

Terminal and Four-Coordinate Vanadium(IV) Phosphinidene Complexes. A Pseudo Jahn–Teller Effect of Second Order Stabilizing the V–P Multiple Bond

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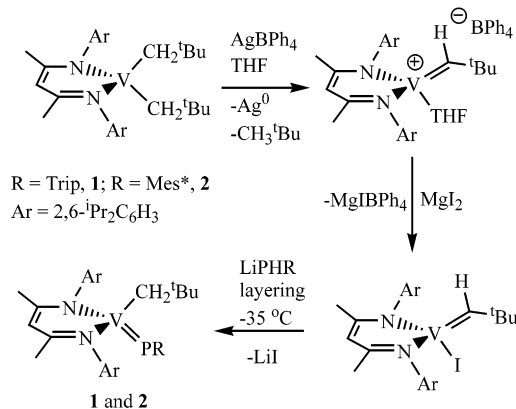
Examples of group 4 and 5 early-transition metal phosphinidenes include only a handful of complexes of Ti,¹ Zr,² Nb,³ and Ta.⁴ Recently, we reported a four-coordinate titanium complex containing a terminal phosphinidene functionality.^{1b} Ti-phosphinidenes are expected to be unstable, because of the hard–soft contrast among these elements. The recent isolation of the first complex containing a Ti=P bond was in part accomplished by stabilizing kinetically this reactive functionality and by applying an α -hydrogen migration strategy using a nucleophilic alkylidene ligand.^{1b,5,6} Inspired by this result, we applied an analogous strategy for preparing a family of four-coordinate complexes with a thus far unknown terminal V=P functionality. We have also determined that these radical species are stabilized not only kinetically but also via a pseudo Jahn–Teller effect of second order.⁷

To prepare a vanadium phosphinidene by α -hydrogen migration, we first synthesized a four-coordinate vanadium–neopentylidene complex [(Nacnac)V=CH^tBu(THF)][BPh₄]⁸ from the one-electron oxidation of (Nacnac)V(CH₂^tBu)₂ (Scheme 1).^{8,9} Anion exchange of BPh₄ for I leads to a much more stable and neutral four-coordinate alkylidene complex of vanadium, (Nacnac)V=CH^tBu(I) (Scheme 1), thus eluding disproportionation reactions.⁸ When a solution of (Nacnac)V=CH^tBu(I) is treated with a primary lithium phosphide salt LiPHR (R⁻ = Trip, Mes*^{*}; Trip = 2,4,6-ⁱPr₃C₆H₂, Mes*^{*} = 2,4,6-^tBu₃C₆H₂), salt elimination is observed concomitant with formation of a highly lipophilic dark residue, which contains a mixture of paramagnetic and diamagnetic products.

However, when an ethereal solution of LiPHR is layered onto a similarly cold Et₂O solution of (Nacnac)V=CH^tBu(I), and the reaction mixture is allowed to react for 4 h at low temperatures, a new product is isolated. The reaction must be rapidly filtered while cold, and the filtrate must be concentrated and kept at low temperatures for 5 days to obtain dark blocks of the paramagnetic material in acceptable yields. Under these conditions, crystals are obtained reproducibly (68%, R = Trip (**1**); 79%, R = Mes*^{*} (**2**), Scheme 1).¹⁰ Crystals of **1** and **2** decompose over several hours at room temperature in solution or in the solid state in the order **1** > **2**, suggesting that these systems are stabilized kinetically depending on the encumbering group on P. We have determined that these are crystals of the vanadium phosphinidene complexes (Nacnac)V=PR(CH₂^tBu). A reasonable proposal is that the formation of complexes **1** and **2** occurs through the putative phosphide intermediate (Nacnac)V=CH^tBu(PHR), which then undergoes α -H migration to furnish the V=PR bond.

Solution magnetic measurements of compounds **1** and **2** are consistent with a d¹ V(IV) paramagnetic species.¹⁰ At room temperature, complexes **1** and **2** exhibit a magnetic moment of 2.09 and 2.14 μ_B , respectively, which is in close agreement with the calculated values obtained by applying the average g_{iso} values from the EPR spectra. In fact, the room-temperature X-band EPR spectra for **1** and **2** not only support the present oxidation state but display

Scheme 1. Synthesis of **1** and **2** from a Four-Coordinate Vanadium(IV) Alkylidene Complex (Nacnac)V=CH^tBu(I)



a 16-line pattern resulting from hyperfine coupling of the unpaired electron to V ($I = 7/2$, 99.6%, $A_{iso} \approx 70$ G) and superhyperfine coupling to P ($I = 1/2$, 100%, $A_{iso} \approx 40$ G),¹¹ respectively (Figure 1).¹⁰

To confirm the proposed connectivity for the vanadium-phosphinidenes generated from the reaction of (Nacnac)V=CH^tBu(I) with 1 equiv of LiPHR, we collected X-ray diffraction data for single crystals from both reactions.¹⁰ The molecular structure for each complex reveals a four-coordinate vanadium center containing a terminal phosphinidene functionality (Figure 2). In the crystal structure of both complexes **1** and **2**, there are two crystallographically independent but chemically equivalent molecules confined in the asymmetric unit.⁹ The geometry at vanadium is best described as distorted tetrahedral, and the short V–P bond length for each derivative is consistent with a metal–ligand multiple bond (**1**, 2.174(4) Å; **2**, 2.1602(6) Å). These values are considerably shorter than those for the four-coordinate vanadium phosphide (Nacnac)V-(PHTrip)₂ (**3**) (V–P_{phosphide} = 2.383(6) and 2.443(5) Å)¹⁰ or vanadium- μ^2 -phosphinidene complexes.^{12,13} In addition, the hybridization of the former alkylidene carbon is now changed, which

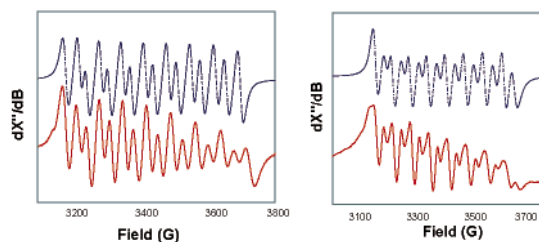


Figure 1. X-band EPR spectra of complexes **1** (left) and **2** (right) recorded at room temperature in toluene. Experimental spectrum is red, and the simulated spectrum is blue. For the line width of **1**, $W_{iso} = 16.5 - 0.5m_1 + 5m_2^2$, and for **2**, $W_{iso} = 20 - 5m_1 + 6m_2^2$. For **1**, $g_{iso} = 1.960$, and for **2**, $g_{iso} = 1.963$.

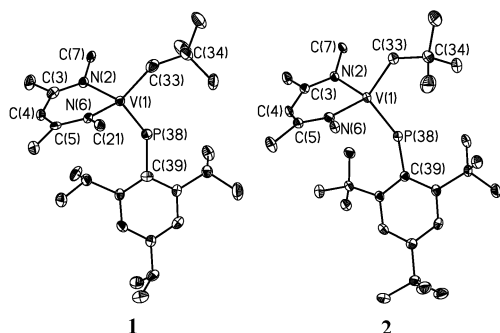


Figure 2. Molecular structures of **1** and **2** with thermal ellipsoids at the 50% probability level. One of two crystallographically independent molecules found in the asymmetric unit, H-atoms, and aryl groups with the exception of the ipso-carbons on the α -nitrogens have been omitted for clarity. One solvent molecule (*n*-hexane) found in the asymmetric unit for the structure of **2** has also been omitted for simplicity.

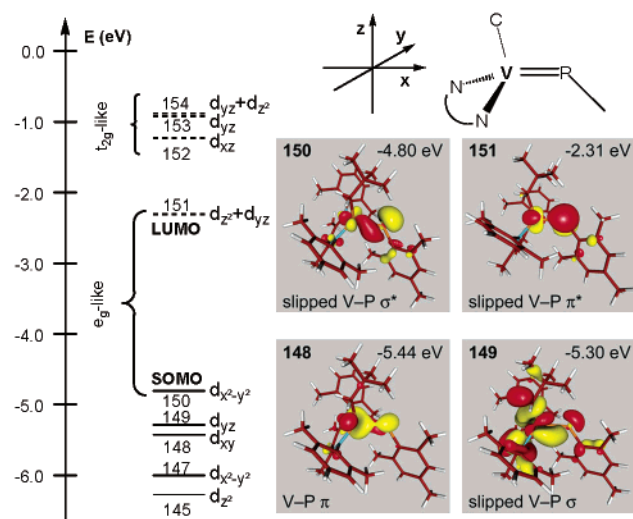


Figure 3. Molecular orbital diagram for the model $(\text{Nacnac})\text{V}=\text{PMe}(\text{CH}_2^t\text{Bu})$. The orbital representations for the LUMO, SOMO, and V–P bonding orbitals (#148–151) are depicted.

is indicated partially by the acute $\text{V}-\text{C}_\alpha-\text{C}_\beta$ angle (**1**, $130.8(3)^\circ$, **2**, $132.5(5)^\circ$) as well as the elongated $\text{V}-\text{C}_\alpha$ bond length (**1**, $2.034(4)$ Å; **2**, $2.053(2)$ Å) relative to that of the former alkylidene precursor ($\text{V}-\text{C}_\alpha-\text{C}_\beta$, $158.7(3)^\circ$; $\text{V}=\text{C}$, $1.787(3)$ Å).⁸ The very short $\text{V}=\text{P}$ bond length could arise from formation of a pseudo triple bond,^{1b,c} but the radical nature of complexes **1** and **2**, coupled with the variable $\text{V}-\text{P}-\text{C}_{\text{ipso}}$ angles, could suggest otherwise (**1**, $136.6(5)^\circ$; **2**, $153.28(6)^\circ$).

To address the factors governing structure and bonding in complexes **1** and **2**, we carried out theoretical calculations on the vanadium phosphinidene model complex $(\text{Nacnac})\text{V}=\text{PMe}(\text{CH}_2^t\text{Bu})$ ($\text{Me} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) using high level density functional theory (DFT).¹⁰ The optimized geometry reproduced the key features of the solid-state structure of **1** expectedly well. Although the singly occupied molecular orbital (SOMO) has $d_{x^2-y^2}$ character and can be construed as ill-suited for bonding with P, the molecule distorts from a tetrahedral geometry to facilitate a bonding interaction of vanadium d-orbital with the PAr ligand (referred to as a slipped σ^*). A structural distortion of the $\text{V}-\text{P}$ σ bond (along the *y*-axis) from a perfect T_d geometry causes substantial intermixing

and energy change of the SOMO (#150) and lowest unoccupied molecular orbital (LUMO, #151, Figure 3). The core distortion can be rationalized intuitively by realizing that the d^1 -configuration of the V(IV) center would give rise to a second-order Jahn–Teller distortion in a homogeneous ligand field.⁷ In addition, the bond order was calculated to be 1.724 from the computed wave function, confirming the double bond character of the $\text{V}-\text{P}$ interaction.

In summary, a strategy for preparing a low-coordinate and terminal titanium phosphinidene complex derived from α -H-abstraction can be expanded to the lighter congener of group 5 transition metals, vanadium. The theoretical and experimental results suggest tantalizingly that complexes **1** and **2** are surprisingly stable, which is in part due to distortion from a tetrahedral environment, consequently stabilizing the $\text{V}-\text{P}$ multiple bond and the orbital housing the unpaired electron. We are currently exploring the reactivity offered by these one-electron metallaradicals containing metal–ligand multiple bonds.

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Supporting Information Available: Complete experimental preparation, computational, and crystallographic data for compounds **1–3** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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