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Synthesis and Structural Characterization of the First Thermally Stable, Neutral, and Electrophilic Phosphinidene Complexes of Vanadium

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ABSTRACT: The first thermally stable, neutral, electrophilic phosphinidene complexes of vanadium, \([\text{CpV} (\text{CO})_3\{\eta^2-P-\text{(NR)}_2\}]\) \((R = \text{Pr} (3a), \text{Cy} (3b))\), have been prepared by the reaction of \([\text{Na}_2\{\text{CpV} (\text{CO})_3\}]\) with \(\text{Cl}_2\text{PNR}_2\). The molecules 3a and 3b have been characterized by microanalysis, IR, and \(^1H\) and \(^31P\) NMR spectroscopy, and for 3a also by single-crystal X-ray diffraction. The structure of 3a exhibits an piano stool geometry closely related to that of \([\text{CpV} (\text{CO})_3\{\eta^2-\text{PM}_{\text{Pr}}\}]\) with an \(\eta^2\)-phosphinidene ligand replacing CO in one of the basal coordination sites of the vanadium atom \((V(1) - P(1) = 2.300(2)\ \text{Å})\). The reactivity of 3a toward a variety of unsaturated substrates: \(\text{PhC} = \text{CPh}, \text{di}-\text{Bu-imidazol-2-ydene}, \text{PhN}_2, \text{and Ph}_{\text{2}}\text{C} = \text{N} = \text{N}\) has been examined to probe the electrophilic (or nucleophilic) character of the low-coordinate P(1) site. In all cases reactions occur exclusively at the phosphinidene phosphorus atom, without CO displacement, a \(\eta^2\)-\text{PNR} complex. The \(\eta^2\)-phosphinidene complexes 12 and 14 lose carbon monoxide to yield derivatives \([\text{CpV} (\text{CO})_3\{\text{P}(\text{NPr})_2\} \text{N} = \text{N} = \text{CPh}_2]\) \((9)\) and \([\text{CpV} (\text{CO})_3\{\text{P}(\text{NPr})_2\text{N}]}\) \((15)\), which contain \(\eta^2\)-\(\text{PN}(\text{N})\)-coordinated phosphainine ligands. An \(\eta^2\)-\(\text{P(NN)}\)-bound phosphainine ligand is present in an isomer of 9, namely, \([\text{CpV} (\text{CO})_3\{\text{P}(\text{NPr})_2\} \text{N} = \text{N} = \text{CPh}_2]\), 13. Complexes 3a, 7, 8, 9, 14, and 15 have been characterized by X-ray crystallography.

INTRODUCTION

Although stable, terminal phosphinidene (phosphanediyl) complexes have been known for less than two decades, the chemistry of this fascinating class of molecules has undergone rapid development in recent years for several substantive reasons: (i) Phosphinidene \((R = P)\) ligands are the heavier congeners of imides \((R = C)\), and are also isolobal with carbenes \((R = 2\text{C})\). Transition metal–phosphinidene complexes are therefore analogous to better known metal–carbenes and imides. In fact, both nucleophilic phosphinidene complexes, \(^4\text{–}20\) with an \(M = P\) double bond formally derived from the combination of triplet RP with a triplet ground state metal fragment, and electrophilic complexes \(^21\text{–}26\) containing essentially \(M = P\) single bonds resulting from singlet RP-singlet metalloic moieties are now well known. The chemistry of these two classes of molecules is now being intensively explored.\(^4\text{–}21\text{,}22\text{,}27\text{–}29\) (ii) The presence and nature of metal–main group element multiple bonding \((M = P, M = P)\) in these complexes is of theoretical and reactivity interest.\(^30\) (iii) In terminal \(M = PR\) molecules, the phosphorus atom is in a low oxidation state \((+1)\) and coordination number \((2)\), providing an opportunity to explore fundamentally different chemistry at a \(P(1)\) center.\(^31\) Low-coordinate nonmetals, deficient in electrons, should exhibit high reactivity. (iv) Like metal–carbene complexes, phosphinidene analogues have considerable potential in phosphaorganic synthesis and catalytic chemistry.\(^4\)

Our own interest in terminal phosphinidene complexes was stimulated by a longstanding interest in chemical transformations at bridging, \(\mu\)-PR ligands in clusters\(^32\text{,}33\) and by the discovery in 2001 of a synthetic route to isolable, cationic, terminal phosphinidene complexes of molybdenum and tungsten, \([\text{Cp}^\ast\text{Fe} (\text{CO})_4\{\text{P}(\text{NPr})_2\}]\), involving halide abstraction from \([\text{Cp}^\ast\text{Fe} (\text{CO})_4\{\text{P}(\text{Cl})\text{NPr}_2\}]\) and \([\text{Cp}^\ast\text{Fe} (\text{CO})_4\{\text{P}(\text{Pr})_2\text{N}]}\) \((M = \text{Mo, W})\), involving halide abstraction from \([\text{Cp}^\ast\text{M} (\text{CO})_3\{\text{P}(\text{Cl})\text{NPr}_2\}]\) and \([\text{Cp}^\ast\text{M} (\text{CO})_3\{\text{P}(\text{Pr})_2\text{N}]}\) \((M = \text{Fe, Ru, Os})\), generated in situ, has been elegantly explored by Mathey\(^36\) and co-workers and Lammertsma et al.\(^37\). The Lammertsma group has recently reported the direct observation of the phosphinidene complex \([\text{W} (\text{CO})_5 (\eta^2-\text{PAr})]\) \((\text{Ar = aryl})\) by electrospray ionization tandem mass spectrometry (ESI-MS/MS), and the chemistry displayed by this reactive species matches that observed in solution.\(^38\)

Over the past few years we have isolated a series of cationic, terminal complexes including the remaining member \([\text{Cp}^\ast\text{Cr} (\text{CO})_3\{\text{P}(\text{NPr})_2\}]\) \(^39\) of the Cr, Mo, W triad, the iron group compounds \([\text{Cp}^\ast\text{Fe} (\text{CO})_3\{\text{P}(\text{NPr})_2\}]\) \((M = \text{Fe, Ru, Os})\), the rhenium cation complex \([\text{Cp}^\ast\text{Re} (\text{CO})_3\{\text{P}(\text{NPr})_2\}]\) \((\text{Ar = aryl})\) by electrospray ionization tandem mass spectrometry (ESI-MS/MS), and the chemistry displayed by this reactive species matches that observed in solution.\(^38\)

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The dark brown complexes \([\text{CPV} \{\text{CO} \}_{3}\eta^{1}\text{-P(NR}_{2}\}]\) (R = 'Pr (3a), Cy (3b)) were formed in quantitative yield via the reaction of \([\text{Na}_{2}] \text{CPV} \{\text{CO} \}_{3}\) with \(\text{Cl}_{2}\text{PNR}_{2}\) (Scheme 1). The high solubility of the compounds resulted in isolation of the compounds in 80% and 62% yield, respectively.

The \(^{31}\text{P}\) NMR spectrum (Figure 1) of 3a shows a broad flat-topped resonance centered at \(\delta\) 1100, whereas the \(^{1}\text{H}\) NMR spectrum shows only the expected Cp and 'Pr resonances. The unusual shape of the \(^{31}\text{P}\) resonance is likely due to coupling to \(^{51}\text{V}\) (I = 7/2) and to N. The 'Pr methyl resonances appear as two sharp doublets (\(\delta\) 1.30 and 1.00), suggesting restricted rotation about the P–N bond on the NMR time scale.

The formulation of 3a was confirmed crystallographically, and the structure (Figure 2) features a typical piano-stool geometry, with the PNPR\(_2\) and three CO ligands occupying the base and a Cp ligand in the apical position. The V(1)–P(1) separation (2.3200(2) Å) is only slightly shorter than a typical V–P single bond length (ca. 2.44 Å) and is longer than the V=P separation (2.1602(6) Å) in the nucleophilic phosphinidene complex \([(\text{Nacnac})\text{V} \{\text{CH}_{2}\text{Bu}\} \{\text{PMes}\}^*\}] (\text{Mes}^* = 2,4,6-\text{Bu}_{3}\text{C}_{6}\text{H}_{2})\).\(^{13}\) The V(1)–P(1) separation in 3a agrees remarkably well with the calculated bond distance for \(\text{CPV} \{\text{CO} \}_{3}\eta^{1}\text{-PH}\) (2.307 Å).\(^{30}\) The PNPR\(_2\) fragment is planar and, in conjunction with the short P(1)–N(1) separation (1.6520(6) Å), indicates a substantial \(\pi\)-interaction between P and N. Complexes 3a/3b are the first thermally stable, neutral, electrophilic phosphinidenes to be reported.

In the present work, we set out to synthesize neutral, terminal phosphinidene complexes in an effort to further explore the limits of stability, the molecular and electronic structures, and the reactivity of these compounds. We describe herein the first neutral and electrophilic, terminal phosphinidene complexes of vanadium, \([\text{CPV} \{\text{CO} \}_{3}\eta^{1}\text{-P(NR}_{2}\}]\) (R = 'Pr, Cy), their reactions with a variety of unsaturated ligands, and the nature of the products.

## RESULTS AND DISCUSSION

Theoretical (DFT) studies of terminal phosphinidene complexes have shown that the character (nucleophilic, electrophilic) of the phosphinidene fragment can be influenced by the metal fragment, particularly the donor or acceptor properties of the ligands and the substituents on the phosphorus atom. Strong donors (e.g., Cp*) favor nucleophilicity and \(\pi\)-acid ligands favor electrophilicity at the metal, while \(\pi\)-donor substituents on phosphorus favor electrophilic behavior.
The reaction of phosphinidene complexes toward alkynes is one of the transformations used to determine whether the phosphinidene is electrophilic or nucleophilic. The isoelectronic electrophilic cation \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\eta^1-\text{P}(\text{NPr}_2)\}]\) reacts readily with nucleophiles such as \(\text{PET}_{3}\), initially forming the phosphine-stabilized phosphinidene adduct \([\text{Cp}^*\text{Mo}(\text{CO})_3\{\eta^1-\text{P}(\text{NPr}_2)\}(\text{PET}_{3})]\) \((5)\), which then loses a CO ligand and forms the new phosphinidene complex \([\text{Cp}^*\text{Mo}(\text{CO})_2\{\eta^1-\text{P}(\text{NPr}_2)\}\{\text{PET}_{3}\}]\) \((6)\), where \(\text{PET}_{3}\) migration from the coordinated \(\text{PNP}_2\) fragment to the metal has occurred.\(^{27}\)

The reaction of phosphinidene complexes toward alkynes is one of the transformations used to determine whether the phosphinidene complexes exhibit nucleophilic or electrophilic characteristics: coordinated electrophilic PR fragments undergo \(2+1\) cycloaddition reactions with alkynes to form three-membered-ring-containing phosphinides,\(^{30}\) whereas their nucleophilic analogues undergo \(2+2\) cycloaddition reactions, affording phosphametallacyclobutene complexes.\(^{3}\)

We found that the addition of diphenylacetylene to \(3a\) (Scheme 2), which displays a broad \(31\text{P}\) NMR resonance centered at \(\delta -19\), affords phosphametallacyclobutene complexes.\(^{3}\)

The electrophilicity of \(3a\) has also been demonstrated by the reaction with the singlet carbene di-\(\text{Bu}\)-imidazol-2-ylidine, which results in the quantitative formation of the phosphine-stabilized phosphinidene adduct \([\text{CpV}(\text{CO})_3\{\eta^2-\text{P}(\text{NPr}_2)\}C(\text{Ph})\{\text{C}(\text{Ph})\}]\) \((7)\), which displays a broad \(31\text{P}\) NMR resonance at \(\delta 72\). The \(1\text{H}\) NMR spectrum of \(8\) shows resonances due to the \(\text{Pr}\) and \(\text{Bu}\) groups, in addition to two downfield signals at \(\delta 7.60\) and 7.79. The non-equivalence of the latter two signals suggests that the carbene fragment is bound to the \(\text{PNP}_2\) fragment via \(\alpha\) rather than the normal \(\text{C2}\) position. The formulation was confirmed via X-ray crystallography (Figure 4), and the structure features an NCN-stabilized phosphinidene complex where the “ylidene” moiety of the NCN carbene precursor has migrated from \(\text{C2}\) to \(\text{C4}\); the binding of the carbene to the phosphinidene phosphorus results in a significant lengthening of the \(\text{V}(1)-\text{P}(1)\) separation to 2.455(2) Å (cf. 2.3200(2) Å in \(3a\)); the other bond distances and angles are unremarkable.

The electrophilicity of \(3a\) has also been demonstrated by the reaction with the singlet carbene di-\(\text{Bu}\)-imidazol-2-ylidine, which results in the quantitative formation of the phosphine-stabilized phosphinidene adduct \([\text{CpV}(\text{CO})_3\{\eta^2-\text{P}(\text{NPr}_2)\}C(\text{Ph})\{\text{C}(\text{Ph})\}]\) \((8)\) (Scheme 2), which displays a broad \(31\text{P}\) NMR resonance at \(\delta 72\). The \(1\text{H}\) NMR spectrum of \(8\) shows resonances due to the \(\text{Pr}\) and \(\text{Bu}\) groups, in addition to two downfield signals at \(\delta 7.60\) and 7.79. The non-equivalence of the latter two signals suggests that the carbene fragment is bound to the \(\text{PNP}_2\) fragment via \(\alpha\) rather than the normal \(\text{C2}\) position. The formulation was confirmed via X-ray crystallography (Figure 4), and the structure features an NCN-stabilized phosphinidene complex where the “ylidene” moiety of the NCN carbene precursor has migrated from \(\text{C2}\) to \(\text{C4}\); the binding of the carbene to the phosphinidene phosphorus results in a significant lengthening of both the \(\text{V}(1)-\text{P}(1)\) and \(\text{P}(1)-\text{N}(1)\) bonds (2.5782(8) \& 1.717(2) Å, respectively), and the long \(\text{P}(1)-\text{C}(15)\) bond (1.888(3) Å) indicates that the latter interaction is primarily donor—acceptor in nature.

A related tungsten phosphinidene complex containing a donor bis(aminoc) cyclopropyldiene moiety has been recently reported by the Bértrand group.\(^{31}\) We have recently reported that the reactions of bimetallic \(\mu\)-phosphinidene complexes \([\text{MN}_{2}(\text{CO})_6\{\mu-\text{P}(\text{NPr}_2)\}]\) and \([\text{CO}_2(\text{CO})_3\{\mu-\text{dpmm}\}\{\mu-\text{P}(\text{NPr}_2)\}]\) afford similar abnormal NCN carbene adducts and that the migration of the ylidene moiety appears to be induced by sterically bulky di-\(\text{R}\)-imidazolylidene \(\text{R}\) groups and the metal-bound ligands or the \(\text{NPr}_2\) group bound to phosphorus.\(^{42}\)

We were also interested in the interaction of \(3a\) with other types of reagents that are typically used to introduce carbene fragments into molecules. For example, the addition of \(\text{Ph}_2\text{C}=\text{N}=\text{N}\) to \(3a\) (Scheme 3) results in the formation of the new complex \([\text{CpV}(\text{CO})_3\{\eta^2-\text{P}(\text{NPr}_2\text{NN}=\text{CPh}_2)\}]\) \((9)\), which displays two \(31\text{P}\)
NMR resonances at δ 93 and -10 in a ratio of approximately 1:2.5.

Single crystals of the new complex were readily obtained, and when dissolved in C₆D₆ the ³¹P NMR spectrum showed the above resonances in the same ratio.

The complex crystallizes as a single isomer, and the X-ray structure (Figure 5) indicates that the diphenylazomethane fragment is bound to the phosphinidene group; carboxyl loss has also occurred with the vacant coordination site taken up by one of the P-bound nitrogens. The V(1)–P(1) and V(1)–N(3) separations (2.5247(4) and 1.900(1) Å, respectively) are long single bonds, whereas P(1)–N(1) and P(1)–N(3) are short single bonds (1.677(1) and 1.686(1) Å, respectively). These results contrast observations obtained with related cationic iron and group VI metal containing phosphinidenes, which, upon reaction with diphenylazomethane, form the complexes [CpFe(CO)₂{η¹-P(NiPr₂)dN-CPh₂}]AlCl₄ (10) and [CpM(CO)₃{η¹-P(NPPr₂)NN=CPh₂}]AlCl₃ (M = Cr, Mo, W) (11), which contain η¹- and η³-phosphadiazaallene ligands, respectively.²² We propose that the reaction sequence to form complex 9 proceeds through the unstable complex 12 (Scheme 3), which then undergoes CO loss to form the product. ³¹P NMR spectra recorded early in the reaction show the presence of a compound with a broad resonance appearing at δ 324, which likely corresponds to complex 12, based on the similarity of the chemical shift to related vanadium complexes (vide supra). Complex 11 displays a downfield ³¹P NMR chemical shift (M = W, δ 125; M = Mo, δ 152; M = Cr, δ 195), and, on the basis of the two resonances appearing in the ³¹P NMR spectrum of complex 9, we suggest that the diphenylazaphosphallene ligand undergoes interconversion between the η²(δ¹P) and η³(δ¹P) 95 binding modes (compound 13) rapidly on the NMR time scale.

Organic azides are commonly used to introduce nitrene fragments (RN) into molecules, and on the basis of the results described above it was of interest to examine the reactivity of complex 3 with PhN₃. The low-temperature addition of PhN₃ to 3a results in N₂ loss and oxidation of the P(I) ligand with the formation of the new phosphaimine complex [CpV(CO)₃{η¹-P(NPPr₂)=NPh}] (14) (Scheme 4). Complex 14 displays a...
bred $^{31}$P NMR resonance centered at $\delta$ 333, and the $^1$H NMR spectrum of 14 shows only the expected Cp, Pr, and Ph signals.

The compound has been characterized crystallographically, and the structure (Figure 6) features a planar stoichiometry with a P-coordinated $\eta^3$-$\text{P}_2\text{NP}=\text{NP}$ ligand, which displays a short V(1)–P(1) interaction (2.362(2) Å) and a planar Pr$_2$NP=NPH ligand. P(1)–N(1) 1.646(3) Å, P(1)–N(2) 1.547(3) Å; the short V–P separation may indicate some back-donation into the vacant p-orbital on phosphorus in the complex (cf. V(1)–P(1) 2.3200(2) Å in [CpV(CO)$_3$($\eta^3$-P(NP)$_2$H)] (3a)). The P=N bond length is similar to the analogous separation (1.545(2) Å) in the free phosphaimine (Me$_2$Si)$_2$NP=NSiMe$_3$. Complex 14 contains a rare example of a coordinated $\eta^3$-phosphaimine ligand.

Orange tricarbonyl complex 14 is unstable and readily loses a CO ligand to form the new green complex [CpV(CO)$_2$($\eta^3$-P(NP)$_2$H)] (15). The $^31$P NMR spectrum of 15 shows a sharp resonance at $\delta$ 111, and the $^1$H NMR spectrum shows signals due to the Cp, Pr, and Ph groups. A single crystal of complex 15 was obtained, and the X-ray structure (Figure 7) shows that carbonyl loss has occurred and that the vacant coordination site has been taken up by the Pr$_2$NP=NPH ligand.

The geometry around phosphorus is significantly pyramidalized and closely resembles that found in donor–acceptor adducts such as [Re(CO)$_3$][P(NP)$_2$(PPPh$_3$)]AlCl$_4$ (28) or in compound 8. The V(1)–P(1) separation (2.528(2) Å) is a long single bond, and N(1) is planar. The V(1)–N(1) separation (1.929(4) Å) is a single bond, whereas the P(1)–N(1) and P(1)–N(2) distances (1.689(5) and 1.673(5) Å, respectively) are slightly shortened single bonds.

### CONCLUSIONS

We have described the synthesis and structural characterization of the first thermally stable, neutral, electrophilic phosphinidene complexes [CpV(CO)$_3$($\eta^3$-P(NR)$_2$)$_2$] (R = Pr (3a); Cy (3b); 3c) and [CpV(CO)$_3$($\eta^3$-P(NP)$_2$H)] (9); in solution 9 interconverts with $\eta^3$-ligand-containing species [CpV(CO)$_3$($\eta^3$-P(NP)$_2$N)=N=CPh$_2$] (11). The addition of Ph$_3$Si to 3a results initially in the formation of an unstable phosphinidene complex, which readily transforms to a new species that contains a four-electron-donor phosphinidene ligand, [CpV(CO)$_3$($\eta^3$-P(NP)$_2$NHP)] (15). The results described above indicate the remarkable utility of electrophilic phosphinidene complexes for the synthesis of new types of phosphorus-containing ligands.

### EXPERIMENTAL SECTION

#### General Comments

All procedures were carried out using standard Schlenk techniques or in an Innovative Technologies glovebox under a nitrogen atmosphere. THF and ether were distilled from Na/ benzophene. Dichloromethane and pentane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper catalyst (pentane). Cp$_2$V$_2$ was vacuum distilled from Na/benzophene. NMR spectra were recorded at 400 MHz ($^1$H) or 161.975 MHz ($^31$P). Cp$_2$PN$_2$R$_2$ (R = Pr, Cy) was prepared according to the literature procedures. CpV(CO)$_3$ and di-Bu-imidazol-2-ylidene were obtained from Stem Chemicals and used as received. All other reagents were obtained from Aldrich and were used as received.

a. ([CpV(CO)$_3$($\eta^3$-P(NR)$_2$)] (R = Pr (3a); Cy (3b)); These compounds were prepared in an analogous fashion, and only the synthesis of compound 3a is described. A 1.212 g (5.314 mmol) sample of Cp$_2$V(CO)$_3$ was added to Na/Hg (1.060 g Na, 46.11 mmol) in 25 mL of THF, and the mixture was stirred overnight, forming a yellow suspension of [Na$_2$V$_2$(CpV(CO)$_3$)]. The suspension was decanted and then cooled to $-45^\circ$C. Cp$_2$PN$_2$R$_2$ (1.201 g, 5.94 mmol) was added, resulting in the formation of a brown solution, which was stirred at room temperature for 30 min, and then the solvent was removed in vacuo. The residue was extracted with 7 × 10 mL of pentane; the extracts were filtered through Celite, combined, and then concentrated to ca. 10 mL. Cooling the mixture to $-45^\circ$C overnight and removing the solvent with a pipet allowed for the isolation of 75% (1.321 g) of compound 3a as a brown crystalline solid. Further concentration of the mother liquor and cooling to $-45^\circ$C overnight routinely afforded an 80% (1.409 g) yield of the product 3a.

b. Cp$_2$V(CO)$_3$($\eta^3$-P(NP)$_2$H) in 1 mL of pentane was stirred at room temperature for 2 h, during which time a crystalline red solid precipitated. The solvent was decanted, and the solid was then washed with 2 mL of cold ($-45^\circ$C) pentane and dried in vacuo. Yield: 70% (83 mg). $^1$H NMR (δ, Cp$_2$V$_2$: 25.0°C): 2.25 (sept., $J_{HH}$ = 6.6 Hz, 6H, CH(CH$_3$)$_2$); 5.80 (s, SH, CH$_2$); 3.89 (m, 1H, CH(CH$_3$)$_2$); 1.30 (d, $J_{HH}$ = 6.6 Hz, 6H, CH(CH$_3$)$_2$); 1.00 (d, $J_{HH}$ = 6.6 Hz, 6H, CH(CH$_3$)$_2$). $^{31}$P NMR (δ, Cp$_2$V$_2$: 25.0°C): 1100 (broad, flat-topped signal). IR (cm$^{-1}$, ether): 1935 (s); 1896 (m); 1868 (s). Anal. Calc. for Cp$_2$V$_2$: C, 66.0; H, 5.7; N, 2.8.

c. [CpV(CO)$_3$($\eta^3$-P(NP)$_2$F)] (4-cyclo-C$_6$H$_5$) ($J_{HH}$ = 6.3 Hz, 1.3–4.5 Bu$_2$C$_6$H$_4$) (18). A 27 mg (0.149 mmol) sample of 1,3-bis(Bu$_2$)imidazol-2-ylidene was added to 50 mg (0.150 mmol) of compound 1a in 1 mL of THF at $-45^\circ$C. The solution
was stirred for 1 h, then pentane was added until incipient precipitation; cooling to −45 °C overnight resulted in the formation of a red crystalline solid. The solvent was decanted, and the solid was then dried in vacuo. Yield: 65% (50 mg). 1H NMR (δ, CDCl₃, 25 °C): 7.79 (s, 1H, =CH); 7.60 (s, 1H, =CH); 4.92 (s, 5H, C₃H₇); 3.68 (sept., JHH = 6.2 Hz, 2H, CH(CH₃)₂); 1.87 (s, 9H, C(CH₃)₃); 1.45 (t, 2H, CH₂(C₃H₇)); 1.35 (bs, 6H, CH(CH₃)₂); 0.97 (bs, 6H, CH(CH₃)₂). 31P NMR (δ, CDCl₃, 25 °C): 72 (br). IR (νCO, cm⁻¹, CHCl₃): 1606 (w); 1261 (s); 1011 (m). Anal. Calcd for C₇₃H₇₇N₉O₃P₂: C, 74.8; H, 6.0; N, 7.1. Found: C, 74.8; H, 6.1; N, 7.2.

| Table 1. Crystallographic Data for Compounds 3a, 7—9, 14, and 15 |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Compound | a, Å | b, Å | c, Å | β, deg | Z |
| 3a | 13.0972(6) | 14.622(2) | 18.301(1) | 12.6247(5) | 12.202(2) |
| 7 | 8.6814(4) | 7.9968(8) | 8.5447(6) | 22.7564(9) | 10.882(2) |
| 8 | 13.8930(7) | 21.098(2) | 18.745(1) | 9.8417(4) | 29.916(2) |
| 9 | 96.581(3) | 92.693(7) | 116.968(3) | 117.801(2) | 74.670(7) |
| 14 | 1581.9(1) | 2464.2(5) | 2612.6(3) | 2429.8(2) | 3971.8(13) |
| 15 | 4.00 | 4.00 | 4.00 | 4.00 | 8.00 |
| D(calcd), Mg/m³ | 1.391 | 1.373 | 1.300 | 1.363 | 1.413 |
| μ, mm⁻¹ | 0.733 | 0.498 | 0.471 | 0.502 | 0.603 |
| refin refins collected | 117.992 | 31.355 | 48.683 | 52.373 | 27.273 |
| indep refins | 11.450 | 2912 | 4570 | 11.063 | 3055 |
| R₁ [F₂ ≥ 2σ(F₂)] | 0.0293 | 0.0550 | 0.0490 | 0.0319 | 0.0492 |
| wR₂ (all data) | 0.0868 | 0.1432 | 0.1523 | 0.1037 | 0.1080 |

The pentane solutions from the above reaction were combined and stirred overnight at room temperature. The mixture was then concentrated to ca. 1 mL and cooled to −45 °C overnight, resulting in the formation of a green crystalline solid. Yield: 50% (154 mg, based on remaining amount of vanadium from the above reaction). 1H NMR (δ, C₆D₆, 25 °C): 7.21—7.10 (m, 4H, C₃H₇); 6.90 (m, 1H, C₃H₇); 5.32 (s, 5H, C₃H₇); 2.65 (m, 2H, CH(CH₂)₂); 1.06 (bs, 6H, CH(CH₂)₂). 31P NMR (δ, C₆D₆, 25 °C): −11. IR (νCO, cm⁻¹, ether): 1668 (s); 1847 (s). Anal. Calcd for C₇₃H₇₇N₉O₃P₂: C, 78.9; H, 6.1; N, 7.2. Found: C, 78.8; H, 6.0; N, 7.2.

**ASSOCIATED CONTENT**

**Supporting Information.** X-ray crystallographic data in CIF format for compounds 3a, 7—9, 14, and 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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