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Synthesis and Characterization of Vanadium(V)–Phosphinimide Complexes

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Synthetic routes to vanadium(V)–phosphinimide derivatives are addressed. Initial synthetic efforts afforded the known compound formulated as $VCl_2(NPPh_3)_3$ which was crystallographically determined to be the salt $[VCl(NPPh_3)_3]Cl$ (**1**). Reactions of the vanadium–imide precursors $VCl_3(NAr)$ (Ar = Ph, C_6H_3-2,6-*i*Pr_2) with $R_3PNSiMe_3$ (R = Ph, *i*Pr, *t*Bu) afforded $VCl_2(NPh)(NPPh_3)$ (**4**), $VCl_2(NPh)(NP\textit{i}Pr_3)$ (**5**), $VCl_2(NPh)(NP\textit{t}Bu_3)$ (**6**), $VCl_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NPPh_3)$ (**7**), $VCl_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NP\textit{i}Pr_3)$ (**8**), and $VCl_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NP\textit{t}Bu_3)$ (**9**) in yields ranging from 72% to 84%. Subsequent alkylation or arylation reactions resulted in $VMe_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NP\textit{t}Bu_3)$ (**10**), $VPh_2(NPh)(NP\textit{t}Bu_3)$ (**11**), $VPh_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NP\textit{i}Pr_3)$ (**12**), and $VPh_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NP\textit{t}Bu_3)$ (**13**) while substitution reactions with $Li[N(SiMe_3)_2]$ and Li[SBn] gave $VCl(N(SiMe_3)_2)(NPh)(NP\textit{t}Bu_3)$ (**14**) and $V(SBn)_2(NC_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)(NP\textit{t}Bu_3)$ (**15**) in yields ranging from 40% to 49% yield. Polarization of the N–P phosphinimide bond and V–N multiple bond character are evidenced by crystallographic data.

Introduction

Throughout the past 10−15 years, the chemistry of transition metal phosphinimide and phosphinimine complexes has been continuously explored.[1,2] In our own work, we have shown that titanium complexes with bulky phosphinimide ligands act as useful precursors to highly active olefin polymerization catalysts.[3,4] In continuing our efforts to explore the chemistry of transition metal phosphinimide complexes, we targeted vanadium(V)−phosphinimide compounds. Relatively few vanadium(V)−phosphinimide complexes have been reported previously. The reactions of VOX_3 (X = Cl, F) with Me_3SiNPR_3 have led to a variety of vanadium(V)−phosphinimide complexes such as $VOCl_2(NPPh_3)$, $VOCl(NPPh_3)_2$, $VCl_3(NPPh_3)_2$, $VOF_2(NPPh_3)$, $VOCl_2(NPPh_2NS(O)Me_2)$, $VCl_2(N(NPPh_2)_2)$, and $VCl_2(NP(CF_3)_2NP(CF_3)NP(CF_3)_2)$,[5−9] whereas reactions of $V(NSiMe_3)Cl_3$ with PR_3Cl_2 or $Me_3SiNP(C_2F_5)_2Cl$ resulted in the vanadium(V)−phosphinimide complexes $V(NPR_3)_nCl_{5-n}$ (R = Ph, $n = 1-4$, $R_3 = MePh_2, Me_2Ph$, $n = 1$) and $VCl_2(NP(C_2F_5)_2NP(C_2F_5)NP(C_2F_5)_2)$, respectively.[9−11] In addition, several groups have reported related vanadium(IV)− and vanadium(III)−phosphinimide derivatives.[12−17] In this paper, we describe our efforts to prepare and characterize V(V)−phosphinimide derivatives. A series of vanadium−imide−phosphinimide complexes are reported. Compounds of this type have very

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recently drawn attention mainly as catalyst precursors for the copolymerization of olefins.[18]

Experimental Section

General Data. All preparations were performed under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glovebox. Solvents were purified employing a Grubbs' type solvent purification system manufactured by Innovative Technology.[19] All organic reagents were purified by conventional methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Avance-300 and 500 spectrometers. All spectra were recorded in C_6D_6 at ambient temperatures unless otherwise noted. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance-300, and chemical shifts are referenced to external 85% H_3PO_4. Line widths at half height are reported in hertz. IR spectra (Nujol mulls) were recorded on a Bruker Vector 22 FT-IR spectrometer. Combustion analyses were done in house employing a Perkin-Elmer CHN series 2400 analyzer. $VOCl_3$, ArNCO (Ar = Ph, C_6H_3-2,6-*i*Pr$_2$), Li[N(SiMe$_3$)$_2$], MeLi, and PhMgBr were used as received from Sigma-Aldrich. VCl_3(NPh) (**2**), VCl_3(NC$_6$H$_3$-2,6-*i*Pr$_2$) (**3**), and R$_3$PNSiMe$_3$ (R = Ph, *i*Pr, *t*Bu) were prepared by modified literature methods.[12,20-22] In the case of a number of the alkyl derivatives, difficulties in purification precluded elemental analyses. In these cases, ^{1}H NMR spectra for these compounds have been deposited as Supporting Information. A few crystals of the known compound [VCl(NPPh$_3$)$_3$]Cl (**1**)[10] were obtained in low yield from the reaction of Ph$_3$PNSiMe$_3$ and VOCl$_3$ and grown in PhMe at 25 °C.[5]

Synthesis of VCl$_2$(NPh)(NPPh$_3$) (4), VCl$_2$(NPh)(NP*i*Pr$_3$) (5), VCl$_2$(NPh)(NP*t*Bu$_3$) (6), VCl$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NPPh$_3$) (7), VCl$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*i*Pr$_3$) (8), and VCl$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*t*Bu$_3$) (9). These compounds were prepared in a similar fashion from **2** or **3**, and thus, one preparation is detailed. A solution of Ph$_3$PNSiMe$_3$ (1.41 g, 4.03 mmol) in 25 mL of PhMe was added at 25 °C to a burgundy solution of VCl$_3$(NPh) (1.00 g, 4.03 mmol) in 40 mL of PhMe. The resulting burgundy solution was heated at reflux for 24 h. The solvent was removed in vacuo, and the product was washed with hexanes (4 × 15 mL). Drying in vacuo for 5 h afforded a brown solid (1.41 g, 72%). Characterization data for **4** follow. ^{1}H NMR δ: 7.49 (dd, 6H, P*o*-Ph, $^{3}J_{H-H} = 8$ Hz, $^{3}J_{P-H} = 13$ Hz), 6.94 (t, 3H, P*p*-Ph, $^{3}J_{H-H} = 6$ Hz), 6.83 (dt, 6H, P*m*-Ph, $^{3}J_{H-H} = 7$ Hz, $^{4}J_{H-H} = 3$ Hz), 6.63 (m, 4H, N*o*-Ph, N*m*-Ph), 6.56 (m, 1H, N*p*-Ph, $^{3}J_{H-H} = 5$ Hz). ^{31}P NMR δ: 22.6 ($\Delta\nu_{1/2} = 605$ Hz). ^{13}C NMR δ: 133.0, 132.9 (d, P*o*-Ph, $^{2}J_{P-C} = 11$ Hz), 129.2 (d, P*m*-Ph, $^{3}J_{P-C} = 13$ Hz), 128.0, 125.4, 124.2. ν_{N-P}: 1132 cm^{-1}. Anal. Calcd: H, 4.12; C, 58.92; N, 5.73. Found: H, 4.31; C, 58.27; N, 5.35. Characterization data for **5** follow: green solid. Yield: 2.43 g, 78%. ^{1}H NMR δ: 7.11 (d, 2H, N*o*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.94 (t, 2H, N*m*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.72 (t, 1H, N*p*-Ph, $^{3}J_{H-H} = 7$ Hz), 1.73 (d(sep), 2H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz, $^{2}J_{P-H} = 11$ Hz), 0.78 (dd, 18H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz, $^{3}J_{P-H} = 17$ Hz). ^{31}P NMR δ: 56.9 ($\Delta\nu_{1/2} = 702$ Hz). ^{13}C NMR δ: 128.7, 125.6, 123.5, 25.4 (d, CHMe$_2$, $^{1}J_{P-C} = 53$ Hz), 16.7. ν_{N-P}: 1135 cm^{-1}. Anal. Calcd: H, 6.77; C, 46.53; N, 7.23. Found: H, 6.78; C, 46.63; N, 6.76. Characterization data for **6** follow: green solid. Yield: 1.41 g, 75%. ^{1}H NMR δ: 7.07 (d, 2H, N*o*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.96 (t, 2H, N*m*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.71 (t, 1H, N*p*-Ph, $^{3}J_{H-H} = 7$ Hz), 1.05 (d, 27H, *t*Bu, $^{3}J_{P-H} = 14$ Hz). ^{31}P NMR δ: 64.4 ($\Delta\nu_{1/2} = 625$ Hz). ^{13}C NMR δ: 128.7, 125.2, 123.1, 42.1 (d, *t*Bu, $^{1}J_{P-C} = 40$ Hz), 29.7. ν_{N-P}: 1122 cm^{-1}. Calcd: H, 7.51; C, 50.36; N, 6.53. Found: H, 7.86; C, 50.51; N, 6.10. Characterization data for **7** follow: greenish brown solid. Yield: 1.37 g, 75%.^{1}H NMR δ: 7.54 (dd, 6H, P*o*-Ph, $^{3}J_{H-H} = 8$ Hz, $^{3}J_{P-H} = 13$ Hz), 6.91 (t, 3H, P*p*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.80 (m, 9H, P*m*-Ph, N*p*-Ph, N*m*-Ph), 3.99 (sep, 2H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz), 1.14 (d, 12H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz). ^{31}P NMR δ: 20.4 ($\Delta\nu_{1/2} = 532$ Hz). ^{13}C NMR δ: 133.4, 133.2 (d, P*o*-Ph, $^{2}J_{P-C} = 11$ Hz), 129.5 (d, (P*m*-Ph, $^{3}J_{P-C} = 13$ Hz) 126.5, 122.8, 29.3, 24.4. ν_{N-P}: 1110 cm^{-1}. Characterization data for **8** follow: green solid. Yield: 2.06 g, 73%. ^{1}H NMR δ: 7.01 (d, 2H, N*m*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.88 (t, 2H, N*p*-Ph, $^{3}J_{H-H} = 7$ Hz), 4.17 (sep, 2H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz), 1.68 (d of sep, 3H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz, $^{2}J_{P-H} = 11$ Hz), 1.39 (d, 12H, CHMe$_2$, $^{3}J_{H-H} = 9$ Hz), 0.77 (dd, 18H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz, $^{3}J_{P-H} = 16$ Hz). ^{31}P NMR δ: 56.3 ($\Delta\nu_{1/2} = 609$ Hz). ^{13}C NMR δ: 144.4, 126.2, 122.8, 29.2, 26.2 (d, PCHMe$_2$, $^{1}J_{P-C} = 53$ Hz), 24.5, 16.7. ν_{N-P}: 1121 cm^{-1}. Characterization data for **9** follow: green solid. Yield: 2.02 g, 84%.^{1}H NMR δ: 7.03 (d, 2H, N*m*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.89 (t, 1H, N*p*-Ph, $^{3}J_{H-H} = 7$ Hz), 4.10 (sep, 2H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz) 1.41 (d, 12H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz), 1.04 (d, 27H, *t*Bu, $^{3}J_{P-H} = 14$ Hz). ^{31}P NMR δ: 62.4 ($\Delta\nu_{1/2} = 732$ Hz). ^{13}C NMR δ: 143.7, 126.0, 122.7, 45.6 (*t*Bu, d, $^{1}J_{P-C} = 41$ Hz), 29.6, 29.3, 24.5. ν_{N-P}: 1115 cm^{-1}.

VMe$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*t*Bu$_3$) (10), VPh$_2$(NPh)(NP*t*Bu$_3$) (11), VPh$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*i*Pr$_3$) (12), and VPh$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*t*Bu$_3$) (13). Alkylation and arylation reactions were performed in a similar manner using MeLi or PhMgBr and the appropriate vanadium dichloride precursor; thus, only one preparation is detailed. A solution of MeLi (0.46 mmol) in Et$_2$O was added at RT to a green solution of **8** (0.10 g, 0.18 mmol) in 30 mL of C$_6$H$_6$. The resulting red solution was stirred for 1 h. The solvent was removed in vacuo, and the product was extracted with hexane. The solution was filtered through Hyflo Super Cel, and removal of the hexane in vacuo afforded a red-brown solid. (0.070 g, 76%). Characterization data for **10** follow. Yield: 0.070 g, 76%. ^{1}H NMR δ: 7.19 (d, 2H, N*m*-Ph, $^{3}J_{H-H} = 8$ Hz), 6.99 (t, 1H, N*p*-Ph, $^{3}J_{H-H} = 8$ Hz), 4.22 (sep, 2H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz), 1.46 (d, 12H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz), 1.39 (s, 6H, CH$_3$), 1.08 (d, 27H, t-Bu, $^{3}J_{P-H} = 14$ Hz). ^{31}P NMR δ: 46.4 ($\Delta\nu_{1/2} = 931$ Hz). ^{13}C NMR δ: 142.4, 128.3, 122.9, 122.5, 41.3 (d, *t*Bu, $^{1}J_{P-C} = 45$ Hz), 29.6, 29.2, 24.4. Characterization data for **11** follow: red solid. Yield: 0.028 g, 48%.^{1}H NMR δ: 8.57 (d, 4H, V*o*-Ph, $^{3}J_{H-H} = 7$ Hz), 7.44 (d, 2H, N*o*-Ph, $^{3}J_{H-H} = 8$ Hz), 7.18 (m, 8H, V*m*-Ph, V*p*-Ph, N*m*-Ph), 6.87 (t, 1H, N*p*-Ph, $^{3}J_{H-H} = 7$ Hz), 1.09 (d, 27H, *t*Bu, $^{3}J_{P-H} = 13$ Hz). ^{31}P NMR δ: 52.7 ($\Delta\nu_{1/2} = 1192$ Hz). ^{13}C NMR δ: 136.1, 129.0, 127.0, 124.0, 122.4, 40.3 (d, *t*Bu, $^{1}J_{P-C} = 43.5$ Hz), 29.3. Characterization data for **12** follow: red solid. Yield: 0.021 g, 36%. ^{1}H NMR δ: 8.34 (d, 4H, V*o*-Ph, $^{3}J_{H-H} = 7$ Hz), 7.45 (d, 2H, N*m*-Ph, $^{3}J_{H-H} = 7$ Hz), 7.16 (m, 6H, V*m*-Ph, V*p*-Ph), 6.98 (t, 1H, N*p*-Ph, $^{3}J_{H-H} = 7$ Hz), 4.46 (sep, 2H, CHMe$_2$, $^{3}J_{H-H} = 6.24$ Hz), 1.73 (d(sep), 3H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz, $^{2}J_{P-H} = 11$ Hz), 1.28 (d, 12H, CHMe$_2$, $^{3}J_{H-H} = 7$ Hz), 0.86 (dd, 18H, CHMe$_2$, $^{3}J_{P-H} = 15$ Hz). ^{31}P NMR δ: 40.5 ($\Delta\nu_{1/2} = 668$ Hz). ^{13}C NMR δ: 143.7, 135.9, 127.0, 123.7, 122.7, 28.3, 25.8 (d, CHMe$_2$, $^{1}J_{P-C} = 56.8$ Hz), 24.7, 16.8. Characterization data for **13** follow: red solid. Yield: 0.025 g, 44%. Crystals grew from hexane at −30 °C. ^{1}H NMR δ: 8.32 (d, 4H, V*o*-Ph $^{3}J_{H-H} = 7$ Hz), 7.22 (d, 4H, N*m*-Ph

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$^3J_{\mathrm{H-H}} = 7$ Hz), 7.20 (t, 2H, V*p*-Ph $^3J_{\mathrm{H-H}} = 5$ Hz), 7.10 (d, 2H, V*m*-Ph, $^3J_{\mathrm{H-H}} = 6$ Hz), 6.98 (t, 1H, N*p*-Ph, $^3J_{\mathrm{H-H}} = 8$ Hz), 4.41 (sep, 2H, $CHMe_2$, $^3J_{\mathrm{H-H}} = 7$ Hz), 1.29 (d, 12H, $CHMe_2$, $^3J_{\mathrm{H-H}} = 7$ Hz), 1.13 (d, 27H, *t*Bu, $^3J_{\mathrm{P-H}} = 13$ Hz). ^{31}P NMR δ: 51.6 ($\Delta\nu_{1/2} = 777$ Hz). ^{13}C NMR δ: 135.4, 126.9, 123.4, 122.5, 29.4, 28.2, 24.8.

Synthesis of $VCl(N(SiMe_3)_2)(NPh)(NPtBu_3)$ (14). A solution of $Li[N(SiMe_3)_2]$ (0.018 g, 0.11 mmol) in THF was added to a cold (−30 °C) green solution of **6** (0.035 g, 0.075 mmol) in toluene. The resulting red solution was stirred for 5 min. The solvent was removed in vacuo, and the product was redissolved in benzene and filtered through Hyflo Super Cel. The removal of benzene afforded a red-brown oil (0.020 g, 49%). ^{1}H NMR (500 MHz, C_6D_6) δ: 7.40 (d, 2H, N*o*-Ph, $^3J_{\mathrm{H-H}} = 8$ Hz), 7.04 (t, 2H, N*m*-Ph, $^3J_{\mathrm{H-H}} = 8$ Hz), 6.76 (t, 1H, N*p*-Ph, $^3J_{\mathrm{H-H}} = 8$ Hz), 1.16 (d, 27H, CMe_2, $^3J_{\mathrm{P-H}} = 13$ Hz), 0.66 (s,18H, $SiMe_3$). ^{31}P NMR δ: 52.3 ($\Delta\nu_{1/2} = 727$ Hz). ^{13}C NMR δ: 128.3, 123.9, 123.7, 41.3 (d, *t*Bu, $^1J_{\mathrm{P-C}} = 45$ Hz), 29.7, 6.1.

Synthesis of $V(SBn)_2(NC_6H_3\text{-}2,6\text{-}iPr_2)(NPtBu_3)$ (15). A 5 mL toluene solution of $VCl_2(NC_6H_3\text{-}2,6\text{-}iPr_2)(NPtBu_3)$ (0.050 g, 0.091 mmol) was added to a 5 mL solution of Li[SBn] (0.027 g, 0.207 mmol) in toluene. The solution turned bright red upon stirring. The solution was stirred for 30 min and filtered through Hyflo Super Cel. The toluene was removed in vacuo, and the resulting red oil was washed with (3 × 5 mL) hexane. The solid was dried in vacuo, and a red solid was collected. Characterization data for **15** follow. Yield: 0.026 g, 40%. ^{1}H NMR δ: 7.53 (d, 4H, V*o*-SCH_2Ph $^3J_{\mathrm{H-H}} = 7$ Hz), 7.15 (m, 4H. N*m*-C_6H_3, V*p*-SCH_2Ph), 7.00 (m, 4H, V*m*-SCH_2Ph), 6.97 (t, 1H, N*p*-C_6H_3, $^3J_{\mathrm{H-H}} = 7$ Hz), 5.17, 5.05 (ABq, 4H, SCH_2Ph, $^3J_{\mathrm{H-H}} = 13$ Hz), 4.43 (sep, 2H, $CHMe_2$, $^3J_{\mathrm{H-H}} = 7$ Hz), 1.46 (d, 12H, $CHMe_2$, $^3J_{\mathrm{H-H}} = 7$ Hz), 1.09 (d, 27H, *t*Bu, $^3J_{\mathrm{P-H}} = 14$ Hz). ^{31}P NMR δ: 54.3 ($\Delta\nu_{1/2} = 511$ Hz). ^{13}C NMR δ: 143.9, 143.1, 129.5, 128.9, 127.1, 124.6, 122.8, 41.8, 41.5 (d, *t*Bu, $^1J_{\mathrm{P-C}} = 31.5$ Hz), 29.7, 29.0, 25.0.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5° < 2θ < 45−50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a Pentium computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[23] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Crystal structure data are provided in Table 1. Additional details are provided in the Supporting Information.

Table 1. Crystallographic Data[a]

	1	**5**	**13**
formula	$C_{60}H_{50}Cl_2N(4)P_3V$	$C_{15}H_{26}Cl_2N_2PV$	$C_{36}H_{54}N_2PV$
fw	1041.79	387.19	596.72
a (Å)	13.646(6)	29.0233(5)	12.220(3)
b (Å)	13.646(6)	8.7868(2)	13.049(6)
c (Å)	47.73(3)	15.51160(10)	13.108(5)
α (deg)	90	90	88.73(3)
β (deg)	90	93.9520(10)	73.30(3)
γ (deg)	120	90	63.48(3)
cryst syst	trigonal	monoclinic	triclinic
V (Å^3)	7697(7)	3946.39(12)	1777.6(12)
space group	$R\bar{3}$	Cc	$P\bar{1}$
d (calcd) g cm^{-1}	1.348	1.303	1.115
Z	6	8	2
abs coeff, μ, mm^{-1}	0.435	0.850	0.348
data collected	11106	9748	2935
data $F_o^2 > 3\sigma(F_o^2)$	2441	5453	2935
variables	200	415	361
R	0.0365	0.0510	0.0797
R_w	0.0974	0.1311	0.1722
GOF	0.994	0.869	1.120

[a] All data were collected at 25° C and with Mo radiation $\lambda = 0.71073$ Å.

Results and Discussion

By analogy to the corresponding titanium chemistry,[3,4,24−26] one might expect that the synthesis of vanadium(V)−phosphinimide complexes would be straightforward. This is not the case. Our initial trials to obtain vanadium(V)−phosphinimide complexes from the reaction of $VOCl_3$ with Me_3SiNPR_3 or $Li[NPR_3]$ led to unresolvable mixtures of species. In repeating the known reaction of $Ph_3PNSiMe_3$ with $VOCl_3$,[5] we obtained multiple products; however, we did isolate a few crystals of the known species formulated as $VCl_2(NPPh_3)_3$ (**1**).[10] While this species was previously proposed to be neutral and have a trigonal bipyramidal geometry about the metal center,[10] X-ray crystallographic data revealed that **1** is in fact the salt $[VCl(NPPh_3)_3]Cl$ (Figure 1). The geometry about vanadium is pseudotetrahedral with N−V−Cl and N−V−N angles of 108.30(11)° and 110.62(10)°, and V−N, V−Cl, and N−P distances of 1.740(3), 2.263(3), and 1.606(3) Å, respectively. The closest approach between the Cl anion and the vanadium center is

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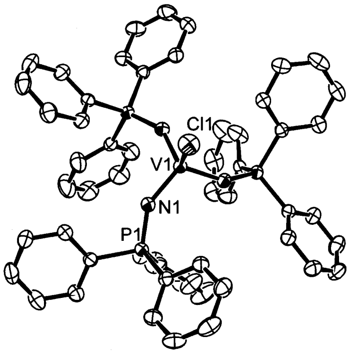

Figure 1. ORTEP drawing of the cation of **1**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances (Å) angles (deg): V(1)−N(1) 1.740(3), V(1)−Cl(1) 2.263(3), P(1)−N(1) 1.606(3), N(1)−V(1)−N(1)′ 110.62(10), N(1)−V(1)−Cl(1) 108.30(11), P(1)−N(1)−V(1) 147.6(2).

8.476 Å. The V−N and N−P bond distances are comparable to those reported for the related salt [V(NPPh$_3$)$_4$]Cl (V−N, 1.769(6) Å; N−P, 1.578(5) Å).[10] The shorter V−N bond and longer N−P bond length in **1** are consistent with the presence of the less electron donating and sterically less demanding Cl. The V−N−P angle in **1** is 147.6(2)°, which is similar to three of the V−N−P angles in [V(NPPh$_3$)$_4$]Cl (141.0(3)°, 146.2(3)°, and 145.8(3)°) but significantly smaller than the fourth V−N−P angle in [V(NPPh$_3$)$_4$]Cl (177.0(3)°). The approximate linearity of the latter V−N−P angle in [V(NPPh$_3$)$_4$]Cl was attributed to crystal packing forces.[10]

The development of facile routes to V(V)−imide complexes[20,27,28] has facilitated the expansion of organometallic chemistry of vanadium(V) complexes.[21,29−65] Reactions of the vanadium−imide-based precursors, VCl$_3$(NAr) (Ar = Ph, C$_6$H$_3$-2,6-*i*Pr$_2$), with R$_3$PNSiMe$_3$ (R = Ph, *i*Pr, *t*Bu) resulted in the straightforward syntheses of VCl$_2$(NPh)(NPPh$_3$) (**4**), VCl$_2$(NPh)(NP*i*Pr$_3$) (**5**), VCl$_2$(NPh)(NP*t*Bu$_3$) (**6**), VCl$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NPPh$_3$) (**7**), VCl$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*i*Pr$_3$) (**8**), and VCl$_2$(NC$_6$H$_3$-2,6-*i*Pr$_2$)(NP*t*Bu$_3$) (**9**), in relatively good yields ranging from 72% to 84%. In the ^{31}P{^{1}H} NMR spectra, all of these compounds exhibited a typically broad flat-top resonance with line-widths at half-height ($\Delta\nu_{1/2}$) that varied from 532 to 732 Hz. Broad signals have also been observed for complexes with a V−P two bond separation, such as V(NPPh$_3$)Cl$_4$.[10] The breadth of the peaks arises from coupling of the ^{31}P nuclei ($I = {}^1/_2$) to the quadrupolar ^{51}V center ($I = {}^7/_2$). In compounds with higher symmetry, such as ([V(NPPh$_3$)$_4$]Cl, the V−P two bond coupling has been resolved.[10,66]

Compound **5** was also crystallographically characterized, revealing an unusual disordering of the molecule in the solid state. There are 2 molecules in the asymmetric unit with two phosphinimide ligands, and with the chlorides and aryl rings of the imide group adopting ordered positions. However, the N(imide) atoms and V atoms are disordered on either side (*para*) of one and in the *meta* positions of the second aryl ring (Figure 2). While a satisfactory crystallographic model of the molecule confirmed the connectivity, a discussion of the metric parameters is not appropriate.

Alkylation of **9** using MeLi and arylation of **6**, **8**, and **9** employing PhMgBr afforded the compounds VMe$_2$(NC$_6$H$_3$-

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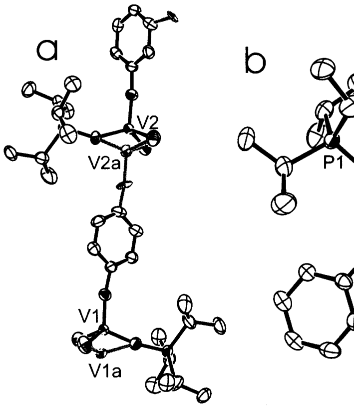
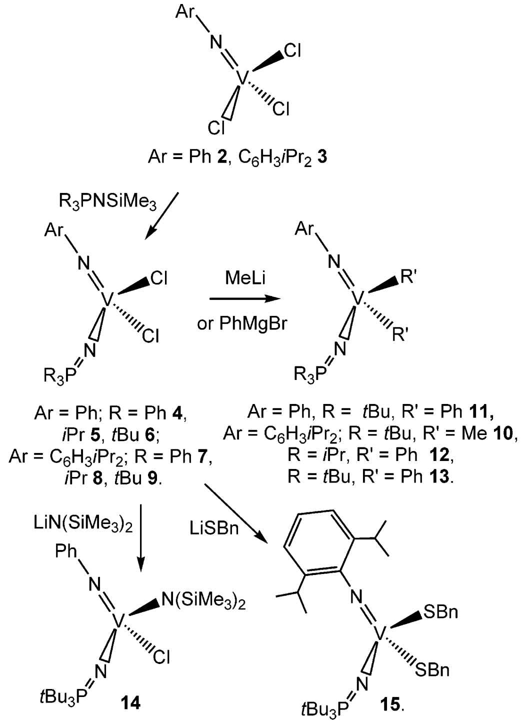


Figure 2. (a) ORTEP drawing of **5** revealing the disorder of the VN atoms. One of the two disordered VN positions shown in gray. (b) ORTEP drawing of one of the molecules of **5** in the asymmetric unit, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity.

Scheme 1



2,6-iPr$_2$)(NPtBu$_3$) (**10**), VPh$_2$(NPh)(NPtBu$_3$) (**11**), VPh$_2$(NC$_6$H$_3$-2,6-iPr$_2$)(NPiPr$_3$) (**12**), and VPh$_2$(NC$_6$H$_3$-2,6-iPr$_2$)(NPtBu$_3$) (**13**), respectively, in acceptable yields ranging from 36% to 76% (Scheme 1). Spectroscopic data were consistent with these formulations. A crystallographic study of **13** confirmed the pseudotetrahedral geometry (Figure 3). The aryl ligands in **13** give rise to V−C distances that average 2.061(10) Å, while the C−V−C angle was found to be 109.5(4)°. The V−N(phosphinimide) bond distance in **13** (1.741(7) Å) is longer than the V−N(imide) bond length of 1.674(7) Å, consistent with multiple bond character in both cases. The V−N(phosphinimide) bond length is markedly longer than that previously reported for VCl$_4$(NPMePh$_2$)(NCMe) (1.655(3) Å)[11] but is comparable to the bond distances previously reported for VOCl$_2$(NPPh$_2$(NS(O)Me$_2$)) (1.716(3) Å)[6] and VOF$_2$(NPPh$_3$) (1.727(4) Å)[7] and to those seen in **1**. These data infer the presence of strong π-donor ligands (oxo, imido, phosphinimido) within the same molecule weaken the V−N(phosphinimide) bond, and increase the net electron density at nitrogen resulting in a shorter N−P bond. This view is consistent with the results of a recently published computational study.[67]

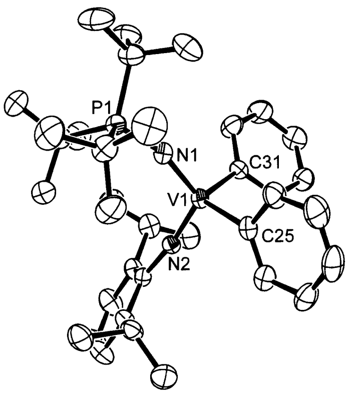


Figure 3. ORTEP drawing of **13**, with 30% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Distances (Å) angles (deg): V(1)−N(2) 1.674(7), V(1)−N(1) 1.741(7), V(1)−C(25) 2.054(8), V(1)−C(31) 2.068(10), P(1)−N(1) 1.589(7), N(2)−C(13) 1.400(10), N(2)−V(1)−N(1) 116.8(3), N(2)−V(1)−C(25) 106.7(4), N(1)−V(1)−C(25) 109.5(3), N(2)−V(1)−C(31) 103.6(3), N(1)−V(1)−C(31) 110.5(4), C(25)−V(1)−C(31) 109.5(4), P(1)−N(1)−V(1) 162.5(5), C(13)−N(2)−V(1) 171.1(7).

Employing **6**, substitution for one of the chloride ligands with an amide ligand was achieved, yielding VCl(N(SiMe$_3$)$_2$)(NPh)(NPtBu$_3$) (**14**) as a red-brown oil in 49% yield. Further amido-substitution could not be achieved presumably due to steric issues. However, the disubstitution reaction involving **9** and Li[SBn] was performed, affording the red, oily product V(SBn)$_2$(NC$_6$H$_3$-2,6-iPr$_2$)(NPtBu$_3$) (**15**) in 40% yield. (Scheme 1). Although these compounds could not be obtained in a crystalline form, the spectroscopic data were consistent with these formulations.

In conclusion, we have found that reactions using commercially available vanadium(V) starting materials did not afford clean routes to vanadium−phosphinimide derivatives. However, the use of V−imide precursors afforded a series of vanadium−imide−phosphinimide derivatives which could be isolated and derivatized. Crystallographic data for **1** and **13** infer V−N(phosphinimide) multiple bond character. However, the presence of strong π-donors such as an imide ligand weakens the V−N(phosphinimide) bond, concurrent shortening of the N−P bond. These data are consistent with the polarized nature of the P−N bond of the phosphinimide ligand.

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Supporting Information Available: Crystallographic data in CIF format and ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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