
H	-1.165694	2.045912	2.583188
C	0.211140	1.450447	5.567410
C	-0.863792	1.112912	6.412623
C	-0.728807	1.200495	7.797537
C	0.477220	1.628752	8.365204
C	1.544608	1.968084	7.533476
C	1.412593	1.883794	6.145031
H	2.242176	2.156701	5.495747
H	2.488349	2.306876	7.959241
H	0.581222	1.698031	9.447540
H	-1.566035	0.926949	8.439056
H	-1.798155	0.761767	5.974194
N	-1.513223	-0.305142	-0.573808
V	-2.681660	-0.393662	-1.781753
N	-1.892287	0.072378	-3.426906
C	-1.092244	1.308421	-3.440680
H	-1.010723	1.711686	-2.427089
H	-0.077472	1.110021	-3.821981
H	-1.559292	2.076338	-4.075424
C	-2.147524	-0.473080	-4.716292
C	-1.636604	-1.728212	-5.079970
C	-1.902604	-2.257493	-6.345672
C	-2.673281	-1.543684	-7.266650
C	-3.175332	-0.288643	-6.910116
C	-2.914802	0.245934	-5.649675
H	-1.033259	-2.280215	-4.359741

H	-1.500365	-3.236482	-6.616054
H	-2.880386	-1.957918	-8.251900
H	-3.788260	0.278541	-7.614759
H	-3.331782	1.212698	-5.366059
N	-3.425815	-2.125882	-1.672444
C	-2.914224	-3.171084	-0.768255
H	-2.496323	-4.009578	-1.352435
H	-3.715587	-3.578048	-0.131509
H	-2.127633	-2.755216	-0.133979
C	-4.685659	-2.462917	-2.264644
C	-5.840190	-2.616097	-1.471824
C	-7.062715	-2.942003	-2.057379
C	-7.158168	-3.125518	-3.441914
C	-6.017443	-2.982077	-4.231823
C	-4.789894	-2.657561	-3.648705
H	-3.898678	-2.554958	-4.265081
H	-6.073564	-3.127515	-5.310387
H	-8.114304	-3.380350	-3.897984
H	-7.949224	-3.046474	-1.431903
H	-5.774909	-2.455482	-0.395908
N	-3.883496	1.011956	-1.367229
C	-3.999168	1.664168	-0.067253
H	-3.239332	1.264194	0.613983
H	-4.995415	1.483555	0.376965
H	-3.867058	2.758464	-0.139299
C	-4.625454	1.618502	-2.421861
C	-5.614412	0.899472	-3.114358
C	-6.298096	1.473293	-4.190027
C	-6.020952	2.783597	-4.583383
C	-5.054292	3.521403	-3.888560
C	-4.365184	2.948401	-2.819882
H	-3.600818	3.522679	-2.295911
H	-4.831289	4.543457	-4.186299
H	-6.555927	3.231003	-5.421511
H	-7.051196	0.889654	-4.713008
H	-5.845700	-0.115794	-2.796755
H	0.020532	1.477744	-0.205214

PH_3 (C_{3v} symmetry)

P	0.000000	0.000000	0.008079
H	1.190622	0.000000	-0.782761
H	-0.595311	-1.031109	-0.782761
H	-0.595311	1.031109	-0.782761

PH_2 (C_{2v} symmetry)

P	0.000000	0.000000	-0.000353
H	1.020353	0.000000	-1.012808
H	-1.020353	0.000000	-1.012808

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