A Contiguous Tricyclic $[P_6]^{2-}$ Framework Spanning Across Two Vanadium(III) Centers.

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ABSTRACT: Complex $[(BDI)VCl(N\{SiMe_3\}_2)]$ (**1**) (BDI^- = $[ArNC(CH_3)]_2CH$, Ar = 2,6-${}^iPr_2C_6H_3$), a precursor readily prepared from metathesis of $[(BDI)VCl_2]$ and $Na[N\{SiMe_3\}_2]$, can be reduced with Na/NaCl in the presence of white P_4 to form a dinuclear species containing two V^{III} centers bridged by a tricyclic $[P_6]^{2-}$ scaffold, namely $[(BDI)V(N\{SiMe_3\}_2)]_2(\mu\text{-}\eta^1:\eta^1\text{-}P_6)$ (**2**). Coordination of the $[P_6]^{2-}$ involves a unique chair-like $\mu\text{-}\eta^1:\eta^1$ binding mode with a contiguous tricyclic hexa-phosphorus unit bridging across the two V centers. Complexes **1** and **2** have been structurally characterized and the pathway towards the formation of the chair-like tricyclic $[P_6]^{2-}$ scaffold in **2** is proposed.

Structural archetypes of P_6 are known to bridge across two metal ions and such catenated scaffolds offer a variety of coordination modes depending on the metal framework. Examples of bridging $L_nM(P_6)ML_n$ involve the more common planar geometry with a $\mu\text{-}\eta^6:\eta^6$ bonding mode (Figure 1A),[1] as well as chair-like $\mu\text{-}\eta^3:\eta^3$ (Figure 1B),[2] bicyclic $\mu\text{-}\eta^3:\eta^3$ (Figure 1C),[3] $\mu\text{-}\eta^2:\eta^2$ (Figure 1D),[4] and a $\mu\text{-}\eta^2:\eta^2$ mode which is best represented as two P−P coupled triphosphirenes reduced each by a powerful Nb^{III} π-base[5] or the dianionic P−P bridged $\mu\text{-}\eta^2:\eta^2$ complex in the case of Al^{III} (Figure 1E).[6] By using a sterically protected vanadium center we now report a new bonding mode of P_6, which involves a unique $\mu\text{-}\eta^1:\eta^1$ arrangement having three contiguous phosphorus rings bridging across the two V^{III} centers in a chair-like fashion (Figure 1F). We propose this unusual scaffold to form via [2+2]-cycloaddition of two V^{III}-phosphirenes where sterics discourage the formation of the well-established *cyclo*-P_3 ligand.[7, 8]

Not long ago we reported the synthesis and spectroscopic studies of *cyclo*-P_3 complexes of V^V.[7] The *cyclo*-P_3 unit can be assembled via the reaction of V^{II} synthons such as $[(BDI)V(\eta^3\text{-}Ntolyl_2)]$ (BDI^- = $[ArNC(CH_3)]_2CH$, Ar = 2,6-${}^iPr_2C_6H_3$; tolyl = 4-MeC_6H_4)[9] and $[(BDI)V(OAr)]_2(\mu_2\text{-}\eta^1:\eta^1\text{-}N_2)$[10] or a bonafide three-coordinate V^{II} complex $[(BDI)V(OAr)]$ with white phosphorus (P_4).[10] More conveniently, the *cyclo*-P_3 framework can be integrated, in one step, via 1e^- reduction of the V^{III} halide precursors $[(BDI)VCl(Ntolyl_2)]$ and $[(BDI)VCl(OAr)]$ in the presence of P_4.[7] Activation of P_4 is quite a complex reaction with various mechanistic scenarios,[11] and it has been shown that steric congestion[12, 13] is a critical factor that can change the outcome of the reaction. For instance, reducing sterics can disfavor isolation of a terminal M≡P ligand and push the reaction to form either a bridging M=P=M or M(*cyclo*-P_3) as shown in the mechanistic studies by Cummins, Rybak-Akimova, Hoff and co-workers.[13] As such, we reasoned that more steric crowding of a low-valent V^{II} ion would discourage the formation of the V(*cyclo*-P_3) ligand framework.

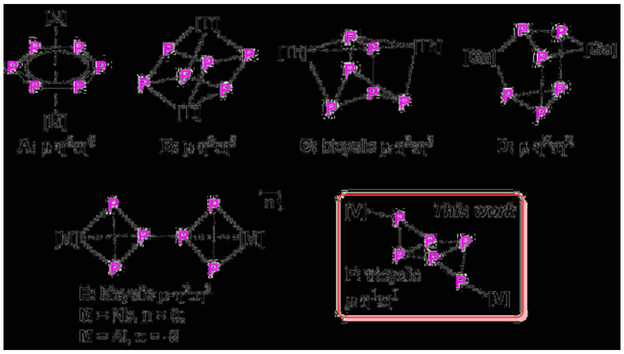


Figure 1. Examples of *cyclo*-P_6 ligands bridging two transition metals (**A-C, E**) and main group metals (**E** and **D**) including the work reported here. **A**: [M] = η^5 substituted cyclopentadienyls of V, Nb, Mo, W; **B**: [Ti] = Cp*Ti; **C**: [Th] = Th(η^5-1,3-${}^tBu_2C_5H_3$); **D**: [Ga] = LGa (L = Dipp(4-(Dipp-imino)pent-2-en-2-yl)amide; Dipp: 2,6-diisopropylphenyl) **E**: [M] = $Nb(OSi^tBu_3)_3$ and [M] = $[K\{Al(SiN^{Dipp})\}]_2$ (SiN^{Dipp}=$\{CH_2SiMe_2NDipp\}_2$); **F**: [V] = $V(BDI)(N\{SiMe_3\}_2)$.

Given that ligands such as $^-Ntolyl_2$ and ^-OAr are known to favor *cyclo*-P_3 formation in a V^{II} ion,[7] we resorted to using the ubiquitous but more sterically encumbering $[N\{SiMe_3\}_2]^-$ ligand with this ion and explored its chemistry with P_4.

Accordingly, treatment of $[(BDI)VCl_2]$[14] with one equiv of $NaN\{SiMe_3\}_2$ in toluene resulted in a color change to dark green over a period of 16 h at room temperature. Separation of the salt followed by crystallization of a concentrated pentane solution cooled to -35 °C afforded green colored crystals of the V^{III} precursor $[(BDI)VCl(N\{SiMe_3\}_2)]$ (**1**) in 64% yield (Scheme 1). Complex **1** is paramagnetic based on the broad resonances spread over 77 to -0.5 ppm[15] and a solution state magnetic susceptibility study is consistent with a V^{III} ion (S = 1) system having two unpaired electrons (μ_{eff} = 2.65 μ_B, 25 °C, C_6D_6). The electronic absorption spectrum of **1** (0.056 mM in THF) displays intense charge transfer bands at 332 nm (ε = 14804 M^{-1} cm^{-1}), 314 (ε = 15732 M^{-1} cm^{-1}), and 268 nm (ε= 14679 M^{-1} cm^{-1}), as well as a very intense LMCT transition at 234 nm (ε = 16804 M^{-1} cm^{-1}) (Figure S5). To conclusively establish the connectivity and geometry of **1**, an X-ray diffraction study of a single crystal (*sc*XRD) was undertaken. Figure 2 shows the molecular structure of **1** revealing the V^{III} center to have a pseudo tetrahedral geometry (τ_4 = 0.87 and τ_δ = 0.80).[16] Similar to other four-coordinate V^{III} systems,[9, 10, 14, 17] the V center in **1** is out of the NCCCN plane to minimize steric congestion around the coordination sphere, and the V−N_{amide} bond distance of 1.931(1) Å is shorter than the V−N_{BDI} bond distances of 1.995(1) Å and 1.991(1) Å. Furthermore, the two -$SiMe_3$ substituents on the amide ligand are oriented perpendicular to the NCCN plane to avoid steric repulsion between the isopropyl and trimethylsilyl substituents.

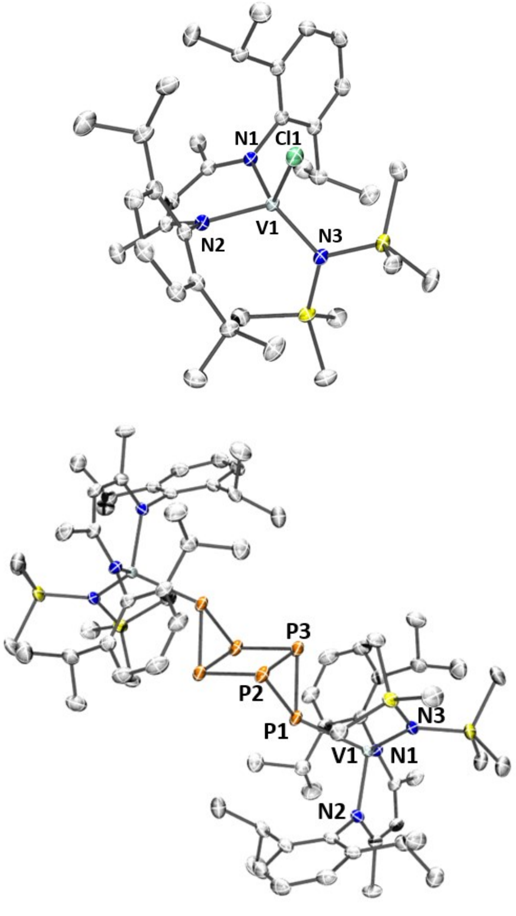
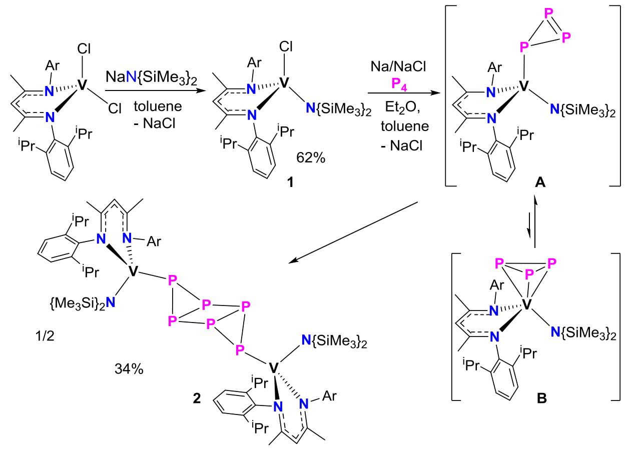


Figure 2. Molecular structures of **1** (top) and **2** (bottom). Thermal ellipsoids are at 50% probability. H-atoms are omitted for clarity.

Having prepared **1**, we then followed a similar protocol to how the previous V^{III} halide precursors were reduced in the presence of P_4. Treatment of **1** with Na/NaCl in Et_2O/toluene in the presence of P_4 at room temperature caused a gradual change in color from dark green to brown. Workup of the reaction mixture and crystallization of the residue from pentane/THF resulted in the formation of $[(BDI)V(N\{SiMe_3\}_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}P_6)$ (**2**) as brown colored crystals in 34% yield. Unlike the known *cyclo*-P_3 complexes of vanadium,[7, 9] complex **2** shows decreased solubility in non-polar solvents. A solid state single crystal XRD (*sc*XRD) study allowed us to identify this species to be the dinuclear $V_2^{III,III}$ system bridged by a P_6 unit, namely $[(BDI)V(N\{SiMe_3\}_2)]_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}P_6)$ (**2**) (Scheme 1 and Figure 2). Although various bridging modes for P_6 are known (*vide supra*, Figure 1), the structure of **2** does offer quite a few surprises. The most salient feature is the geometry of the P_6 framework, which has a chair-like conformation resulting from the fusion of 3-4-3 P-based rings to give the tricyclo[3.1.0.0^{2,4}]hexaphosphane bridging motif. Such a tricyclic framework bridges each V^{III} center via binding through one of the P-atoms. Since complex **2** crystallizes in $P2_1/n$ space group, an inversion center at the centroid of the P_4 ring symmetrically relates the two halves, specifically the fragments $[(BDI)V(N\{SiMe_3\}_2)(\eta^1\text{-}P_3)]$ (**A**, Scheme 1) and a mirror plane perpendicular to the P_4 ring and passing through each of the V atoms, relates each half of the molecule within **A**. Each P-atom about the P_6 ligand is pyramidalized, with P1−P2 and P1−P3 bond distances being 2.1850(7) and 2.1740(7) Å in accord with single bonds, and P2−P3' and P2−P3 bond distances of 2.2612(7) and 2.2348(8) Å being slightly longer than a P−P single bond.[18] The P_4 square in complex **2** with PPP bond angles of 91.7(3)° and the cyclic P_3 rings with PPP bond angles of 60.3(2)° are linked by a slightly obtuse angle of 94.99(3)°. The V−P distance of 2.4391(6) Å is also in agreement with V^{III} phosphido-like given the similarity to distances found in the four-coordinate V^{III} $[(BDI)V(PHTrip)_2]$ (Trip = 2,4,6-$^iPr_3C_6H_2$; V−$P_{phosphide}$ = 2.383(6) and 2.443(5) Å)[19] and other vanadium-phosphido and μ^2-phosphinidene complexes.[20] The geometry of the four-coordinate V^{III} ion (τ_4 = 0.82 and τ_δ = 0.80)[16] is quite similar to that of precursor **1** and implies an overall similar electronic structure of the d^2-metal ion. These features are also corroborated by the similar electronic absorption spectrum of **2** (0.013 mM in THF) at 372 nm (ε = 44531 M^{-1} cm^{-1}), 358 nm (ε = 49077 M^{-1} cm^{-1}), 272 (ε = 51000



Scheme 1. Synthesis of complex **1** and subsequent reduction in the presence of P_4 to form the P_6 bridged dimer **2**. Two likely proposed intermediates are shown *enroute* to **2**.

M^{-1} cm^{-1}), and 228 nm (ε = 76462 M^{-1} cm^{-1}) (Figure S6). As a result, complex **2** is paramagnetic and a solution-state Evans shows a μ_{eff} = 3.60 μ_B (25 °C, C_6D_6) in accord with a high-spin and dinuclear $V_2^{III,III}$.

The formation of complex **2** is not only structurally unique but also interesting in how the tricyclic ring forms and binds. Following reduction of **1** to divalent [(BDI)V(N{$SiMe_3$}$_2$)],[15] P_4 is then reductively converted to what we speculate to be the phosphirene intermediate **A** (Scheme 1). This reaction in and of itself is quite intriguing and complex since it likely operates via a bimolecular pathway akin to what was originally proposed by Cummins, Rybak-Akimova, and Hoff based on a combination of thermochemical, kinetic, and quantum chemical studies using P_4 and [Mo(N[^{t}Bu]Ar')$_3$] (Ar' = 3,5-$Me_2C_6H_3$).[13] However, the steric nature of the [N{$SiMe_3$}$_2$]$^-$ in **1** most likely discourages further reduction of the P=P motif in **A** to furnish a more thermodynamically stable *cyclo*-P_3 complex [(BDI)V(N{$SiMe_3$}$_2$))(*cyclo*-P_3)] (**B**). We hypothesize that the V^{III} is not a powerful π-base hence discouraging formation of a bicyclic scaffold like the one described in Figure 1E. Likewise, formation of a putative phosphido [(BDI)V(P)(N{$SiMe_3$}$_2$)] with extrusion of P_2 would not be as thermodynamically favored, so the system instead chooses to undergo [2+2]-cycloaddition chemistry involving the reactive P=P bonds to furnish the tricyclic $[P_6]^{2-}$ framework in **2**. Examples of such dimerization of phosphirene fragments have been reported in the literature.[21]

In conclusion, we have shown how steric tuning of a monoanionic ligand in a species such as [(BDI)V(L)] (L^- = Ntolyl$_2$, OAr, N{$SiMe_3$}$_2$) discourages the formation of the *cyclo*-P_3 ligand when L is the bulkier [N{$SiMe_3$}$_2$]$^-$ ligand. This feature also hints to the reactive nature of P=P bonds and the weaker π-basicity of V^{III} thus allowing us to isolate a new archetype of P_6.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, NMR and UV-vis spectroscopies. This material is available free of charge via the Internet at http://pubs.acs.org.

Accession codes

CCDC structures 2225084 and 2225085 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic DataCentre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

HMDS: $^-$N{$SiMe_3$}$_2$, ^{i}Pr: *iso*-propyl, Cp*: pentamethylcyclopentadienyl, Me: methyl, BDI^- = [ArNC(CH_3)]$_2$CH, Ar = 2,6-^{i}Pr$_2C_6H_3$

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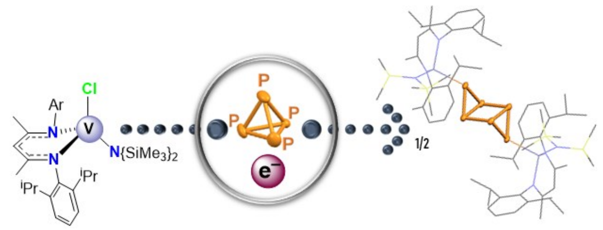
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