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Communication

Synthesis of phosphanaphthalenes and *nido*-carborane fused six-membered phosphacycles

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ABSTRACT

A simple method to synthesize luminescent λ^5-phosphanaphthalenes and zwitterionic *nido*-carborane fused six-membered phosphacycles was developed from the reaction of *ortho*-phosphinobenzoaldehydes or *ortho*-phosphinocarboranylaldehydes with an electron-deficient alkyne, respectively. Similar results were obtained with the imino analogues.

Currently, six-membered phosphacycle based fluorophores have attracted considerable attention in a variety of fields, ranging from coordination chemistry [1] to optical material science [2]. Among these six-membered phosphacycles, λ^5-phosphinine is one of the less-studied areas since most of the known λ^5-phosphinines are nonemissive [3]. Although the recent results highlighted the fascinating optical and electronic properties of λ^5-phosphinines, but the efficient methods to access luminescent λ^5-phosphinines are very limited [4,2c,2d]. Matveeva and Kostyuk developed a series of heterocyclization of phosphonium ylides derivatives with acetylenes to give λ^5-phosphinines [5,3]. But the photophysical chemistry of these λ^5-phosphinines has never been discussed. Several fluorescent 2,4,6-triaryl-λ^5-phosphinines were synthesized [6,2b,2d] and Müller developed the first blue λ^5-phosphinine emitter based OLED very recently [7]. After diligent studies on a serendipitous result, Hayashi discovered simple access to a new tunable fluorophore, 2,6-dicyano-λ^5-phosphinine [2c]. It will be useful to develop new methods for the construction of diversified luminescent λ^5-phosphinines with the hypothesis that structural diversity will lead to diverse photophysical properties.

Herein, we present a facile, high-yielding protocol to luminescent λ^5-phosphanaphthalenes that relies on the intramolecular Michael addition of the *in-situ* formed zwitterionic carbenoid species to aldehyde.

Recently, our group developed a series of intramolecular ring-closing reactions for the synthesis of annulated six-membered phosphacycles [8]. Kwon and co-workers reported an interesting three-component coupling reaction of trialkylphosphines, methyl phenylpropiolate, and 4-pyridinecarboxaldehyde to give stable tetravalent phosphonium enolate zwitterions [9]. Thus, we envisioned that *ortho*-phosphinobenzoaldehydes would react with an electron-deficient alkyne DMAD to form zwitterionic phosphonium heterocycle **2**, which would eventually lead to the formation of λ^5-phosphanaphthalenes **3** *via* an intramolecular addition to a carbonyl group (Scheme 1) [10]. A clean reaction of 2-diphenylphosphinobenzaldehyde with DMAD was observed by ^{31}P NMR (5 ppm) spectroscopy. However, neither starting material nor product was obtained after workup and purification.

We hypothesized that the reaction provided the desired phosphacycle **3**, the keto/enol tautomerization gave the unstable **3′** in Scheme 2 which decomposed during the workup procedure. If the hydrogen transfer process is blocked by alkylation of the hydroxy group of **3**, the stable λ^5-phosphanaphthalene **4** might be isolated (Scheme 2).

An alkylation procedure was added after the formation of zwitterionic phosphonium **3** from the reaction of *ortho*-phosphinobenzoaldehyde with DMAD. The THF solution of the crude reaction mixture was treated with NaH (3 equiv.) at 0 °C for half-hour, then benzyl bromide (4 equiv.) was added, and the reaction mixture was refluxed for 1 h. It is gratifying to see the desired λ^5-phosphinine **4a** was isolated in 80% yield after chromatography (Fig. 1). A series of 4-alkyloxyl-λ^5-phosphinines was obtained

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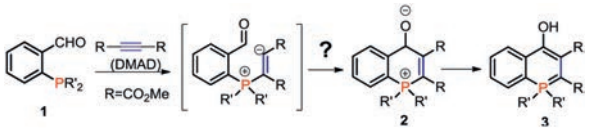
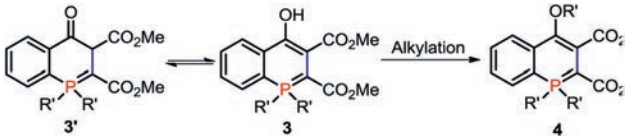


Scheme 1. Proposed reaction of **1** with electron-deficient alkyne.



Scheme 2. Tautomerization of phosphanaphthalenes.

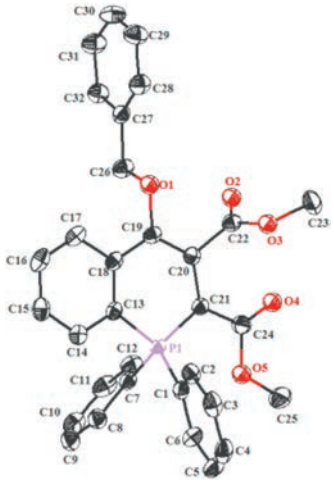
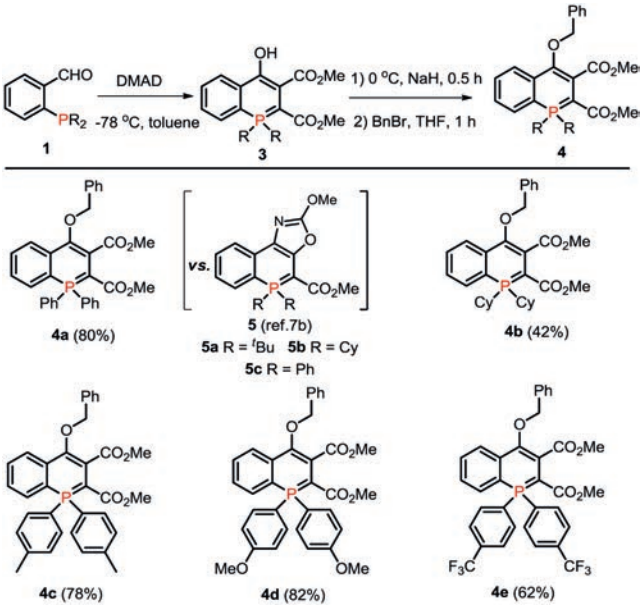
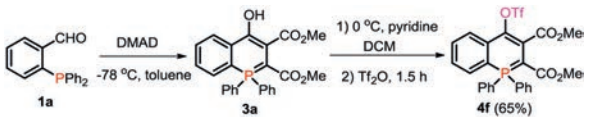


Fig. 1. X-ray crystal structure of **4a**. The level set for thermal ellipsoids of all atoms is 30%. All the hydrogen atom have been omitted for clarity. Main bond lengths (Å) and angles (deg): C13-C18 1.411(3), C19-C20 1.358(3), C21-C20 1.446(3), C1-P1 1.809(2), P1-C7 1.821(2), P1-C13 1.791(2), P1-C21 1.734(2), C1-P1-C7 107.95(11), C13-P1-C1 107.66(11), C13-P1-C7 107.11(11), C21-P1-C1 114.57(11), C21-P1-C7 113.63(12), C21-P1-C13 105.49(12). CCDC: 1999936.



Scheme 3. Synthesis of phosphanaphthalenes.



Scheme 4. Synthesis of **4f**.

(Scheme 3). Higher reaction efficiencies were observed with neutral (**4a**, **4c**) or electron-rich (**4d**) aryl-substituted phosphine than electron-deficient aryl-substituted **4e**. A low yield was obtained with cyclohexyl substituted **4b**. All of these λ^5-phosphanaphthalenes are luminescent under UV light excitation.

It should be noted that replacing NaH and benzyl bromide with pyridine and Tf_2O provided trifluoromethanesulfonate (OTf) substituted **4f** (Scheme 4), and the transition metal catalyzed cross-coupling with **4f** is currently underway.

The X-ray crystal structure analysis showed **4a** containing a well delocalized cyclic ylidic structure with a small torsion angle (C20-C21-P1-C13, 6.2°(2)). The P-C(CO_2Me) bond (P1-C21 1.734(2) Å) is shorter than that of the intracyclic P-C(Ph) bond (P1-C13 1.791(2) Å), while the bond distances of the phosphacyle are ranged from 1.358 Å to 1.446 Å. These data indicated that the luminescent **4a** has a more planar phosphacycle and much shorter P-C(CO_2Me) bond length than those of nonemissive **8a** and **9**. We have found that the photophysics of λ^5-phosphanaphthalenes **5** (Scheme 3) [7b] depends significantly upon the nature of the exocyclic substituents on phosphorus, because the luminescent bulky alkyl, ^{t}Bu (**5a**) and Cy (**5b**), -substituted products are more planar than the nonemissive phenyl substituted **5c**. It should be noted that the phenyl substituted **4a** is also more planar than the tricyclic fused analogue **5c**, which indicates that structural and photophysical features of λ^5- phosphanaphthalenes can be tuned by not only the exocyclic substituents on phosphorus but also the substitution pattern of the phospha-ring.

Recently, the three-dimensional (3D) aromaticity, electron-withdrawing property, and the formation of negatively charged *nido*-carborane *via* deboronation endow the *ortho*-carborane with many unique advantages as a building block [11,12a,12b]. Therefore, it would be interesting to replace the aryl with a carboranyl backbone. Surprisingly, the reaction of phosphinocarboranylaldehyde with DMAD provided different results. A stable white solid was isolated without alkylation. The ^{31}P NMR analysis indicated that the white solid containing two types of phosphorus compounds, the major one exhibits a resonance at 28 ppm, while the minor one has a chemical shift of 14 ppm. Fortunately, the structure of the major product **8a** was solved by the crystal analysis (Fig. 2). Since the mixture has one ^{1}H NMR resonance at 13 ppm, a putative enol tautomer **8a'** was assigned for the minor product in the mixture (Scheme 5).

After treated with DDQ, the two tautomers were converted into a single product **9**, which was fully characterized by multinuclear NMR spectroscopy, high-resolution mass spectrometry (HR-MS), and X-ray diffraction. As shown in the X-ray crystal structure (Fig. 2), **9** has a much shorter distance (C16-C17 1.339(3) Å) between the two CO_2Me groups than that (1.486(3) Å) of **8a** and a more planar phosphacycle. To the best of our knowledge, these compounds represent the first examples of carborane fused six-membered phosphacycle [12].

Replacing the phenyl substituents with electron-neutral methyl (Scheme 6, entry 2), electron-donating methoxy (entry 3), and electron-withdrawing CF_3 (entry 4) substituted aryl groups provided similar tautomerized products, with keto tautomer as the major one. A little bit lower yield was obtained with CF_3 (**8d** +**8d'**, 60% isolated yield) substituted derivative.

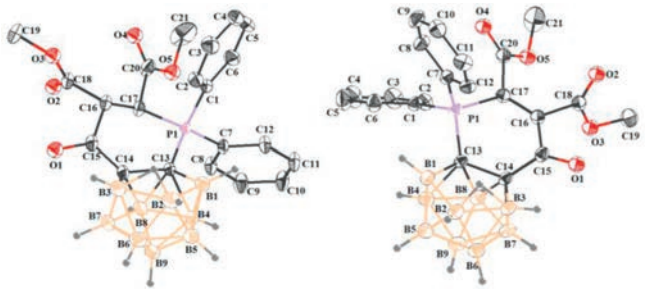
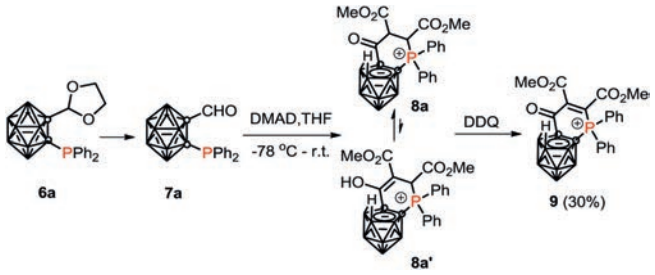
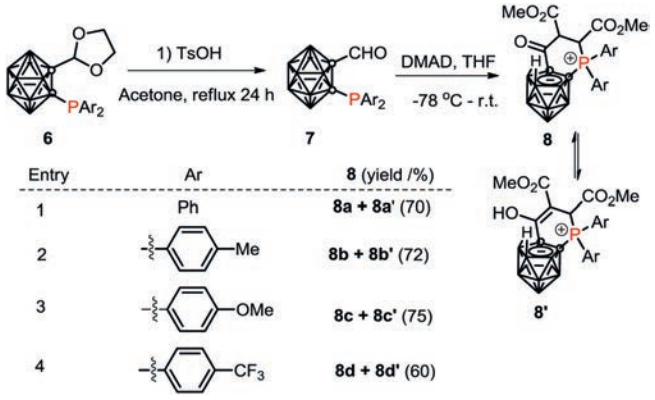


Fig. 2. X-ray crystal structure of **8a** (left). The level set for thermal ellipsoids of all atoms is 30%. Except for the hydrogen atom on the carborane, it has been omitted for clarity. Main bond lengths (Å) and angles (deg): C13-C14 1.576(3), C14-C15 1.486 (3), C15-C16 1.520(3), C16-C17 1.547(3), C1-P1 1.792(2), P1-C7 1.789(2), P1-C17 1.834(2), P1-C13 1.787(2), C1-P1-C17 105.91(10), C7-P1-C1 109.64(10), C1-P1-C13 112.87(10), C17-P1-C7 112.87(10), C7-P1-C13 110.59(10), C17-P1-C13 106.72(10), C14-C13-P1 118.51(15). CCDC: 1999934. X-ray crystal structure of **9** (right). The level set for thermal ellipsoids of all atoms is 30%. Except for the hydrogen atom on the carborane, it has been omitted for clarity. Main bond lengths (Å) and angles (deg): C13-C14 1.570(3), C14-C15 1.479(3), C15-C16 1.512(3), C16-C17 1.339(3), C1-P1 1.791 (2), P1-C7 1.789(3), P1-C17 1.802(3), P1-C13 1.785(2), C1-P1-C17 108.42(12), C7-P1-C1 111.10(12), C7-P1-C17 108.46(12), C13-P1-C1 112.72(12), C13-P1-C7 109.24(11), C13-P1-C17 106.72(12), C14-C13-P1 117.43(17). CCDC: 1999935.



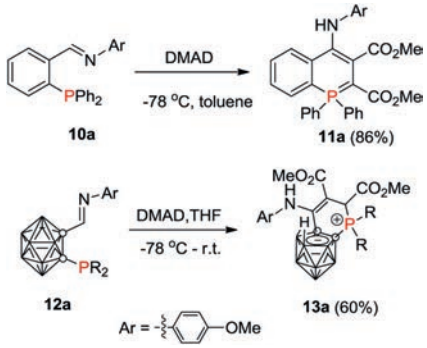
Scheme 5. The *nido*-carborane fused phosphacycles.



Scheme 6. Synthesis of zwitterionic *nido*-carborane fused P-heterocycles.

When the reaction was carried out with imino derivatives **10a**, 4-amino-λ^5-phosphinine **11a** was obtained as a sole product directly without enamine to imine tautomerization. A similar phenomenon was observed with iminocarborane **12a** (Scheme 7).

With these diverse λ^5-phosphanaphthalenes molecules in hand, we next turned our attention to their photophysical properties by recording UV–vis and emission spectra in DCM at a low concentration (1×10^{-5} mol/L) as shown in Table 1 and Fig. 3. *nido*-Carborane fused phosphacycles **8a-d**, **9** and **13a** are non-emissive. Compared with **8a-d**, λ^5-phosphanaphthalenes **4a-d** exhibit moderate fluorescent efficiency and bathochromic shift in



Scheme 7. Synthesis of amino-substituted phosphacycles.

Table 1
Photophysical data of **4a**, **4b**, **4c**, **4d**, **11a**.

Compound	log ε	λmax (nm)[a]	λem (nm)[a]	Φf[b]
4a	3.86	424	543	0.10
4b	3.79	423	518	0.19
4c	3.44	424	534	0.15
4d	3.81	423	527	0.13
11a	3.68	419	566	0.07

[a] Measured in CH_2Cl_2 (1×10^{-5} mol/L). Emission maxima upon excitation at the absorption maximum wavelengths.
[b] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±5% errors.

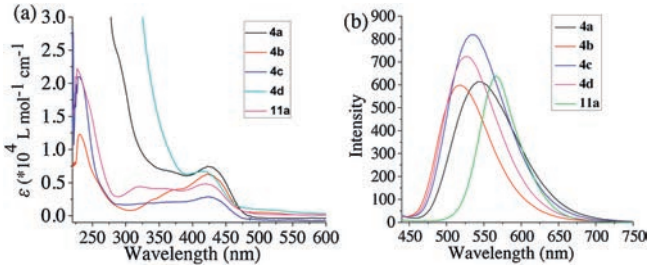


Fig. 3. (a) UV–vis absorption of **4a**, **4b**, **4c**, **4d**, **11a** in CH_2Cl_2 (1×10^{-5} mol/L) at 298 K. (b) PL spectra of **4a**, **4b**, **4c**, **4d**, **11a** in CH_2Cl_2 (1×10^{-5} mol/L) at 298 K.

their absorption wavelengths, due to the presence of an extended π-conjugation system. A low fluorescence quantum yield was observed with 4-amino-λ^5-phosphinine **11a**.

In summary, a one-pot reaction of easily accessible phosphine derivatives with DMAD was developed to synthesize the unknown zwitterionic *nido*-carborane fused six-membered phosphacycles and a new series of luminescent λ^5-phosphanaphthalenes. This new result also highlighted the planarity of λ^5-phosphinine is crucial to their luminescence, which can be tuned by the exocyclic substituents on phosphorus and substitution pattern of the ring. Further applications of this synthetic method and utilizations of the luminescent λ^5-phosphanaphthalenes are underway in our group.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.11.018.

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