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A Stable Dialkylphosphinyl Radical

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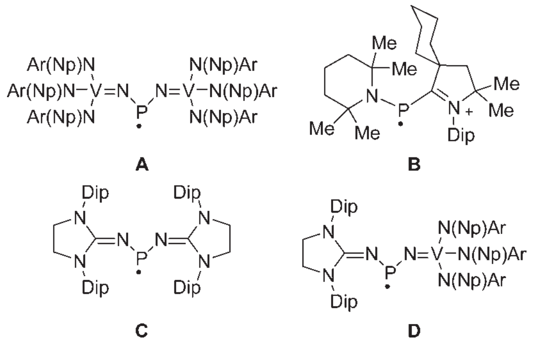
S Supporting Information

ABSTRACT: Dialkylphosphinyl radical **1** was synthesized as thermally stable yellow crystals and found to be monomeric both in solution and in the solid state. EPR spectrum showed that the spin density of **1** is mainly localized on the 3p orbital of the dicoordinated phosphorus atom. A distinct absorption band due to the electronic transition from nonbonding electron pair orbital to singly occupied 3p orbital on the phosphorus atom of **1** was observed at 445 nm in solution. Phosphinyl radical **1** underwent facile reaction with carbon tetrachloride, hydrogen abstraction, and a unique reaction with a persistent radical, galvinoxyl, giving a cyclic phosphaalkene and a silylether.

Phosphinyl radicals are fascinating reactive intermediates in phosphorus chemistry because they have a bifunctional dicoordinated phosphorus center with an unpaired electron and a lone pair.[1] Although several persistent phosphinyl radicals stabilized by kinetic and resonance stabilization have been reported,[2] stable phosphinyl radicals that do not dimerize in the solid state[1b] are still quite rare. Very recently, stable phosphinyl radicals and related phosphinyl radical ions were synthesized by Cummins et al.[3] and Bertrand et al.[4,5] (Chart 1). These radicals have at least one nitrogen substituent that can affect the electronic properties of the phosphorus center.

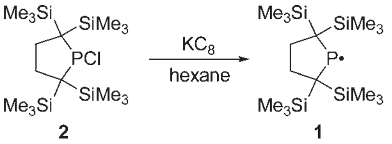
Chart 1. Stable Dicoordinated Phosphorus Centered Radicals[a]



[a]Np = neopentyl, Ar = 3,5-dimethylphenyl, Dip = 2,6-diisopropylphenyl.

Neutral dialkylphosphinyl radicals, which are least perturbed electronically by substituents and should be suitable for investigation of intrinsic properties of phosphinyl radicals such as electronic structures and reactivity, have not been isolated as a monomeric form in the solid state. Bis(trimethylsilyl)methyl (Dis)-substituted phosphinyl radical, $Dis_2P\cdot$ reported by Lappert and Power et al. exists as a monomeric form in the gas phase and in solution but it dimerizes to give the corresponding diphosphane Dis_2PPDis_2 upon crystallization.[6] We have extensively explored the chemistry of isolable dialkyl-substituted divalent species of group-14 elements (silylene, germylene, and stannylene) utilizing a helmet-shaped bidentate alkyl ligand, 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl (R^H_2).[7] The successful synthesis of these species prompted us to examine the synthesis of dialkylphosphinyl radical utilizing the R^H_2 ligand. We report herein synthesis, structure, and reactions of the first stable dialkylphosphinyl radical, 2,2,5,5-tetrakis(trimethylsilyl)-1-phosphacyclopentane-1-yl ($R^H_2P\cdot$, **1**), which is monomeric both in solution and in the solid state.

Phosphinyl radical **1** was synthesized as air-sensitive yellow crystals in 57% yield on a multigram scale by the reduction of the corresponding dialkylchlorophosphine **2**[8] with potassium graphite in hexane at room temperature for 19 days (eq 1). The ^1H NMR spectrum of the yellow crystals shows no signals except for very weak signals due to a trace amount of hydrophosphine R^H_2PH (**3**) and hexane used as solvent for crystallization.[9] Radical **1** is highly air sensitive but thermally very stable; it can survive at room temperature for several months in an inert atmosphere both in 3-methylpentane (3-MP) solution and in the solid state.



(1)

X-ray analysis showed that **1** exists as a monomeric form in the solid state as shown in Figure 1. The shortest distance between the dicoordinated phosphorus centers of 6.9414(5) Å is far longer than the sum of van der Waals radii of two phosphorus atoms (3.6 Å)[10a] indicating that **1** is monomeric in the solid state. The P−C bond length of **1** [1.869(1) Å] is within the range of standard P−C single bond lengths (1.84−1.87 Å)[10b] but slightly shorter than those of hydrophosphine **3** [1.886(2) and 1.885(2) Å]. The C1−P−C4 angle of **1** of 96.16(6)° is comparable to that of **3** [96.28(7)°].

EPR spectrum of **1** in 3-MP at 298 K showed a doublet signal (g-factor = 2.0086) due to a coupling with one ^{31}P nucleus (Figure 2a). The hyperfine coupling constant (hfc) due to ^{31}P nucleus, $a(^{31}P)$ of 9.07 mT, is in the range of typical hfc's of the pertinent phosphinyl radicals (6.5−9.6 mT)[1−6] and close to those of structurally similar $Dis_2P\cdot$ (9.63 mT)[6] and related transient dialkylphosphinyl radicals (9.57 mT for $Me_2P\cdot$[11a] and 9.67 mT for i-$Pr_2P\cdot$[11b]). On the basis of the intensity relative

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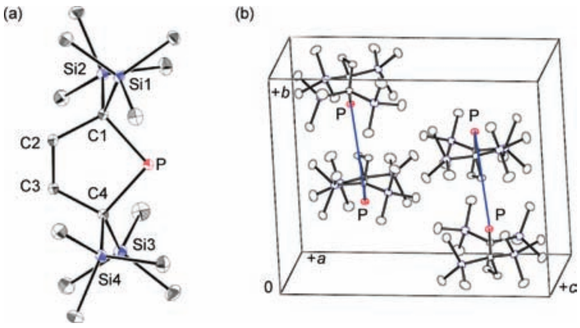


Figure 1. (a) Molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P−C1 1.869(1); P−C4 1.869(1); C1−C2 1.562(2); C2−C3 1.538(2); C3−C4 1.562(2); C1−Si1 1.913(1); C1−Si2 1.916(1); C4−Si3 1.914(1); C4−Si4 1.916(1); C1−P−C4 96.16(6). (b) A packing diagram of **1**. The shortest distance between the dicoordinated phosphorus atoms shown as a blue line is 6.9414(5) Å.

to those of the major doublet signal, the doublet satellite signals with the hfc of 1.73 mT are assigned to signals due to the four trimethylsilyl ^{29}Si nuclei.[12]

EPR spectrum of **1** in 3-MP glass matrix displayed typical axial symmetry (Figure 2b). The *g*-factors and hfc tensors were determined as follows: $g_{//}$ = 2.0013, $a_{//}(^{31}\mathrm{P})$ = 27.9 mT, $g_{\perp}$ = 2.0084, and $a_{\perp}(^{31}\mathrm{P})$ = 0.49 mT. Accordingly, the isotropic and anisotropic coupling constants are a_{iso} = 9.63 mT and a_{aniso} = 9.14 mT, respectively. On the basis of the comparison with hfc's of atomic phosphorus,[13] 70% and 2% spin are localized on the 3p(P) and 3s(P) orbitals in **1**, respectively. The spin localization of **1** is significantly higher than those of the hitherto known radicals **B**[4] [57% and 2% for 3p(P) and 3s(P)] and **C**[5] [62% and 2% for 3p(P) and 3s(P)].

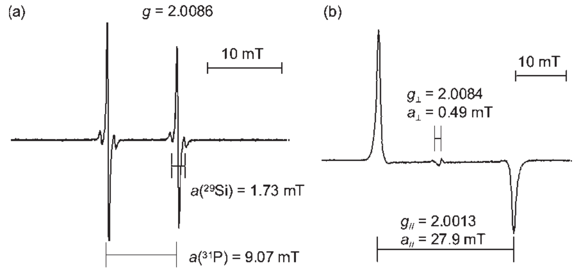


Figure 2. EPR spectra of **1** in (a) 3-methylpentane (3-MP) solution at 298 K and (b) 3-MP frozen solution at 112 K.

Theoretical calculations were carried out to obtain further insight into the electronic structure of **1**.[14] The optimized structure ($\mathbf{1}_{\mathrm{opt}}$) calculated at the UB3LYP/6-31G(d) level well reproduced the structure of **1** determined by X-ray analysis. The SOMO of $\mathbf{1}_{\mathrm{opt}}$ calculated at the UHF/6-31G(d) level was almost pure 3p orbital on the dicoordinated phosphorus atom with small contribution of $\sigma^*(\mathrm{Me_3Si{-}C})$ orbitals, while the HOMO of $\mathbf{1}_{\mathrm{opt}}$ was a nonbonding orbital on the phosphorus atom (Figure 3). The Mulliken spin densities on phosphorus atom and each silicon atom of $\mathbf{1}_{\mathrm{opt}}$ calculated at the UM05-2X/def2-SVP level are 0.90 and 0.02−0.03, respectively, which are consistent with the considerably high spin localization on the phosphorus atom and the existence of small $3p(\mathrm{P}){-}\sigma^*(\mathrm{Me_3Si{-}C})$ orbital interactions of **1**.[15] The spin density on the phosphorus atom of $\mathbf{1}_{\mathrm{opt}}$ is slightly smaller than that of parent 1-phosphacyclopentane-1-yl, $\mathbf{1}_{\mathrm{H}}$ (1.00), suggesting that radical **1** is thermodynamically stabilized to some extent due to the $3p(\mathrm{P}){-}\sigma^*(\mathrm{Me_3Si{-}C})$ interactions. This is supported by the isodesmic reaction (eq 2) showing that radical $\mathbf{1}_{\mathrm{opt}}$ is more stable than $\mathbf{1}_{\mathrm{H}}$ by 6.8 kcal mol^{-1} at the (U)B3LYP/6-31G(d) level.

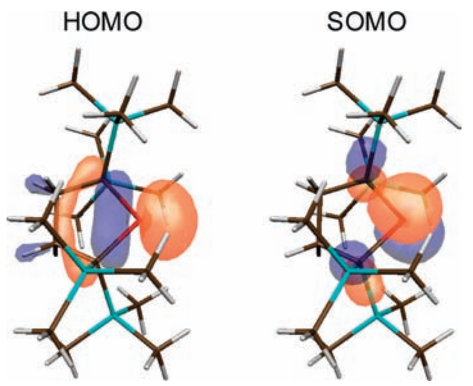
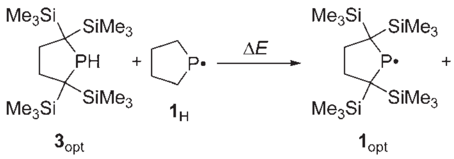


Figure 3. Highest occupied molecular orbital (HOMO, left) and singly occupied molecular orbital (SOMO, right) of $\mathbf{1}_{\mathrm{opt}}$ calculated at the UHF/6-31G(d)//UB3LYP/6-31G(d) level.



(2)

UV−vis spectrum of **1** in 3-MP showed two distinct absorption bands at 445 nm (ε 157, band I) and 304 nm (ε 1790, band II) (Figure 4). Band I is the origin of the yellow color of **1**. Judging from TD-DFT calculations of $\mathbf{1}_{\mathrm{opt}}$, band I is assignable to n(P) → 3p(P) transition (HOMO-SOMO transition).[14] To the best of our knowledge, this is the first observation and characterization of electronic transitions of phosphinyl radical by UV−vis spectroscopy. Band II is assigned to overlapped transitions of σ(C−P) → 3p(P) and $\sigma(\mathrm{C{-}SiMe_3}) \rightarrow 3p(\mathrm{P})$.[16]

Compound **1** shows high reactivity as a phosphinyl radical toward various reagents even though the phosphorus center of **1** is highly protected by the helmet-shaped $\mathrm{R^H_2}$ ligand (Chart 2).

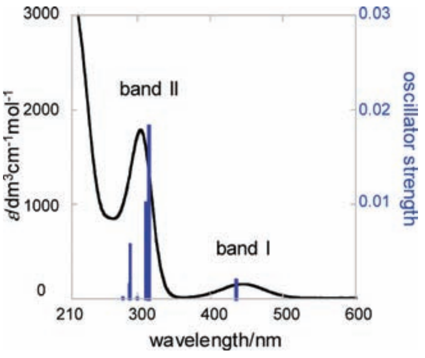
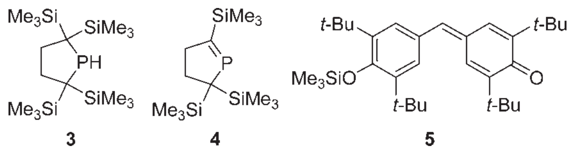


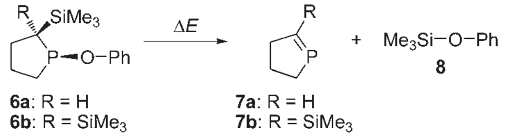
Figure 4. UV−vis absorption spectrum of **1** in 3-MP at room temperature. Superimposed vertical blue bars indicate band positions and oscillator strengths of $\mathbf{1}_{\mathrm{opt}}$ calculated at the TD-UB3LYP/6-311+G(d,p)//UB3LYP/6-31G(d) level.

Chart 2. Reaction Products



The reaction of **1** with carbon tetrachloride in hexane completed within a minute to afford chlorophosphine **2** in 49% yield.[17] Hydrogen abstraction of **1** from cyclohexa-1,4-diene in the dark condition also occurred within 3 days to give the corresponding hydrophosphine **3** and benzene in 99 and 49% yields, respectively. This is the first example of hydrogen abstraction of phosphinyl radical from a hydrocarbon. The reaction of **1** with a persistent oxygen-centered radical, galvinoxyl, afforded interesting products, phosphaalkene **4** and trimethylsilyl ether **5** instead of a simple radical recombination product.

Possible mechanism for formation of **4** and **5** can involve the radical coupling between phosphinyl radical center of **1** and terminal oxygen atom of galvinoxyl followed by elimination of silyl ether **5** to give phosphaalkene **4**.[18] In the latter process, severe steric repulsion between geminal trimethylsilyl groups would be responsible for the facile elimination of silyl ether **5** giving phosphaalkene **4**. Consistent with this explanation, the theoretical calculations for the model reactions (eq 3) at the B3LYP/6-31G(d) level show that the reaction of **6a** (R = H) giving **7a** and **8** is slightly exothermic ($\Delta E = -0.2$ kcal mol^{-1}), while that of more sterically congested **6b** (R = $SiMe_3$) giving **7b** and **8** is considerably exothermic ($\Delta E = -10.0$ kcal mol^{-1}).



(3)

Further investigations of the reactivity of **1** are in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and full characterizations for **1**−**5**, details of theoretical calculations, and X-ray crystallographic data of **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Molecular structures of chlorophosphine **2** and hydrophosphine **3** were determined by single crystal X-ray diffraction study. For details, see Supporting Information.

(9) Purity of **1** was estimated to be >98% on the basis of NMR and EPR spectroscopies.

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(12) The $a(^{29}Si)$ value of **1** is similar to those of the isoelectronic anion radical of 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopentane-1,1-diyl (1.28−1.70 mT). Ishida, S.; Iwamoto, T.; Kira, M. *J. Am. Chem. Soc.* **2003**, *125*, 3212.

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(14) TD-DFT calculations were carried out at the UB3LYP/6-311+G(2df,p)//UB3LYP/6-31G(d) level. The shapes of Kohn−Sham orbitals were quite similar to those of the corresponding molecular orbitals calculated at the UHF/6-31G(d) level. Details including full citations are in Supporting Information.

(15) Spin densities estimated by theoretical calculations are usually higher than those by powder pattern EPR spectrum.[4,5]

(16) TD-DFT calculations showed that the position of HOMO-SOMO transition (band I) of $\mathbf{1}_H$ was the same as that of $\mathbf{1}_{opt}$ (437 nm),

while no transition band corresponding to band II was predicted for $\mathbf{1}_{\mathrm{H}}$, suggesting that $Me_3Si{-}C$ orbitals are responsible for the band II of **1**.

(17) Chlorophosphine **2** did not react with CCl_4. Although the facile reaction of **1** with CCl_4 giving chlorophosphine **2** in nonpolar hexane suggested chlorine abstraction of **1** from CCl_4, we failed identifying the fate of the CCl_3 moiety, and hence, heterolytic pathway may not be ruled out.

(18) This phosphaalkene formation proceeded in neutral condition is in contrast to phospha-Peterson reaction in basic conditions. For an example, see: Yam, M.; Chong, J. H.; Tsang, C.-W.; Patrick, B. O.; Lam, A. E.; Gates, D. P. *Inorg. Chem.* **2006**, *45*, 5225.