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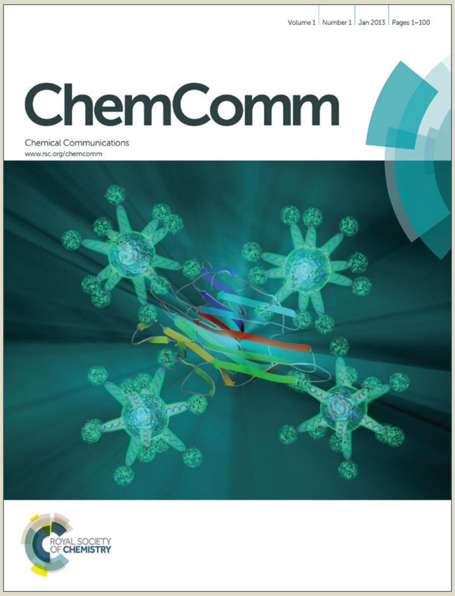

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Formation of phosphanoxy-substituted phosphaalkenes via sterically promoted cleavage of the P=P diphosphene bond

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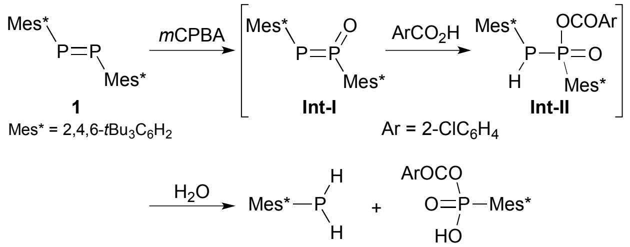
The reaction of a kinetically stabilized diphosphene (Mes*P=PMes*: Mes* = 2,4,6-tri-*tert*-butylphenyl) with an organolithium reagent and an acyl halide afforded the corresponding phosphanoxy-substituted phosphaethene [((phosphinidene)methoxy)phosphine] via sterically-promoted bond-cleavage of the P–P bond.

In 1981, Yoshifuji and co-workers succeeded in isolating and characterizing a "phosphobenzene" derivative by using bulky 2,4,6-tri-*tert*-butylphenyl (Mes*) groups.[1] This isolable diphosphene (**1**) has stimulated synthetic studies of various low-coordinated heavier main group elements through use of the kinetic stabilization technique.[2,3] In contrast, the sterically congested double bond has shown several unique reactive properties.



Scheme 1. Reaction of diphosphene **1** with *m*CPBA resulting the P–P bond cleavage.

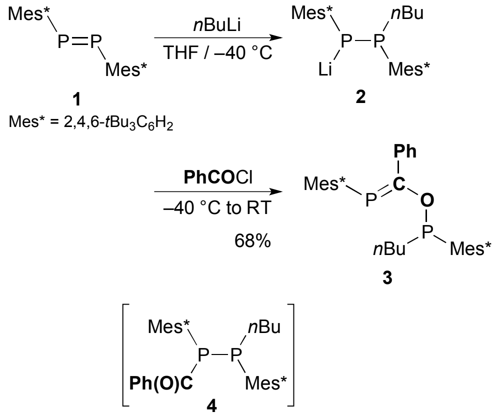
For example, diphosphene **1** undergoes a bond-cleavage reaction providing a primary phosphine (Mes^*PH_2) and a phosphonic acid monoester [Mes*P(O)(OH)(OCOAr)] (Scheme 1).[4] In this reaction, the intermediate oxophosphanylidenephosphorane (**Int-I**) is attacked by the resultant *m*-chlorobenzoic acid, and the facile P–P bond cleavage of **Int-II** occurs in the presence of water. Therefore, the steric encumbrance around the diphosphane structure can induce these unique bonding properties. In addition, a bulky diphosphane bearing four bis(trimethylsilyl)methyl groups may exhibit facile homolytic cleavage providing the phosphinyl radicals.[5]

In the course of our research on low-coordinated phosphines, we have explored the sterically promoted P–P bond cleavage of **1** for synthesizing of structurally attractive phosphorus compounds. The conversion of **1** into several phosphacumulenes via additions of dihalocarbene species has been reported, indicating that this approach may be a suitable for constructing P2 molecular skeletons in low-coordination states.[6,7]

Here we report that treating **1** with an organolithium reagent and an acyl halide induced formal P–P cleavage leading to phosphanoxy-substituted phosphaalkenes.[8] The structure and physicochemical properties of the novel phosphaalkene derivative were investigated. Additionally, we discuss the formal P–P cleavage based on DFT calculations.

Diphosphene **1** was prepared according to a reported procedure,[1] and was reacted with 1 equiv of *n*-butyllithium to generate the corresponding anionic diphosphane (**2**)[9] at –40 °C. Subsequently a solution of anion **2** was quenched with benzoyl chloride (Scheme 2). Structural analyses confirmed that the yellow product purified by recrystallization (AcOEt/MeCN, 80 °C) was a single diastereomer of novel phosphanoxy-substituted phosphaalkene **3** (68% yield). The predicted benzoyl-substituted diphosphane (**4**) was not isolated at all. Crystalline **3** was air-stable and slightly unstable on silica gel.

In the ^{31}P NMR spectrum, the sp^2-phosphorus of **3** was observed at a higher field (167 ppm) than most of hydrocarbon-substituted phosphaalkenes[2] because of the –OP(*n*Bu)Mes* moiety at the β-position, and the sp^3-phosphorus was observed around 135 ppm. The canonical structure of the phosphanoxy-substituted phosphaalkene [Mes^*P^-–C(Ph)=O^+–P(*n*Bu)Mes*] affected the ^{31}P NMR shift.[10] Compared with the J_{PP} coupling constant of most acyclic 1,3-diphosphapropenes,[11] this compound's J_{PP} of 135 Hz was smaller because of the increase in the P···P distance. In the ^{13}C NMR, the P=C carbon had a relatively low-field chemical shift (195 ppm). Figure 1 shows the X-ray structure of **3**. The *E*-isomeric P=C–O–P< skeleton exhibited an *s*-cis type conformation. The P···P distance of 3.062 Å indicated no covalent bonding character between the phosphorus atoms. The P1–C2 distance confirmed the double bond structure and was comparable to that of 2-siloxy-substituted phosphaalkenes.[12] The skeletal parameters of **3** were similar to those of most Mes*-substituted phosphaalkenes.[2,13] The steric bulkiness induced remarkable distortion of the Mes* aromatic rings into the boat-like structures.[14] The 2-phenyl group and the P=C plane formed a twisted conformation with a torsion angle of 30°. The P1–C1–O–P2 torsion angle of 14.1(1)° indicated an interaction between the P=C π-bond and the lone pair, which was consistent with the ^{31}P NMR data. The UV-Vis spectrum of **3** showed absorptions from 300 to 400 nm. TD-DFT calculations [wB97XD/6-31G(d,p)][15,16] for **3** suggested that the small and large absorptions mainly arose from the HOMO to LUMO (340 nm) and HOMO-1 to LUMO (300 nm) transitions, respectively (Figure 2, see also Supplementary Information). The large contribution of the lone pair to the sp^2-phosphorus in the HOMO and π-orbital of the P=C bond to HOMO-1 is consistent with the experimentally observed UV-Vis propertyies. Additionally, the phenyl ring in the 2-position contributed strongly to the frontier orbitals.



Scheme 2. P–P bond cleavage of diphosphene **1** affording phosphaalkene (methylenephosphine) **3**.

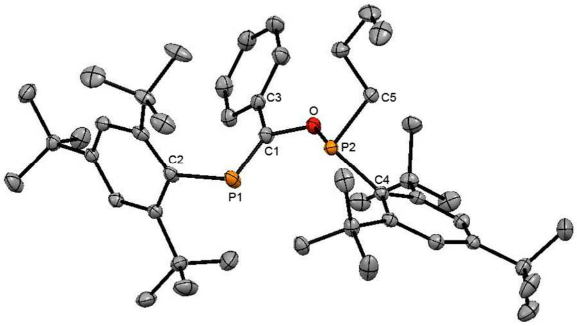


Figure 1. An ORTEP drawing for **3** (50% probability levels). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.702(1), P1–C2 1.847(1), C1–C3 1.487(2), C1–O 1.395(2), P2–O 1.682, P2–C4 1.860(1), P2–C5 1.841(1), P1···P2 3.062(1), C1–P1–C2 103.7(1), P1–C1–C3 134.2(1), P1–C1–O 117.3(1), C3–C1–O 108.5(1), C1–O–P2 120.9(1), O–P2–C4 97.1(1), O–P2–C5 110.3(1), C4–P2–C5 96.7(1).

The formation of **3** indicated formal cleavage of the phosphorus-phosphorus bond of **1** and concomitant creation of the P–O bond in the reaction procedures with an alkyllithium and an acyl halide. This is comparable to the Becker method of synthesizing phosphaalkenes via silyl migration.[17] The steric encumbrance around the phosphorus atoms would induce P–P cleavage in the putative reaction intermediate or transition state. To understand the steric effects promoting the P–P cleavage of **1** leading to the phosphanoxy-substituted phosphaalkene, we performed DFT calculations[16] for the model compounds (Figure 3). For methyl-substituted **3A** and **4A**, the acetyl-substituted diphosphane structure **4A** was energetically preferable. However, **4B** bearing the 2,6-di-*tert*-butylphenyl groups was less stable than the phosphaalkene **3B**, which was consistent with the experimental results. Thus, the steric encumbrance should induce the P–P cleavage of putative intermediate **4B**.[18,19] Alternatively, taking into account the possible unusual P–P bonding character in the sterically congested environment, a mechanism through a phosphanyl radical pair formed by homolytic cleavage is also possible.[5,20] Variable temperature NMR monitoring of the reaction mixture of **1**, butyllithium, and benzoyl chloride revealed that the initial product putatively bearing a P–P bond [δ_P 2.4, –2.8; J_{PP} = 360.3 Hz, at –40 °C] completely disappeared at 25 °C, and formation of **3** was observed at 0 °C together with unidentified products. We are currently characterizing the observed intermediates.

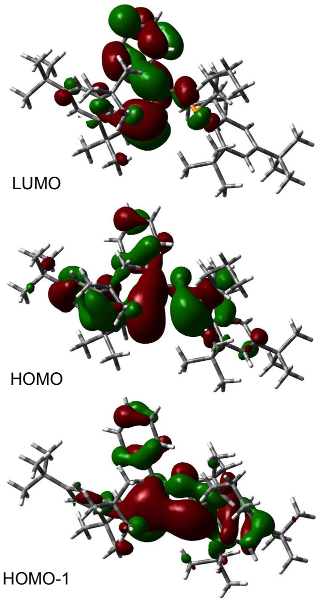


Figure 2. Decisive molecular orbitals of **3** for the UV-Vis spectroscopic property [B3LYP/6-31G(d)].

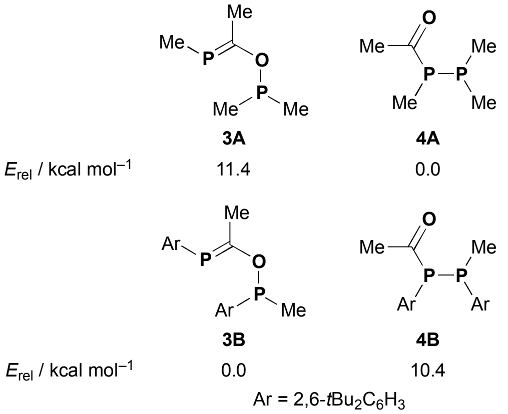
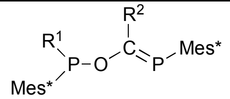


Figure 3. DFT-calculated relative energies of the model compounds for **3** and **4** [B3LYP/6-31G(d)].

The procedure shown in Scheme 2 prompted us to synthesize several phosphanoxy-substituted phosphaalkenes with organolithium reagents and acyl halides. We prepared air-tolerant crystalline **5**–**8** together with **3** (Table 1). Acyl chlorides bearing electron-deficient and electron-rich aryl substituents were used for the P–P cleavage of **2** and the corresponding phosphaalkenes **5** and **6** were isolated. Pivaloyl chloride was used to prepare **7**. The diphoshanyl anion generated from **1** and phenyllithium at room temperature was reacted with benzoyl chloride to give **8** in moderate yield. All the phosphanoxyl-substituted phosphaalkenes were air-tolerant crystalline compounds and able to be purified by recrystallization. Thus, these products would be suitable to coordination chemistry and catalysis.

Table 1. Preparation of phosphanoxy-substituted phosphaalkenes via the P=P cleavage.



Compound	R^1	R^2	Yield (%)
3	*n*Bu	Ph	68
5	*n*Bu	4-$CF_3C_6H_4$	42
6	*n*Bu	4-$MeOC_6H_4$	74
7	*n*Bu	*t*Bu	41
8	$Ph^{a)}$	Ph	55

a) Reaction of **1** with phenyllithium was performed at RT.

Conclusions

In conclusion, we have established a synthetic procedure for air-tolerant crystalline phosphanoxy-substituted phosphaalkenes via the sterically promoted P–P bond cleavage of the diphosphene **1**. The structural and physicochemical properties of **3** were analyzed, and the metathesis-like reaction was analyzed further based on DFT calculations. These novel phosphanoxy-substituted phosphaethenes could be used for developing unique application in fields such as coordination chemistry and catalysis. Additionally, we are currently attempting to elucidate the reaction mechanism, with particular focus on the P–P bond cleavage.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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18 Transition state from **4A** to **3A** was optimized and indicated activation energy of 41.2 kcal/mol. See Supplementary Information.

19 Attempts to optimize a possible transition state from **4B** to **3B** resulted in fail.
20 Compound **4B** exhibited almost closed shell characters in a CASSCF calculation. See Supplementary Information.