

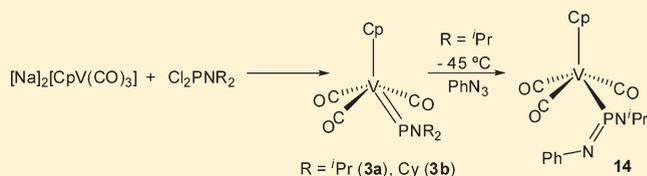
Synthesis and Structural Characterization of the First Thermally Stable, Neutral, and Electrophilic Phosphinidene Complexes of Vanadium

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S Supporting Information

ABSTRACT: The first thermally stable, neutral, electrophilic phosphinidene complexes of vanadium, $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{NR}_2)\}]$ ($\text{R} = \textit{i}\text{Pr}$ (**3a**), Cy (**3b**)), have been prepared by the reaction of $[\text{Na}]_2[\text{CpV}(\text{CO})_3]$ with Cl_2PNR_2 . The molecules **3a** and **3b** have been characterized by microanalysis, IR, and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, and for **3a** also by single-crystal X-ray diffraction. The structure of **3a** exhibits a piano stool geometry closely related to that of $\text{CpV}(\text{CO})_4$ with an η^1 -phosphinidene ligand replacing CO in one of the basal coordination sites of the vanadium atom ($\text{V}(1)\text{-P}(1) = 2.300(2)$ Å). The reactivity of **3a** toward a variety of unsaturated substrates: $\text{PhC}\equiv\text{CPh}$, di-*t*-Bu-imidazol-2-ylidene, PhN_3 , and $\text{Ph}_2\text{C}=\text{N}=\text{N}$ has been examined to probe the electrophilic (or nucleophilic) character of the low-coordinate P(I) site. In all cases reactions occur exclusively at the phosphinidene phosphorus atom, without CO displacement, affording examples of P-coordinated phosphirene $[\text{CpV}(\text{CO})_3\{\text{P}(\text{N}^i\text{Pr}_2)\text{CPh}=\text{CPh}\}]$ (**7**), abnormal NCN carbene adduct $[\text{CpV}(\text{CO})_3\{\text{P}(\text{N}^i\text{Pr}_2)\text{-4-cyclo-C}_3\text{H}_2\text{-1,3-(N}^i\text{Bu)}_2\}]$ (**8**), diazaphosphaimine $[\text{CpV}(\text{CO})_3\{\text{P}(\text{N}^i\text{Pr}_2)=\text{N}-\text{N}=\text{CPh}_2\}]$ (**12**), and P-coordinated phosphaimine $[\text{CpV}(\text{CO})_3\{\text{P}(\text{N}^i\text{Pr}_2)=\text{NPh}\}]$ (**14**) complexes. The η^1 -phosphaimine complexes **12** and **14** lose carbon monoxide to yield derivatives $[\text{CpV}(\text{CO})_2\{\text{P}(\text{N}^i\text{Pr}_2)\text{N}-\text{N}=\text{CPh}_2\}]$ (**9**) and $[\text{CpV}(\text{CO})_2\{\text{P}(\text{N}^i\text{Pr}_2)=\text{NPh}\}]$ (**15**), which contain η^2 -(P,N)-coordinated phosphaimine ligands. An η^3 -(P,N,N)-bound phosphaimine ligand is present in an isomer of **9**, namely, $[\text{CpV}(\text{CO})_2\{\text{P}(\text{N}^i\text{Pr}_2)\text{N}-\text{N}=\text{CPh}_2\}]$, **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,¹ the chemistry of this fascinating class of molecules has undergone rapid development in recent years for several substantive reasons: (i) Phosphinidene ($\text{R}-\text{P}$) ligands are the heavier congeners of imides ($\text{R}-\text{N}$) and are also isolobal with carbenes (R_2C).^{2,3} Transition metal–phosphinidene complexes are therefore analogous to better known metal–carbenes and imides. In fact, both nucleophilic phosphinidene complexes,^{4–20} with an $\text{M}=\text{P}$ double bond formally derived from the combination of triplet RP with a triplet ground state metal fragment, and electrophilic complexes^{21–26} containing essentially $\text{M}-\text{P}$ single bonds resulting from singlet RP–singlet metallic moieties are now well known. The chemistry of these two classes of molecules is now being intensively explored.^{4,21,22,27–29} (ii) The presence and nature of metal–main group element multiple bonding ($\text{M}=\text{P}$, $\text{M}\equiv\text{P}$) in these complexes is of theoretical and reactivity interest.³⁰ (iii) In terminal $\text{M}-\text{PR}$ 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(I) center.³¹ Low-coordinate nonmetals, deficient in electrons, should exhibit high reactivity. (iv) Like metal–carbene complexes, phosphinidene analogues have considerable potential in phosphoorganic synthesis and catalytic chemistry.⁴

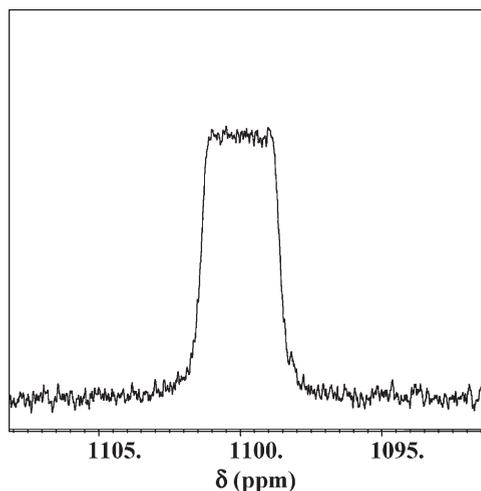
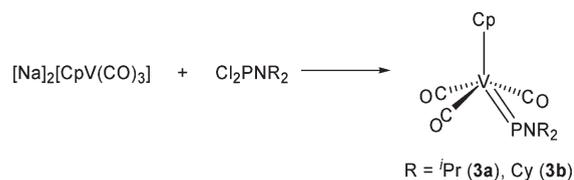
Our own interest in terminal phosphinidene complexes was stimulated by a longstanding interest in chemical transformations at bridging, μ -PR ligands in clusters^{32,33} and by the discovery in 2001 of a synthetic route to isolable, cationic, terminal phosphinidene complexes of molybdenum and tungsten, $[\text{Cp}^*\text{M}(\text{CO})_3\{\text{PN}^i\text{Pr}_2\}]\text{AlCl}_4$ ($\text{M} = \text{Mo}, \text{W}$), involving halide abstraction from $[\text{Cp}^*\text{M}(\text{CO})_3\{\text{P}(\text{Cl})\text{N}^i\text{Pr}_2\}]$.³⁴ At the time these were the first fully characterized, electrophilic, terminal phosphinidene complexes, although NMR spectroscopic evidence had been reported³⁵ for a related iron cation, $[\text{Cp}^*\text{Fe}(\text{CO})_2\{\text{PN}^i\text{Pr}_2\}]^+$, and the phosphoorganic chemistry of transient electrophilic phosphinidenes such as $[(\text{CO})_5\text{W}=\text{PR}]$ and $[(\text{CO})_4\text{Fe}=\text{PR}]$, generated in situ, had been elegantly explored by Mathey³⁶ and co-workers and Lammertsma et al.³⁷ The Lammertsma group has recently reported the direct observation of the phosphinidene complex $[\text{W}(\text{CO})_5(\eta^1\text{-PAr})]$ ($\text{Ar} = \text{aryl}$) 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 $[\text{Cp}^*\text{Cr}(\text{CO})_3\{\text{PN}^i\text{Pr}_2\}]^+$ of the Cr, Mo, W triad, the iron group compounds $[\text{Cp}^*\text{Fe}(\text{CO})_2\{\text{PN}^i\text{Pr}_2\}]^+$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$), the rhenium cation

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Scheme 1

Figure 1. ³¹P NMR spectrum of compound 3a.

$[\text{Re}(\text{CO})_5\{\text{PN}^i\text{Pr}_2\}]^+$, and the cobalt complex $[\text{Co}(\text{CO})_3(\text{PPh}_3)\{\text{PN}^i\text{Pr}_2\}]^+$.^{21,23–25,34} These molecules, all of which have been structurally characterized, display several important features. They are thermally stable, despite in some notable cases, such as the Re and Co compounds, the lack of sterically encumbered substituents on the metal or phosphorus ligand. The thermal stability of $[\text{Re}(\text{CO})_5\{\text{P}(\text{N}^i\text{Pr}_2)\}]^+$ compared to the reported instability of the isoelectronic $[\text{W}(\text{CO})_5(\text{PR})]$ is particularly notable. Clearly it would seem that electronic factors, including the presence of donor substituents on the nonmetal, are responsible for the enhanced stability of the Re cation. Close examination of metal–phosphorus bond lengths in this set of compounds confirms that the M–P bond has mostly single-bond character with a modest shortening due to $\text{M}d\pi\text{--P}p\pi$ back-donation. The latter is strengthened when a CO group is displaced by a stronger donor phosphine, thus supporting the bonding model.²⁷ Chemically these phosphinidene complexes are clearly electrophilic, forming adducts via P–P bond formation at the phosphinidene phosphorus atom with phosphines and diphosphines,^{8,27,28} affording P-bound phosphirenes with alkynes,²³ generating P-coordinated phosphalkenes and phosphamines with diazoalkanes and organic azides,²² and undergoing four-electron, two-step oxidation at the P(I) center with sulfur.³⁹ Such reactions parallel the properties of transient electrophilic phosphinidenes $[(\text{CO})_5\text{W}=\text{PR}]$ as demonstrated by Mathey.³⁶

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 π -acid ligands favor electrophilicity at the metal, while π -donor substituents on phosphorus favor electrophilic behavior.

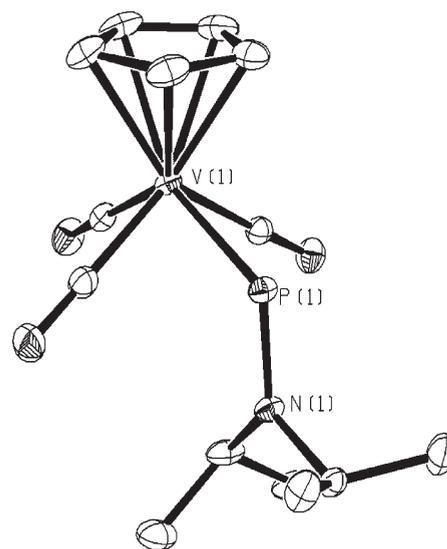


Figure 2. ORTEP diagram of compound 3a. Selected bond lengths (Å) and angles (deg): V(1)–P(1) 2.3200(2); P(1)–N(1) 1.6520(6); V(1)–P(1)–N(1) 120.65(2); P(1)–N(1)–C(4) 117.54(4); P(1)–N(1)–C(7) 127.79(4).

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, $[\text{CpV}(\text{CO})_3\{\text{P}(\text{NR}_2)\}]$ (R = ⁱPr, Cy), their reactions with a variety of unsaturated ligands, and the nature of the products.

RESULTS AND DISCUSSION

The dark brown complexes $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{NR}_2)\}]$ (R = ⁱPr (3a), Cy (3b)) were formed in quantitative yield via the reaction of $[\text{Na}]_2[\text{CpV}(\text{CO})_3]$ with Cl_2PNR_2 (Scheme 1). The high solubility of the compounds resulted in isolation of the compounds in 80% and 62% yield, respectively.

The ³¹P NMR spectrum (Figure 1) of 3a shows a broad flat-topped resonance centered at δ 1100, whereas the ¹H NMR spectrum shows only the expected Cp and ⁱPr resonances. The unusual shape of the ³¹P resonance is likely due to coupling to ⁵¹V ($I = 7/2$) and to N. The ⁱPr methyl resonances appear as two sharp doublets (δ 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 PN^iPr_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 $[(\text{Nacnac})\text{V}(\text{CH}_2^t\text{Bu})(=\text{P}^i\text{Mes}^*)]$ ($\text{Mes}^* = 2,4,6\text{-}^t\text{Bu}_3\text{-C}_6\text{H}_2$).¹¹ The V(1)–P(1) separation in 3a agrees remarkably well with the calculated bond distance for $\text{CpV}(\text{CO})_3=\text{PH}$ (2.307 Å).³⁰ The N^iPr_2 fragment is planar and, in conjunction with the short P(1)–N(1) separation (1.6520(6) Å), indicates a substantial π -interaction between P and N. Complexes 3a/3b are the first thermally stable, neutral, electrophilic phosphinidenes to be reported

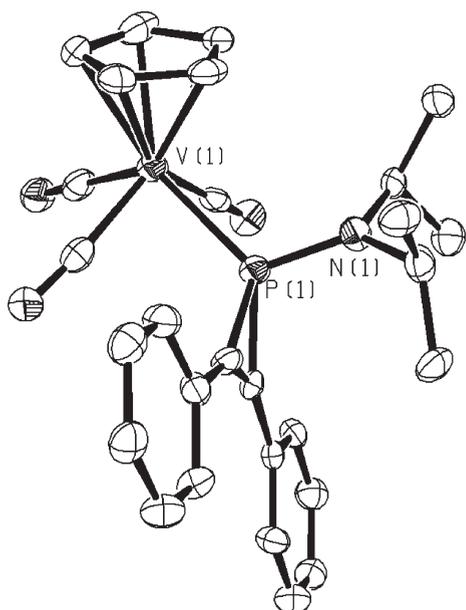
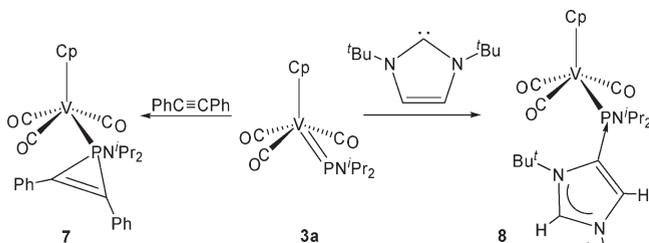


Figure 3. ORTEP diagram of compound 7. Selected bond lengths (Å) and angles (deg): V(1)–P(1) 2.455(2); P(1)–N(1) 1.684(4); P(1)–C(10) 1.791(5); P(1)–C(11) 1.778(5); V(1)–P(1)–N(1) 117.5(2); V(1)–P(1)–C(10) 127.7(2); V(1)–P(1)–C(11) 124.2(2); N(1)–P(1)–C(10) 111.4(2); N(1)–P(1)–C(11) 111.1(2); P(1)–N(1)–C(18) 126.9(3); P(1)–N(1)–C(21) 117.0(3); C(10)–P(1)–C(11) 43.9(2).

Scheme 2



and are also the first electrophilic phosphinidene complexes of vanadium.

The isoelectronic electrophilic cation $[\text{Cp}^*\text{Mo}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\}]\text{AlCl}_4$ (**4**) reacts readily with nucleophiles such as PEt_3 , initially forming the phosphine-stabilized phosphinidene adduct $[\text{Cp}^*\text{Mo}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)(\text{PEt}_3)\}]\text{AlCl}_4$ (**5**), which then loses a CO ligand and forms the new phosphinidene complex $[\text{Cp}^*\text{Mo}(\text{CO})_2(\text{PEt}_3)\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\}]\text{AlCl}_4$ (**6**), where PEt_3 migration from the coordinated PNR_2 fragment to the metal has occurred.²⁷ The addition of PEt_3 to $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\}]$ (**3a**), however, causes no change, and this led us to speculate whether **3** would display electrophilic or nucleophilic reactivity. 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 phosphirenes,⁴⁰ whereas their nucleophilic analogues undergo 2+2 cycload-

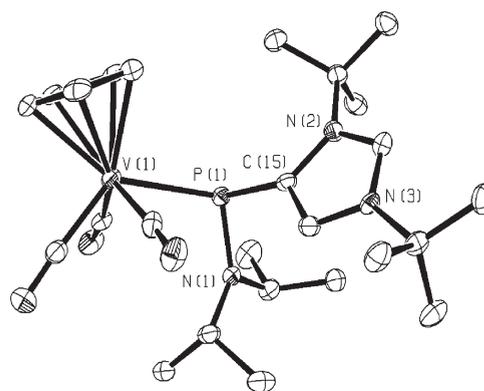


Figure 4. ORTEP diagram of compound 8. Selected bond lengths (Å) and angles (deg): V(1)–P(1) 2.5782(8); P(1)–N(1) 1.717(2); P(1)–C(15) 1.888(3); N(2)–C(15) 1.420(3); N(2)–C(17) 1.337(3); N(3)–C(16) 1.372(3); N(3)–C(17) 1.331(3); C(15)–C(16) 1.365(4); V(1)–P(1)–N(1) 110.47(8); V(1)–P(1)–C(15) 111.18(8); N(1)–P(1)–C(15) 101.7(1).

dition²⁰ reactions, affording phosphametallacyclobutene complexes.³ We found that the addition of diphenylacetylene to **3a** (Scheme 2) results in the quantitative formation of the crystallographically characterized (Figure 3) phosphirene complex $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\text{C}(\text{Ph})=\text{C}(\text{Ph})\}]$ (**7**), which displays a broad ^{31}P NMR resonance centered at $\delta -19$.

Binding of the alkyne to the phosphinidene phosphorus results in a significant lengthening of the V(1)–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-*t*-Bu-imidazol-2-ylidene, which results in the quantitative formation of the donor–acceptor adduct $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)(4\text{-cyclo-C}_3\text{H}_2(\text{N}^i\text{Bu})_2)\}]$ (**8**) (Scheme 2), which displays a broad ^{31}P NMR resonance at $\delta 72$. The ^1H NMR spectrum of **8** shows resonances due to the ^iPr and *t*-Bu groups, in addition to two downfield signals at $\delta 7.60$ and 7.79 . The nonequivalence of the latter two signals suggests that the carbene fragment is bound to the PN^iPr_2 fragment via C4 rather than the normal 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 C2 to C4; the binding of the carbene to the phosphinidene phosphorus results in substantial lengthening of both the V(1)–P(1) and P(1)–N(1) bonds (2.5782(8) and 1.717(2) Å, respectively), and the long P(1)–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(amino)cyclopropylidene moiety has been recently reported by the Bertrand group.⁴¹ We have recently reported that the reactions of bimetallic μ -phosphinidene complexes $[\text{Mn}_2(\text{CO})_8\{\mu\text{-P}(\text{N}^i\text{Pr}_2)\}]$ and $[\text{Co}_2(\text{CO})_4\{\mu\text{-dppm}\}\{\mu\text{-P}(\text{N}^i\text{Pr}_2)\}]$ afford similar abnormal NCN carbene adducts and that the migration of the ylidene moiety appears to be induced by steric interactions between bulky di-*R*-imidazolylidene *R* groups and either the metal-bound ligands or the N^iPr_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 $[\text{CpV}(\text{CO})_2\{\eta^2\text{-P}(\text{N}^i\text{Pr}_2)\text{NN}=\text{CPh}_2\}]$ (**9**), which displays two ^{31}P

Scheme 3

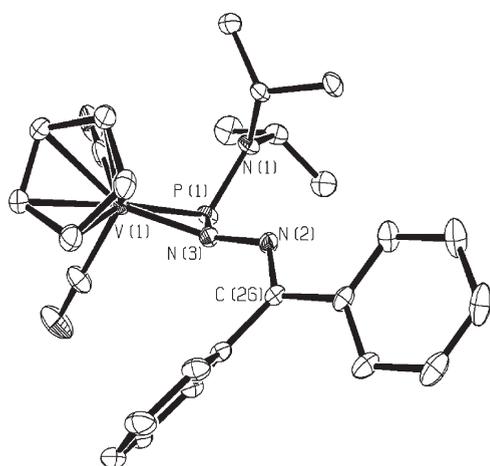
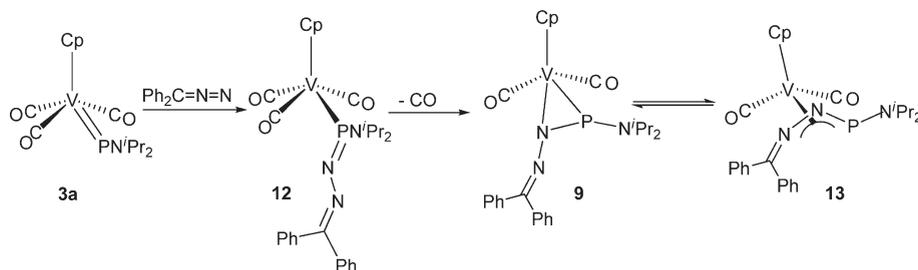


Figure 5. ORTEP diagram of compound **9**. Selected bond lengths (Å) and angles (deg): V(1)–P(1) 2.5247(4); V(1)–N(3) 1.900(1); P(1)–N(1) 1.677(1); P(1)–N(3) 1.686(1); N(2)–N(3) 1.388(2); N(2)–C(26) 1.294(2); V(1)–P(1)–N(1) 112.02(4); V(1)–P(1)–N(3) 48.79(4); V(1)–N(3)–P(1) 89.32(5); V(1)–N(3)–N(2) 141.73(9); N(1)–P(1)–N(3) 107.02(6); P(1)–N(3)–N(2) 122.50(9); N(3)–N(2)–C(26) 118.3(1).

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 C_6D_6 the ^{31}P 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 diphenyldiazomethane fragment is bound to the phosphinidene group; carbonyl 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 diphenyldiazomethane, form the complexes $[\text{CpM}(\text{CO})_2\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)=\text{N}-\text{N}=\text{CPh}_2\}]\text{AlCl}_4$ (**10**) and $[\text{CpM}(\text{CO})_3\{\eta^3\text{-P}(\text{N}^i\text{Pr}_2)\text{NN}=\text{CPh}_2\}]\text{AlCl}_4$ (M = Cr, Mo, W) (**11**), which contain η^1 - and η^3 -phosphadiazallene 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. ^{31}P 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

Scheme 4

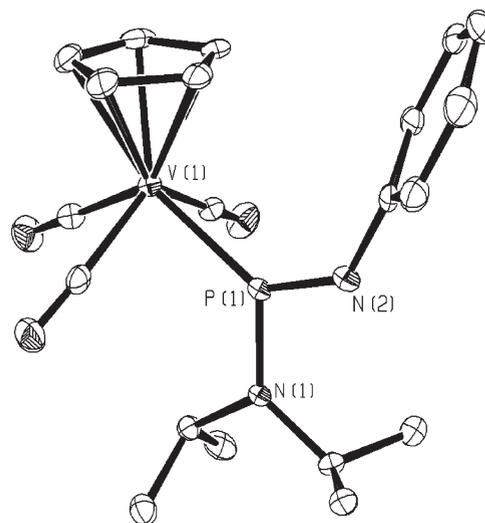
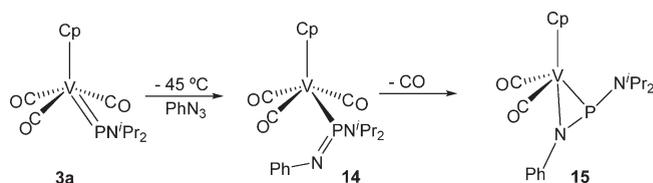


Figure 6. ORTEP diagram of compound **14**. Selected bond lengths (Å) and angles (deg): V(1)–P(1) 2.362(1); P(1)–N(1) 1.646(3); P(1)–N(2) 1.547(3); V(1)–P(1)–N(1) 122.7(1); V(1)–P(1)–N(2) 132.0(1); N(1)–P(1)–N(2) 105.2(2).

11 displays a downfield ^{31}P 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 ^{31}P NMR spectrum of complex **9**, we suggest that the diphenyldiazaphosphallene ligand undergoes interconversion between the η^2 ($\delta(^{31}\text{P}) -10$) and η^3 ($\delta(^{31}\text{P}) 95$) 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 PhN_3 . The low-temperature addition of PhN_3 to **3a** results in N_2 loss and oxidation of the P(I) ligand with the formation of the new phosphaimine complex $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)=\text{NPh}\}]\text{AlCl}_4$ (**14**) (Scheme 4). Complex **14** displays a

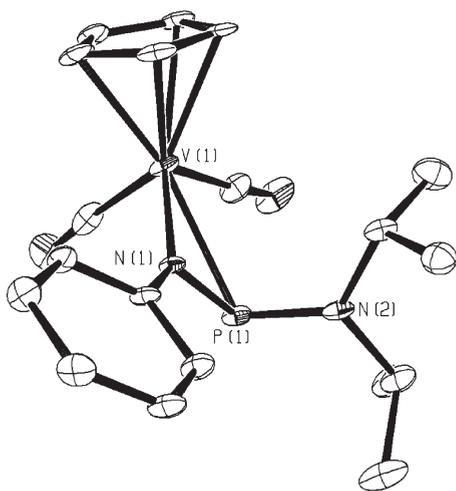


Figure 7. ORTEP diagram for compound **15**: Selected bond lengths (Å) and angles (deg): V(1)–P(1) 2.528(2); V(1)–N(1) 1.929(4); P(1)–N(1) 1.689(5); P(1)–N(2) 1.673(5); V(1)–P(1)–N(1) 49.7(2); V(1)–P(1)–N(2) 112.9(2); V(1)–N(1)–P(1) 88.4(2); N(1)–P(1)–N(2) 107.3(2).

broad ^{31}P NMR resonance centered at δ 333, and the ^1H NMR spectrum of **14** shows only the expected Cp, ^iPr , and Ph signals.

The compound has been characterized crystallographically, and the structure (Figure 6) features a piano stool geometry with a P-coordinated $\eta^1\text{-Pr}_2\text{NP}=\text{NPh}$ ligand, which displays a short V(1)–P(1) interaction (2.362(2) Å) and a planar $^i\text{Pr}_2\text{NP}=\text{NPh}$ 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 $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\}]$ (**3a**)). The P=N bond length is similar to the analogous separation (1.545(2) Å) in the free phosphimine (Me_3Si) $_2\text{NP}=\text{NSiMe}_3$.⁴³ Complex **14** contains a rare example of a coordinated η^1 -phosphimine ligand.

Orange tricarbonyl complex **14** is unstable and readily loses a CO ligand to form the new green complex $[\text{CpV}(\text{CO})_2\{\eta^2\text{-P}(\text{N}^i\text{Pr}_2)\text{NPh}\}]$ (**15**). The ^{31}P NMR spectrum of **15** shows a sharp resonance at δ –11, and the ^1H NMR spectrum shows signals due to the Cp, ^iPr , 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 NPh fragment. The geometry around phosphorus is significantly pyramidalized and closely resembles that found in donor–acceptor adducts such as $[\text{Re}(\text{CO})_5\{\text{P}(\text{N}^i\text{Pr}_2)(\text{PPh}_3)\}]\text{AlCl}_4$ (**2**)⁸ 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 $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{NR}_2)\}]$ (R = ^iPr (**3a**); Cy (**3b**)); the complexes are also the first electrophilic phosphinidene complexes of vanadium. The electrophilic nature of the complexes is clearly indicated by the reaction of **3a** with diphenylacetylene and di- ^tBu -imidazol-2-ylidene, which form phosphirene and abnormal carbene-stabilized phosphinidene complexes, respectively. The reaction of complex **3a** with diphenyldiazomethane provides a novel, structurally

characterized complex, $[\text{CpV}(\text{CO})_3\{\eta^2\text{-P}(\text{N}^i\text{Pr}_2)\text{N}=\text{CPh}_2\}]$ (**9**); in solution **9** interconverts with η^3 -ligand-containing species $[\text{CpV}(\text{CO})_2\{\eta^3\text{-P}(\text{N}^i\text{Pr}_2)\text{N}=\text{CPh}_2\}]$ (**13**). The addition of PhN_3 to **3a** results initially in the formation of an unstable phosphaimine complex, which readily transforms to a new species that contains a four-electron-donor phosphaimine ligand, $[\text{CpV}(\text{CO})_2\{\eta^2\text{-P}(\text{N}^i\text{Pr}_2)\text{NPh}\}]$ (**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/benzophenone. Dichloromethane and pentane were purified using solvent purification columns containing alumina (dichloromethane) or alumina and copper catalyst (pentane). C_6D_6 was vacuum distilled from Na/benzophenone. NMR spectra were recorded at 400 MHz (^1H) or 161.975 ($^{31}\text{P}\{^1\text{H}\}$). Cl_2PNR_2 (R = ^iPr , Cy)⁴⁴ and $[\text{Na}]_2[\text{CpV}(\text{CO})_3]$ ⁴⁵ were prepared according to the literature procedures. $\text{CpV}(\text{CO})_4$ and di- ^tBu -imidazol-2-ylidene were obtained from Strem Chemicals and used as received. All other reagents were obtained from Aldrich and were used as received.

a. $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{NR}_2)\}]$ (R = ^iPr (**3a**); R = 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 $\text{CpV}(\text{CO})_4$ 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 $[\text{Na}]_2[\text{CpV}(\text{CO})_3]$. The suspension was decanted and then cooled to –45 °C. $\text{Cl}_2\text{PN}^i\text{Pr}_2$ (1.201 g, 5.944 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 °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 °C overnight routinely afforded an 80% (1.409 g) combined yield of the product. **3a**: ^1H NMR (δ , C_6D_6 , 25 °C): 5.25 (sept, $^3J_{\text{HH}} = 6.6$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$); 5.04 (s, 5H, C_5H_5); 3.89 (m, 1H, $\text{CH}(\text{CH}_3)_2$); 1.30 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 1.00 (d, $^3J_{\text{HH}} = 6.6$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$). ^{31}P NMR (δ , C_6D_6 , 25 °C): 1100 (broad, flat-topped signal). IR (ν_{CO} , cm^{-1} , ether): 1953 (s); 1896 (m); 1868 (s). Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{PV}$: C, 50.8; H, 5.8; N, 4.2. Found: C, 50.6; H, 6.2; N, 4.2. **3b**: Yield: 62%. ^1H NMR (δ , C_6D_6 , 25 °C): 5.08 (s, 5H, C_5H_5); 4.91 (m, 1H, Cy); 3.73 (m, 1H, Cy); 2.21 (m, 2H, Cy); 1.78–1.40 (m, 18H, Cy). ^{31}P NMR (δ , C_6D_6 , 25 °C): 1111. IR (ν_{CO} , cm^{-1} , ether): 1952 (s); 1893 (m); 1867 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_3\text{PV}$: C, 58.4; H, 6.6; N, 3.4. Found: C, 58.5; H, 6.6; N, 3.5.

b. $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\text{C}(\text{Ph})=\text{C}(\text{Ph})\}]$ (**7**). A 40 mg (0.224 mmol) sample of diphenylacetylene was added at –45 °C to 74 mg (0.223 mmol) of $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)\}]$ in 1 mL of pentane. The mixture 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 °C) pentane and dried in vacuo. Yield: 70% (83 mg). ^1H NMR (δ , C_6D_6 , 25 °C): 7.90 (m, 4H, C_6H_5); 7.20–7.15 (m, 4H, C_6H_5); 7.06 (m, 2H, C_6H_5); 4.43 (s, 5H, C_5H_5); 3.38 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$); 1.00 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). ^{31}P NMR (δ , C_6D_6 , 25 °C): –19 (br). IR (ν_{CO} , cm^{-1} , ether): 1956 (s); 1870 (s, shoulder); 1862 (s). Anal. Calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_3\text{PV}$: C, 66.0; H, 5.7; N, 2.8. Found: C, 65.8; H, 5.3; N, 3.0.

c. $[\text{CpV}(\text{CO})_3\{\eta^1\text{-P}(\text{N}^i\text{Pr}_2)(4\text{-cyclo-C}_3\text{H}_2\text{-1,3-(N}^t\text{Bu)}_2)\}]$ (**8**). A 27 mg (0.149 mmol) sample of 1,3-bis(^tBu)imidazol-2-ylidene was added to 50 mg (0.150 mmol) of compound **1a** in 1 mL of THF at –45 °C. The solution

Table 1. Crystallographic Data for Compounds 3a, 7–9, 14, and 15

	3a	7	8	9	14	15
formula	C ₁₄ H ₁₉ NO ₃ PV	C ₂₈ H ₂₉ NO ₃ PV	C ₂₅ H ₃₉ N ₃ O ₃ PV	C ₂₆ H ₃₀ N ₃ O ₂ PV	C ₂₀ H ₂₄ N ₂ O ₃ PV	C ₁₉ H ₂₄ N ₂ O ₂ PV
fw	331.21	509.43	511.50	498.46	422.32	394.31
T, K	125(2)	373(2)	373(2)	273(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	P2(1)/c	P2(1)/c	P2(1)/n	Cc	Pcba	P2(1)/n
unit cell dimens						
a, Å	13.0972(6)	14.622(2)	18.301(1)	12.2647(5)	12.202(2)	12.935(5)
b, Å	8.7514(4)	7.9968(8)	8.5447(6)	22.7564(9)	10.882(2)	10.411(4)
c, Å	13.8930(7)	21.098(2)	18.745(1)	9.8417(4)	29.912(6)	15.338(6)
β, deg	96.581(3)	92.693(7)	116.968(3)	117.801(2)		94.670(7)
V, Å ³	1581.9(1)	2464.2(5)	2612.6(3)	2429.8(2)	3971.8(13)	2058.8(14)
Z	4	4	4	4	8	4
D(calcd), Mg/m ³	1.391	1.373	1.300	1.363	1.413	1.272
μ, mm ⁻¹	0.733	0.498	0.471	0.502	0.603	0.573
reflins collected	117 992	31 355	48 683	52 373	27 273	7858
independ reflns	11 450 [R(int) = 0.0386]	2912 [R(int) = 0.2227]	4570 [R(int) = 0.1010]	11 063 [R(int) = 0.0387]	3055 [R(int) = 0.0337]	1808 [R(int) = 0.0654]
R ₁ [F _o ² ≥ 2σ(F _o ²)]	0.0293	0.0550	0.0490	0.0319	0.0492	0.0594
wR ₂ (all data)	0.0868	0.1432	0.1523	0.1037	0.1080	0.1493

was stirred for 1 h, and then pentane was added until incipient precipitation; cooling to $-45\text{ }^{\circ}\text{C}$ 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 , CD₂Cl₂, 25 $^{\circ}\text{C}$): 7.79 (s, 1H, =CH); 7.60 (s, 1H, =CH); 4.92 (s, 5H, C₅H₅); 3.68 (sept, ³J_{HH} = 6.2 Hz, 2H, CH(CH₃)₂); 1.87 (s, 9H, C(CH₃)₃); 1.61 (s, 9H, C(CH₃)₃); 1.23 (br s, 6H, CH(CH₃)₂); 0.97 (br s, 6H, CH(CH₃)₂). ³¹P NMR (δ , CD₂Cl₂, 25 $^{\circ}\text{C}$): 72 (br). IR (ν_{CO} , cm⁻¹, CH₂Cl₂): 1962 (w); 1891 (s); 1795 (s). Anal. Calcd for C₂₅H₃₉N₃O₃PV: C, 58.7; H, 7.7; N, 8.2. Found: C, 58.4; H, 7.4; N, 8.1.

d. [CpV(CO)_n{η^m-P(NⁱPr₂)(NN=CPh₂)}] (n = 2, m = 2 (**9**); n = 3, m = 1 (**12**); n = 2, m = 3 (**13**)). A 44 mg (0.227 mmol) sample of Ph₂C=N=N was added at $-45\text{ }^{\circ}\text{C}$ to 75 mg (0.226 mmol) of [CpV(CO)₃{η¹-P(NⁱPr₂)}] in 1 mL of THF. After 10 min a sample of the reaction mixture was taken and the ³¹P and ¹H NMR spectra were recorded, showing the presence of a small amount of compound **12**, in addition to complexes **9** and **13**. The mixture was stirred for 1 h, and then the solvent was removed in vacuo. The green solid was dissolved in a minimum volume of pentane and then cooled to $-45\text{ }^{\circ}\text{C}$ overnight, resulting in the formation of a green crystalline solid. **9**: ¹H NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 6.81–7.60 (m, 10H, C₆H₅); 5.15 (s, 5H, C₅H₅); 2.88 (sept, ³J_{HH} = 6.7 Hz), 2H, CH(CH₃)₂); 1.22 (m, 12H, CH(CH₃)₂). ³¹P NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): -11. IR (ν_{CO} , cm⁻¹, ether) for mixture of **9** and **13**: 1957 (s); 1927 (m); 1870 (s); 1859 (s). **12**: ¹H NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 6.75–7.50 (m, 10H, C₆H₅); 5.09 (s, 5H, C₅H₅); 3.25 (m, 2H, CH(CH₃)₂); 1.12 (m, 12H, CH(CH₃)₂). ³¹P NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 384 (br). This compound is unstable, and it was not possible to obtain an IR spectrum or microanalytical data. **13**: Yield 75% (84 mg). ¹H NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 6.81–7.65 (m, 10H, C₆H₅); 5.12 (s, 5H, C₅H₅); 3.34 (m, 2H, CH(CH₃)₂); 1.09 (m, 12H, CH(CH₃)₂). ³¹P NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 94. Anal. Calcd for C₂₆H₂₉N₃O₃PV: C, 62.7; H, 5.9; N, 8.4. Found: C, 62.5; H, 6.1; N, 8.0.

e. [CpV(CO)₃{η¹-P(NⁱPr₂)=NPh}] (**14**). A solution of 88 mg (0.739 mmol) of PhN₃ in 3 mL of THF was added dropwise to 244 mg (0.736 mmol) of [CpV(CO)₃{η¹-P(NⁱPr₂)}] in 10 mL of THF at $-80\text{ }^{\circ}\text{C}$. The mixture was warmed to room temperature and stirred for 45 min, resulting in the formation of a yellow-green solution. The solvent was removed in vacuo, and the residue extracted with pentane (4 × 5 mL); the extracts were filtered through Celite, and the solvent was

concentrated until precipitation (ca. 3 mL). After cooling overnight to $-45\text{ }^{\circ}\text{C}$ the orange solid was washed with 2 × 5 mL of cold pentane and then dried in vacuo. Yield: 30% (93 mg). ¹H NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 7.08 (m, 2H, C₆H₅); 6.81 (m, 1H, C₆H₅); 6.61 (m, 2H, C₆H₅); 4.48 (s, 5H, C₅H₅); 3.53 (m, 2H, CH(CH₃)₂); 1.27 (d, ³J_{HH} = 5.4 Hz, CH(CH₃)₂). ³¹P NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): 323 (broad, flat-topped signal). This compound is not stable, and we were unable to obtain microanalysis.

e. [CpV(CO)₂{η²-P(NⁱPr₂)NPh}] (**15**). 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 $-45\text{ }^{\circ}\text{C}$ 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 $^{\circ}\text{C}$): 7.21–7.10 (m, 4H, C₆H₅); 6.90 (m, 1H, C₆H₅); 5.32 (s, 5H, C₅H₅); 2.65 (m, 2H, CH(CH₃)₂); 1.06 (br s, 6H, CH(CH₃)₂); 0.98 (br s, 6H, CH(CH₃)₂). ³¹P NMR (δ , C₆D₆, 25 $^{\circ}\text{C}$): -11. IR (ν_{CO} , cm⁻¹, ether): 1968 (s); 1857 (s). Anal. Calcd for C₁₉H₂₄N₂O₂PV: C, 58.9; H, 6.1; N, 7.1. Found: C, 58.8; 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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■ REFERENCES

(1) Cowley, A.; Pellerin, B.; Atwood, J. L.; Bott, S. G. *J. Am. Chem. Soc.* **1990**, *112*, 6734.

- (2) Aktas, H.; Mulder, J.; Kanter, F. J. J. d.; Slootweg, J. C.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *J. Am. Chem. Soc.* **2009**, *131*, 13531.
- (3) *Phosphorus: The Carbon Copy*; Dillon, K. B. M., F.; Nixon, J. F., Ed.; John Wiley & Sons: Ltd.: Chichester, 1998.
- (4) Aktaş, H.; Slootweg, J.; Lammertsma, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2102.
- (5) Termaten, A. T.; Aktas, H.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Organometallics* **2003**, *22*, 1827.
- (6) Termaten, A. T.; Nijbacker, T.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem.—Eur. J.* **2003**, *9*, 2200.
- (7) Wicker, B. F.; Scott, J.; Andino, J. G.; Gao, X.; Park, H.; Pink, M.; Mindiola, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 3691.
- (8) *Science of Synthesis*; Slootweg, J. C.; Lammertsma, K., Eds.; Georg Thieme Verlag: Stuttgart, 2009; Vol. 42.
- (9) Aktas, H.; Slootweg, J. C.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *J. Am. Chem. Soc.* **2009**, *131*, 6666.
- (10) Bailey, B. C.; Huffman, J. C.; Mindiola, D. J.; Weng, W.; Ozerov, O. V. *Organometallics* **2005**, *24*, 1390.
- (11) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 1924.
- (12) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170.
- (13) Zhao, G.; Basuli, F.; Kilgore, U. J.; Fan, H.; Aneetha, H.; Huffman, J. C.; Wu, G.; Mindiola, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 13575.
- (14) Figueroa, J. S.; Cummins, C. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 984.
- (15) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 3846.
- (16) Waterman, R.; Hillhouse, G. L. *Organometallics* **2003**, *22*, 5182.
- (17) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2003**, *125*, 13350.
- (18) Termaten, A. T.; Nijbacker, T.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Organometallics* **2002**, *21*, 3196.
- (19) Termaten, A. T.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Chem.—Eur. J.* **2003**, *9*, 3577.
- (20) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914.
- (21) Graham, T. W.; Cariou, R. P. Y.; Sánchez-Nieves, J.; Allen, A. E.; Udachin, K. A.; Regragui, R.; Carty, A. J. *Organometallics* **2005**, *24*, 2023.
- (22) Graham, T. W.; Udachin, K. A.; Carty, A. J. *Chem. Commun.* **2005**, 5890.
- (23) Sánchez-Nieves, J.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 2404.
- (24) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 2657.
- (25) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2003**, *22*, 3927.
- (26) Kilgore, U. J.; Fan, H.; Pink, M.; Urnezus, E.; Protasiewicz, J. D.; Mindiola, D. J. *Chem. Commun.* **2009**, 4521.
- (27) Sterenberg, B. T.; Senturk, O. S.; Udachin, K. A.; Carty, A. J. *Organometallics* **2007**, *26*, 925.
- (28) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 4463.
- (29) Vaheesar, K.; Bolton, T. M.; East, A. L. L.; Sterenberg, B. T. *Organometallics* **2009**, *29*, 484.
- (30) Ehlers, A. W.; Baerends, E. J.; Lammertsma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2831.
- (31) Ellis, B. D.; Macdonald, C. L. B. *Coord. Chem. Rev.* **2007**, *251*, 936.
- (32) Scoles, L.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Inorg. Chem.* **2005**, *44*, 2766.
- (33) Scoles, L.; Yamamoto, J. H.; Brissieux, L.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Inorg. Chem.* **2001**, *40*, 6731.
- (34) Sterenberg, B. T.; Carty, A. J. *J. Organomet. Chem.* **2001**, 617–618, 696.
- (35) Nakazawa, H.; Buhro, W. E.; Bertrand, G.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 3433.
- (36) Mathey, F. *Dalton Trans.* **2007**, 1861.
- (37) Wit, J. B. M.; van Eijkel, G. T.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2596.
- (38) Jansen, H.; Samuels, M.; Couzijn, E.; Slootweg, J.; Ehlers, A.; Chen, P.; Lammertsma, K. *Chem.—Eur. J.* **2010**, *16*, 1454.
- (39) Graham, T. W.; Udachin, K. A.; Zgierski, M. Z.; Carty, A. J. *Can. J. Chem.* **2007**, *85*, 885.
- (40) Sánchez-Nieves, J.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 2404.
- (41) Huy, N. H. T.; Donnadiou, B.; Bertrand, G.; Mathey, F. *Chem. Asian J.* **2009**, *4*, 1225.
- (42) Graham, T. W.; Udachin, K. A.; Carty, A. J. *Chem. Commun.* **2006**, 2699.
- (43) Pohl, S. *Chem. Ber.* **1979**, *112*, 3159.
- (44) Shimidzu, T.; Yamana, K.; Maikuma, S. *Tetrahedron Lett.* **1984**, *25*, 4237.
- (45) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635.