DOI: 10.1002/anie.200700059

VIP Phosphorus Radicals

An Isolable and Monomeric Phosphorus Radical That Is Resonance-Stabilized by the Vanadium(IV/V) Redox Couple**

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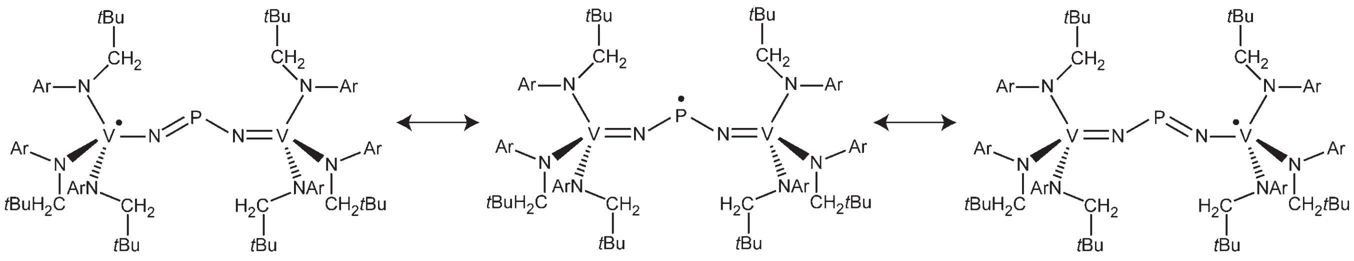
Dedicated to Professor Herbert W. Roesky

The synthesis of isolable radicals involving the heavier main-group elements represents a significant chemical challenge.[1] Sterically stabilized phosphorus-centered radicals which are persistent and monomeric in solution have been synthesized.[2–4] Of particular note are the "jack-in-the-box" diphosphines of Lappert, Power, and co-workers, which dissociate into sterically stabilized and persistent radicals upon solvation.[5,6] Also, a *p*-phosphaquinone radical anion has been studied[7] and the resonance-stabilized 1,3-diphosphaallyl[8] and diphosphanyl[9] radicals have been isolated. Yet the synthesis of a neutral phosphorus radical that exists as a monomer even in the solid state has been elusive. Herein we report such a phosphorus radical, a radical that is electronically stabilized by the ability to delocalize its P-radical character onto a pair of nitridovanadium metalloligands. Prior to tackling the synthesis, our quantum chemical calculations predicted that the magnitude of the electronic stabilization relative to $^{\bullet}PH_2$ would be on the order of 24 kcal mol^{-1}.

One significant difference between transition metals and the heavier main-group elements is that the former are generally susceptible to one-electron redox chemistry, whereas the latter are more limited to electron-pair chemistry.[1] This distinction prompted our choice of two nitridovanadium(V) trisanilide moieties as ligands for the stabilization of divalent phosphorus. Hence, contributing resonance structures with vanadium(IV) character would stabilize a P-centered radical (Scheme 1). In addition, *N*-neopentylanilide ligands would add a degree of steric protection to a radical with the target formula $[^{\bullet}P\{NV[N(Np)Ar]_3\}_2]$ (**1**; Np = neopentyl, Ar = 3,5-$Me_2C_6H_3$).

The reaction of sodium azide with the vanadium(III) precursor $[V\{N(Np)Ar\}_3]$ (**2**) cleanly generates the sodium salt of nitride anion $[N{\equiv}V\{N(Np)Ar\}_3]^{1-}$ (**3**) as a fine yellow powder in a single step in 77% yield. A similar reaction has been described previously for the *tert*-butyl derivative $[V\{N(tBu)Ar\}_3]$.[10] We exploited the nucleophilicity of anion **3** through its reaction with 0.5 equivalents of PCl_3 to generate the red-brown radical precursor $[ClP\{NV[N(Np)Ar]_3\}_2]$ (**1**-Cl) in 48% yield after separation from $[ClV\{N(Np)Ar\}_3]$ (**2**-Cl), which is generated as a by-product of the reaction, as confirmed by independent synthesis.[11] Each pair of neopentyl methylene protons on the anilide ligands of **1**-Cl is diastereotopic as assessed by ^1H NMR spectroscopy, owing to the pyramidal geometry at the phosphorus atom.

Access to target radical **1** is provided by the one-electron reduction of **1**-Cl, which can be effected by a variety of reducing agents. One such reductant, the potent chlorine-atom abstractor $[Ti\{N(tBu)Ar\}_3]$,[12–14] reacts rapidly with **1**-Cl in diethyl ether solution to smoothly generate [ClTi{N-



Scheme 1. Resonance stabilization of radical **1** provided by the vanadium(IV/V) redox couple.

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[**] We thank the U.S. National Science Foundation for support of this research through grant CHE-0316823 and through a predoctoral fellwoship to N.A.P, and the MIT Undergraduate Research Opportunities Program for support of P.A. We also would like to thank Prof. Dr. Anthony Spek (Utrecht) for his validation of the crystal structure of **1**.

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(tBu)Ar}$_3$] and the radical **1**, the identities of which were confirmed by NMR and EPR spectroscopy (see below). This reaction suggests that the chlorine atom in **1**-Cl is sufficiently sterically accessible to form a bridge to the crowded titanium center in the process of Cl-atom transfer. For synthetic purposes and for easy separation, **1**-Cl can also be cleanly reduced to **1** with potassium graphite.[3] Crystallization of the reaction product from pentane provides dark brown crystals of **1** in 77 % yield. The ^{1}H NMR spectrum of **1** consists only of two broad resonances at $\delta = 1.4$ and 2.8 ppm. The solution magnetic susceptibility of **1** was measured by the Evans method[15,16] and yielded a magnetic moment of 1.67 μ_B, consistent with the presence of a single unpaired electron.

The EPR spectrum of **1** shows a complex splitting pattern. This spectrum was modeled with hyperfine couplings to two ^{51}V nuclei ($I = 7/2$, 99.75 %, $A_{iso} = 23.8$ G) and one ^{31}P nucleus ($I = 1/2$, 100 %, $A_{iso} = 42.5$ G).[17] The simulated and experimental spectra are presented in Figure 1. The large value of the ^{31}P coupling is indicative of substantial radical character on the phosphorus atom, while the ^{51}V coupling indicates some degree of vanadium(IV) character. A comparison of these values to those of other phosphorus(II) and vanadium(IV) complexes can be found in Table 1. These data show that both the ^{51}V and ^{31}P hyperfine couplings are smaller than in traditional localized P^{II} and V^{IV} radicals, consistent with a significant degree of delocalization.

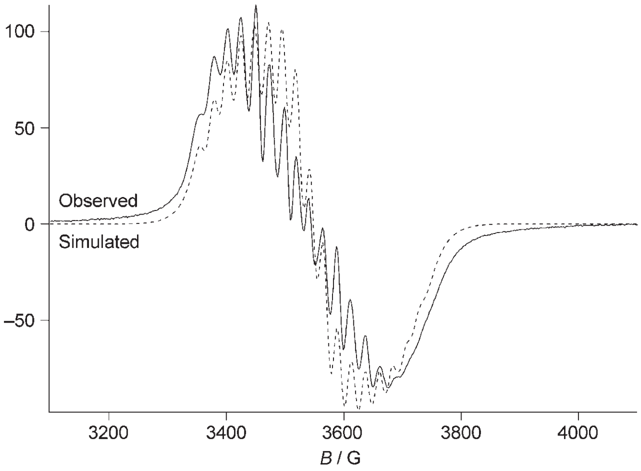

Figure 1. Observed and simulated EPR spectrum of **1**. Hyperfine coupling constants and g values are listed in Table 1.

To further illuminate the delocalization of the unpaired electron in this system, quantum chemical calculations on the model system [$^{\bullet}$P{NV[N(Me)Ph]$_3$}$_2$] (**1m**) were performed by using the ADF package,[18] with **1m** restricted to C_2 symmetry; the rotational axis was the z axis and the NPN moeity was positioned in the xz plane. These calculations predict that the major orbital contributions to the SOMO (Figure 2) are the phosphorus 3p$_y$ orbital (31.30 %) and the vanadium 3d$_{xy}$ (39.49 % over two vanadium atoms) and 3d$_{x^2-y^2}$ (8.33 %) orbitals. The combined EPR and computational data indicate that both the phosphorus-centered and vanadium-centered radical resonance structures (Scheme 1) contribute substantially to the electronic structure of **1**.

Table 1: Hyperfine coupling constants and g values of selected P^{II} and V^{IV} radicals in toluene at about 25 °C (unless otherwise indicated).

Radical species	A_{iso} [G]	g_{av}
[P{NV[N(Np)Ar]$_3$}$_2$]	42.5 (^{31}P), 23.8 (^{51}V)	1.984[a]
P(OMes*)$_2$	82 (^{31}P)	1.999[19]
P(Mes*)(OtBu)	100 (^{31}P)	2.005[19]
P[CH(SiMe$_3$)$_2$]$_2$	96.3 (^{31}P)	2.009[20]
P[N(SiMe$_3$)$_2$]$_2$	91.8 (^{31}P)	2.008[20]
P[Mes*][C$_6$H$_2$(tBu)$_2$O]$^-$	93 (^{31}P)	2.007[b],[4]
P[CH(SiMe$_3$)$_2$][NiPr$_2$]	63 (^{31}P), 3.7 (^{14}N)	2.005[20]
P[NiPr$_2$][N(SiMe$_3$)$_2$]	77.2 (^{31}P), 5.2 (^{14}N)	2.007[20]
P[CH(SiMe$_3$)$_2$][NMe$_2$]	65 (^{31}P)	2.008[20]
[ClV{N(Np)Ar}$_3$]	67.9 (^{51}V)	1.973[a]
[ClV{(Me$_3$SiNCH$_2$CH$_2$)$_3$N}]	147 (^{51}V)	1.963[c],[21]
[V(CH$_2$SiMe$_3$)$_4$]	54.5 (^{51}V)	1.968[22]
[V(NMe$_2$)$_4$]	65 (^{51}V)	1.975[d],[23]
[V(NEt$_2$)$_4$]	66 (^{51}V)	1.977[e],[24]

[a] This work. [b] THF (295 K). [c] Toluene glass (92 K). [d] Frozen CyMe (120 K). [e] Benzene (ca. 300 K). Mes* = 2,4,6-tBu$_3$C$_6$H$_2$.

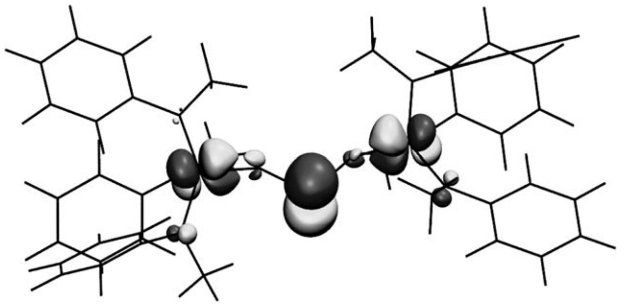

Figure 2. SOMO of **1m**, showing delocalization of the radical throughout the V-NPN-V π system.

The solid-state structure of radical **1** was determined by single-crystal X-ray diffraction,[25] which revealed a monomer with no close contacts involving the two-coordinate phosphorus atom. The structure shows the expected geometry with a bent N-P-N linkage (110.9(3)°; Figure 3a). Viewed from another perspective, radical **1** can be thought of as a mixed-valence vanadium(IV/V) system with a bridging NPN ligand, a ligand which to our knowledge has not been described previously in transition-metal chemistry. This ligand is formally a heavy-azide analogue, a class of molecules that has garnered attention from our group and others.[26–30] The electron delocalization represented by the resonance structures in Scheme 1 has the effect of contracting the P–N bonds by about 0.055 Å and lengthening the V–N bonds by approximately 0.036 Å when compared to localized single P–N and double V–N bonds, such as those in **1**-SePh (see below).

Radical **1** undergoes reactions at its phosphorus center to generate new phosphorus–element bonds. For example, reaction between **1** and 0.5 equivalents PhEEPh (E = S, Se) cleanly generates dark red-brown, diamagnetic [PhEP{NV[N(Np)Ar]$_3$}$_2$] (**1**-EPh). That bond formation takes place at the phosphorus center was confirmed by the

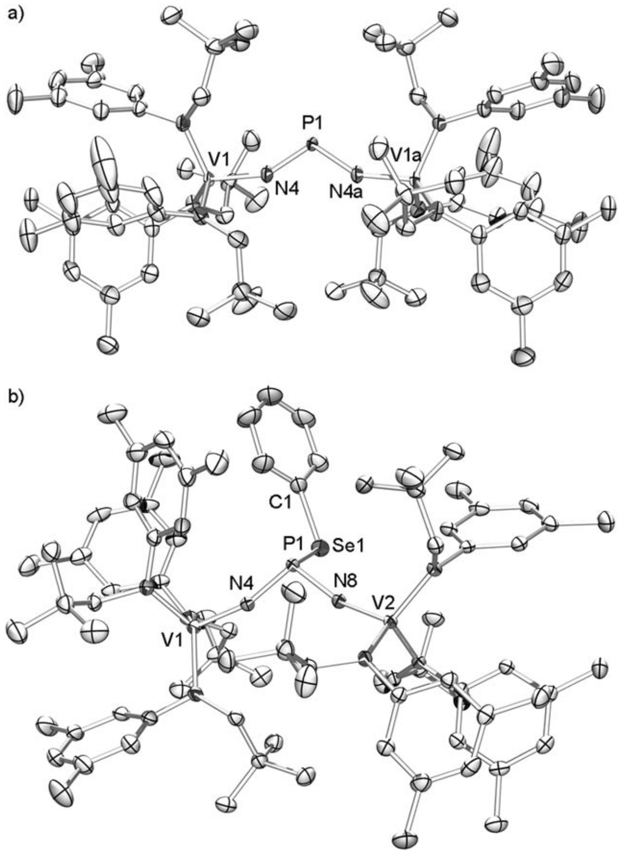

Figure 3. a) Molecular structure of **1** with 50% probability ellipsoids. Selected bond lengths [Å] and angles [°]: V1-N4 1.724(2), P1-N4 1.630(7), P1-N4a 1.614(7); P1-N4-V1 148.9(3), N4-P1-N4a 110.9(3), P1-N4a-V1a 150.8(3). b) Molecular structure of **1**-SePh with 50% probability ellipsoids. Selected bond lengths [Å] and angles [°]: C1-Se1 1.910(4), Se1-P1 2.3021(9), P1-N8 1.674(2), P1-N4 1.681(2), V1-N4 1.6824(19), N8-V2 1.6930(19); C1-Se1-P1 101.62(15), N8-P1-N4 103.63(10), N8-P1-Se1 98.23(8), N4-P1-Se1 102.49(8), P1-N4-V1 162.68(13), P1-N8-V2 160.46(14).

presence of only a single anilide ligand environment as assessed by ^{1}H NMR spectroscopy (again with diastereotopic neopentyl methylene units), by the presence of ^{31}P,^{77}Se coupling ($J_{\text{PSe}} = 327$ Hz) in the ^{77}Se NMR spectrum of **1**-SePh, and by a single-crystal X-ray diffraction study on **1**-SePh (Figure 3b). Additionally, treatment of **1** with 0.5 equivalents of *p*-tetrachlorobenzoquinone generates dark-red, diamagnetic [{{[Ar(Np)N]$_3$VN}$_2$P}$_2$(μ-OC$_6$Cl$_4$O)] (**4**). The ^{1}H NMR spectrum of **4** is similar to those of **1**-EPh, except that the resonances, especially those of the methylene and *ortho* aryl protons, are broadened in a manner indicative of restricted rotation. All three of these radical-reaction products are generated in nearly quantitative yield (> 95%), as assessed by ^{1}H NMR spectroscopy in the presence of an internal standard. Treatment of radical **1** with milder reagents including white phosphorus and Gomberg's dimer, both of which often react with less-stabilized radicals,[3,31,32] gave rise to negligible reaction at room temperature.

As a measure of the radical stability in **1**, the homolytic bond-dissociation energy of the P–H bond in the model compound [HP{NV[N(Me)Ph]$_3$}$_2$] (**1m**-H) was calculated by using DFT methods. The P–H bond in **1m**-H was computed to be 24 kcal mol^{-1} weaker than that in PH$_3$ (using the isodesmic reaction **1m**-H + PH$_2$→**1m** + PH$_3$, for which $\Delta E = -24$ kcal mol^{-1}), thus putting the P–H bond strength in **1**-H at roughly 58 kcal mol^{-1}.[33] The predicted weakness of the P–H bond in **1m**-H is indicative of a large stabilization provided by the delocalization of the unpaired electron as discussed above. Accordingly, the synthesis of **1**-H, a potential potent H-atom donor, has proven to be elusive. No reaction was observed between **1** and the common H-atom sources *n*Bu$_3$SnH, *n*Bu$_2$SnH$_2$, and [(η^5-C$_5$H$_5$)(CO)$_3$MoH][34,35] in diethyl ether at room temperature. A synthesis of **1**-H from **1**-Cl was attempted by using one equivalent of LiHBEt$_3$ as a hydride source. When LiHBEt$_3$ was added to a solution of **1**-Cl at room temperature, a rapid reaction was observed with vigorous gas evolution. When assayed by low-temperature ^{1}H NMR spectroscopy in [D$_8$]toluene, the reaction did not proceed below −20 °C. As the reaction mixture warmed, the generation of H$_2$ ($\delta = 4.49$ ppm) and **1** was observed. On the basis of bond-dissociation enthalpy calculations of **1m**-H, the generation of H$_2$ from two equivalents of the putative intermediate **1**-H is a thermodynamically feasible process [Eq. (1)].

$$\mathbf{1}\text{-Cl} + \text{LiHBEt}_3 \rightarrow \mathbf{1} + \frac{1}{2}\,\text{H}_2 + \text{LiCl} + \text{BEt}_3 \qquad (\mathbf{1})$$

Herein we have reported on [$^{\bullet}$P{NV[N(Np)Ar]$_3$}$_2$] (**1**), a neutral phosphorus radical that is a stable monomer even in the solid state. While this molecule undergoes selected radical bond-formation reactions at its phosphorus center, the resonance stabilization provided by the two vanadium metalloligands tempers its reactivity to a significant extent. It is expected that the P-radical character of the system may be tuned, for example, by changing the metal center in the metalloligands (for example, Nb in place of V). In addition, the easily synthesized redox-active metalloligand[36,37] employed here may be useful for the stabilization of radicals centered on other heavy main-group elements.

Received: January 5, 2007

Keywords: metalloligands · phosphorus · radicals · resonance stabilization · vanadium

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