

Molecular-Strain Driven Phosphinidene Reactivity of a Phosphanorcaradiene

Yizhen Chen,^{[a][b]} Dongmin Wang^{[a][b]} Li Zhang,^[c] and Gengwen Tan^{*[a][b]}

Dedication ((optional))

[a] Y. Chen, D. Wang, and Prof. Dr. G. Tan

Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, Guangdong Basic Research Center of Excellence for Functional Molecular Engineering, School of Chemistry, IGCME, Sun Yat-sen University, Guangzhou 510275, China
E-mail: tangw55@mail.sysu.edu.cn

[b] Y. Chen, D. Wang, and Prof. Dr. G. Tan

Innovation Center for Chemical Sciences, Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

[c] Dr. L. Zhang

School of Electronic Engineering, Guangxi University of Science and Technology, Liuzhou 545000, China

Supporting information for this article is given via a link at the end of the document. ((Please delete this text if not appropriate))

Abstract: Herein we report straightforward synthesis, characterization and reactivity studies of a phosphanorcaradiene, in which one of the benzene rings in the flanking fluorenyl substituents is intramolecularly dearomatized through attachment to the phosphorus atom. It was facilely obtained by the reduction of phosphorus(III) dichloride $M^{\delta}\text{Fluid}^{\text{bu}}\text{-PCl}_2$ supported by a hydrindacene substituent with potassium graphite. Despite being thermally robust, it serves as an elegant precursor for transient phosphinidene. It reacted with trimethylphosphine and isonitrile to yield phosphanylidene-phosphorane and 1-phospha-3-azaallene, respectively. Moreover, it was capable of activating ethylene and 4-tertbutylphenylacetylene to afford [1+2] cycloaddition products, as well as oxidative cleavage of Si-H and N-H bonds to yield secondary phosphines. All the reactions proceeded smoothly at room temperature without the presence of transition metals. The driving force for these reactions is most likely the high ring-constraint of the three-membered PC_2 ring and recovery of the aromaticity of the benzene ring.

Carbene insertion into aromatic rings to produce cycloheptatrienes (CHTs) and norcaradienes (NCDs) developed by Büchner and Curtius in 1885 is a powerful method for the conversion of stable aromatic compounds to more reactive systems (Figure 1).^[1] The equilibria between CHTs and NCDs have been well-established.^[2] Recent reports have shown that CHTs and NCDs can serve as carbene precursors via retro-Büchner reactions.^[3] Phosphorus is viewed as carbon copy.^[4] Phosphinidenes are neutral monocoordinate and monovalent phosphorus species possessing six valence electrons. Such species are isoelectronic to well-explored carbenes^{[5],[6]} and tetrylenes.^[7] In contrast, most phosphinidenes are transient species because of their exceptionally high reactivity.^[8] The sole isolable example of phosphinidene was synthesized by Bertrand and coworkers.^[9] Therefore, the chemical properties of phosphinidenes have been demonstrated mainly by generating transient species with suitable precursors.

Phosphepines, phosphorus analogs of CHTs, were first synthesized by Märkl et al. in the 1980s,^[10] followed by the groups of Tsuchiya^[11] and Lammertsma.^[12] The Lammertsma group showed that phosphepine transition metal (TM) complex I could act as a versatile metallo-phosphinidene precursor to activate a variety of substrates.^[13] In addition, several P(III)

precursors, including phosphatetrahdrane II,^[14] 7-phosphanorbornadiene III,^[15] dibenzo derivatives IV^[16] and phosphirane-TM complexes,^[17] have been utilized for phosphinidene reactivity studies. Notably, phosphinidene transfer with these materials must be promoted through heating or via TM catalysts.

In contrast to phosphepines, phosphanorcaradienes, which are phosphorus analogs of NCDs, have higher molecular-constraints and thereby exhibit inherent high reactivity, making isolation in the condensed state a formidable task. On this basis, such compounds may be ideal synthons for accessing transient phosphinidenes via phosphorus-type retro-Büchner reactions. However, only one free phosphanorcaradiene has been reported by Stephan and coworkers. It was synthesized through demetalation of a phosphepine-gold complex, while its reactivity as a phosphinidene precursor for small molecule activation has not been fully disclosed.^[18]

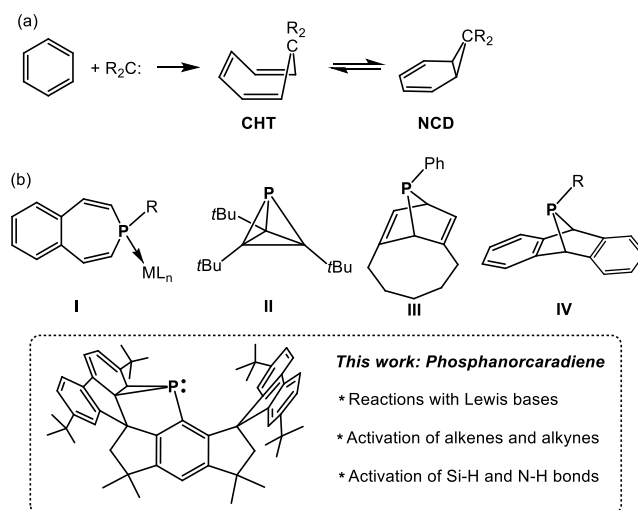
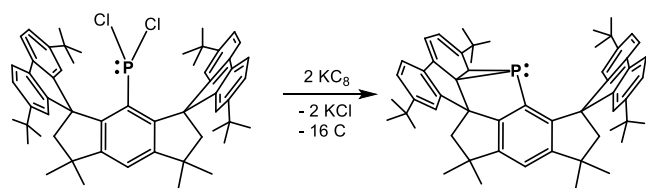


Figure 1. (a) Schematic depiction of Büchner ring expansion and the equilibria between CHTs and NCDs; (b) Selected examples of P(III) precursors as synthons of transient phosphinidenes.

Our group has continuous research interests in synthesizing low-coordinate main-group species, and has successfully

isolated and structurally characterized several heavier analogs of free carbynes^[19] and nitrenes,^[20] as well as main-group multiple bonds^[21] supported by sterically encumbered hydrindacene ligands.^[22] Encouraged by these results, we continued our research to pursue isolable phosphinidenes.^[23] In this contribution, we report straightforward synthesis, characterization and reactivity studies of a phosphanorcaradiene **1**. These investigations revealed that it can serve as an elegant synthon of phosphinidene due to the release of molecular-strain.^[24] This is the first study in which the transition metal-free activation of alkenes, alkynes, silanes and amines at room temperature was achieved with phosphanorcaradiene.



Scheme 1. Synthesis of phosphanorcaradiene **1**.

With the aim of synthesizing a stable phosphinidene, we carried out the reduction of the phosphorus(III) dichloride $M^s\text{Fluid}^{\text{bu}}\text{-PCl}_2$ ^[21b] with two molar equivalents of potassium graphite in THF; however, phosphanorcaradiene **1** was obtained in 75% yield as a yellow solid instead of the expected product (Scheme 1). One of the benzene rings in the flanking fluorenyl moieties is intramolecularly dearomatized through attachment to the phosphorus atom. The formation of the PC_2 three-membered ring leads to a decrease in the symmetry and complex ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The proton signal in the PC_2 ring was shown at δ 2.54 ppm. A sharp singlet signal at δ -155.1 ppm was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in C_6D_6 solution, similar to that of phosphiranes.^[9, 25] Interestingly, **1** can be heated to 100 °C in C_6D_6 solution for one hour without noticeable decomposition under an inert atmosphere, but it is highly air- and moisture-sensitive and yields intractable mixtures when exposed to air or dry oxygen. The synthesis of **1** is more straightforward in comparison to that of the phosphanorcaradiene reported by Stephan and coworkers.^[18]

Single crystals of **1** suitable for X-ray diffraction analysis were obtained by layering *n*-hexane in a toluene solution at 4 °C.^[26] It crystallizes in the monoclinic space group *P*1. There are two independent enantiomers present in one crystal unit cell due to the chirality of the P atom. One of the molecules is shown in Figure 2, which unambiguously reveals the connection of the P atom to two C atoms of the flanking fluorenyl group. The distances of P1–C27 (1.973(5) Å) and P1–C28 (1.985(5) Å) are substantially longer than those of P1–C1 (1.847(4) Å) and the P–C distances of the PC_2 ring in phosphiranes.^[9, 25] Consistently, the C27–P1–C28 angle (43.78(19)°) is more acute. Moreover, the P atom deviates from the position expected for atoms attached to a phenyl group as evidenced by the large difference between the bond angles of C2–C1–P1 (111.7(3)°) and C6–C1–P1 (131.7(4)°). These data suggest that the PC_2 ring in **1** bears a greater ring-strain than phosphiranes.

The electronic structure of **1** was further elucidated by density functional theory (DFT) calculations at the BP86+D3BJ/def2-

SVP level. The HOMO represents the bonding orbitals of the C_2P ring and the C–C π -orbitals of the linked C_6 ring (Figure 2). The lone pair of P atom is shown in the HOMO-4, and the LUMO contains the π^* -antibonding orbitals of the fluorenyl moiety linked to the P atom. Additionally, natural bond orbital (NBO) and intrinsic bond orbital (IBO)^[27] analyses were conducted to gain insight into the bonding character of **1**. The Wiberg bond indices (WBIs) of the P1–C27 (0.83) and P1–C28 (0.78) bonds are substantially smaller than that of the P1–C1 bond (1.08), suggesting that they are relatively weaker than the P1–C1 bond. P1–C27(C28) σ -bonds are formed by the overlap of the 3p orbitals at P1 and the 2p orbitals at C27(C28) (Figure S1). The 3p orbitals at the P atom and the 2p orbitals at the C atoms provided more than 90% of the bonding electrons in the P1–C27(C28) bonds. These orbitals are significantly different from the P1–C1 σ -bond, which is formed by the 3p orbital with the partial s character of P1 and the sp^2 hybrid orbital of C1.

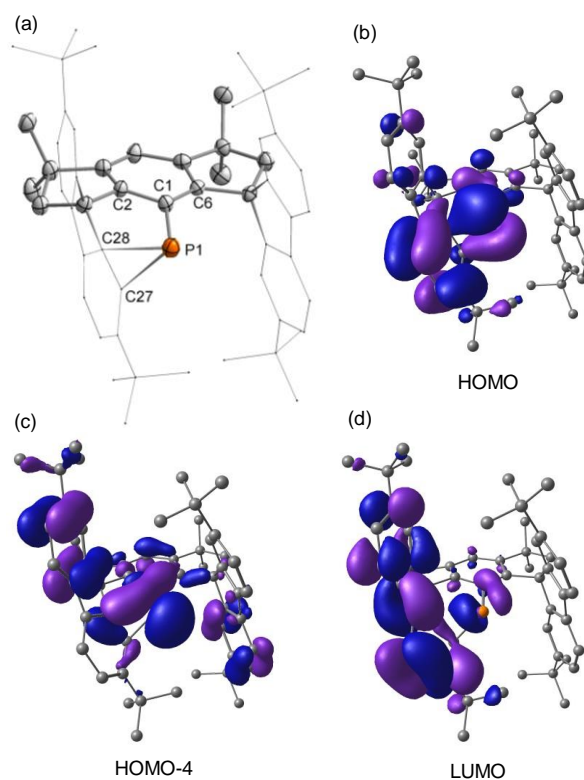


Figure 2. (a) Thermal ellipsoid drawings of the molecular structure of **1**. All hydrogen atoms are omitted, and the fluorenyl moieties are shown in a wireframe style for clarity. (b-d) Selected frontier molecular orbitals of **1**.

To further explore the electronic structure of the C_2P ring of **1**, the quantum theory of atoms in molecules (QTAIM) and electron localization function (ELF) analyses were carried out.^[28] The QTAIM calculations indicate that there are three bond critical points (BCPs) among the P1, C27 and C28 atoms (Figure S2). In addition, the bond paths between P1 and C27(C28) slightly deviate away from the P1–C27(C28) axes. Furthermore, the ELF plots exhibit a twisted region with highly localized electron density between each C and P in the C_2P ring (Figure S3).

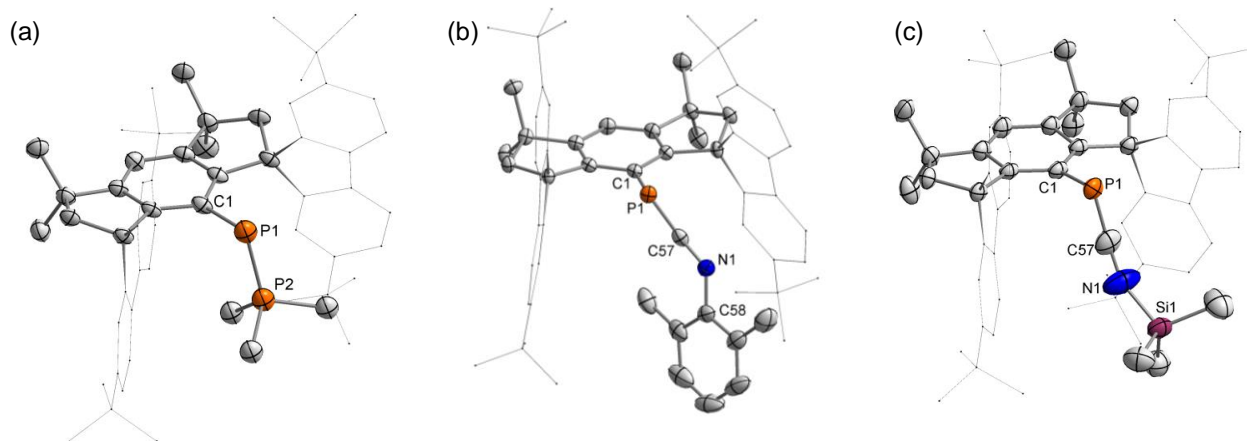
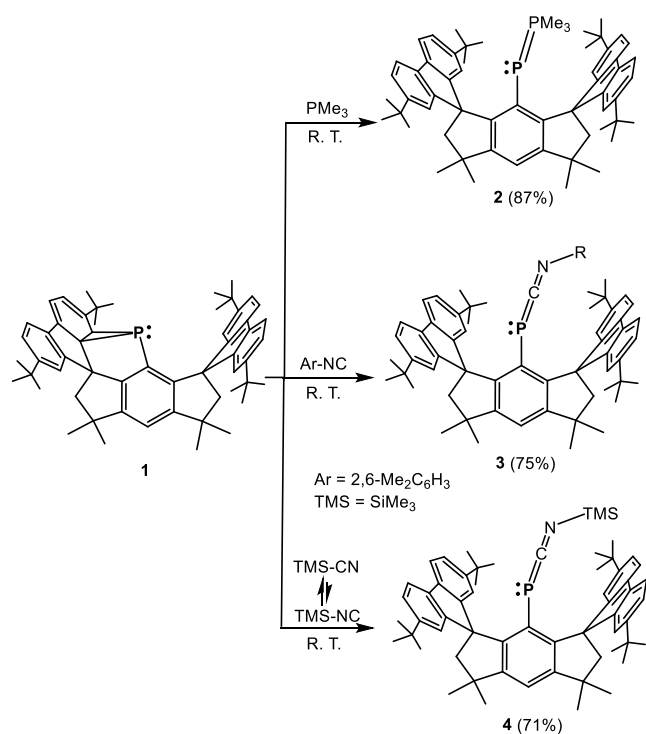


Figure 3. Thermal ellipsoid drawings of the molecular structures of **2-4**. All hydrogen atoms are omitted, and the fluorenyl moieties are shown in a wireframe style for clarity.



Scheme 2. Reactions of **1** with Lewis bases **2-4**.

The formation of **1** can be simplified to [2+1] cycloaddition of a transient phosphinidene with a C=C double of the flanking fluorenyl group. We previously reported the isolation of triplet stibinidene^[20a] and bismuthinidenes,^[20b] which are heavy congeners of the proposed phosphinidene. A comparison of the calculated energies between triplet phosphinidene, singlet phosphinidene and **1** showed that **1** has the lowest energy, which is 6.4 kcal/mol lower than that of triplet phosphinidene, and that the singlet-triplet energy of free phosphinidene is 20.8 kcal/mol (Figure S4).

With understanding of the electronic structure, it is anticipated that **1** can act as a phosphinidene synthon through the dissociation of relatively weak P1–C27(C28) bonds and the

release of molecular-strain.^[29] Accordingly, the reactivity of **1** toward Lewis bases was tested (Scheme 2). It reacted smoothly at room temperature with trimethylphosphine to afford phosphanylidene-phosphorane **2**, which was isolated in 87% yield. **2** exhibits ³¹P NMR resonance signals at δ –0.9 and –157.8 ppm with a coupling constant of $^1J_{P-P} = 603$ Hz. The high-field signal is comparable to those of reported phosphanylidene-phosphoranes,^[30] which have been utilized as phospho-Wittig reagents.^[31] Moreover, treatment of **1** with 2,6-dimethylphenylisocyanide and trimethylsilylnitrile both afforded 1-phospha-3-azaallenes **3** and **4** in high yields, respectively. ³¹P resonances were observed at δ –152.3 and –190.5 ppm in the ³¹P{¹H} NMR spectra. The formation of **4** can be interpreted by the equilibrium between trimethylsilylnitrile and trimethylsilylisocyanide,^[32] and the latter species has a greater propensity to react with **1**. A similar reaction pattern between disilyne and trimethylsilylnitrile has been reported by Sekiguchi and coworkers.^[33]

The dicoordinate phosphorus atoms in **2-4** were revealed by SC-XRD analysis (Figure 3). The P–P distance of 2.1306(15) Å and the C1–P1–P2 bond angle of 102.03(11)° in **2** are comparable to those in DmpP=PMe₃ (Dmp = 2,6-Me₂C₆H₃; 2.084(2) Å and 106.79(13)°, respectively).^[34] The P=C=N fragments in **3** and **4** are almost linear with P–C–N bond angles of 168.82(18)° and 168.0(3)°, respectively. Moreover, the P1–C57 (1.668(2) and 1.651(4) Å) and C57–N1 (1.200(3) and 1.212(5) Å) bonds feature double bond characteristics. These geometric parameters are reminiscent of (phosphino)phosphinidene-isonitriles reported by Bertrand and coworkers,^[35] and are consistent with their cumulene-like properties.

The ability of **1** to activate alkenes and alkynes was further investigated (Scheme 3). Exposure of **1** to 1 atm. of ethylene atmosphere at room temperature led to the formation of phosphirane **5** in moderate yield. The ³¹P{¹H} NMR resonance was shown at δ –229.2 ppm, similar to that of 1-mesitylphosphirane (δ –238.9 ppm).^[29e] Complete consumption of **1** with an excess amount of 4-tertbutylphenylacetylene at room temperature was observed after 12 h, and phosphirene **6** was isolated in 65% yield. A single resonance signal was observed at δ –171.3 ppm in the ³¹P{¹H} NMR spectrum of **6**. The formation of **5** and **6** under mild conditions is most likely

attributed to the decrease in the ring-strain and recovery of aromaticity at the six-membered ring in **1**, which is striking since phosphinidene transfer to alkenes with **II** and **IV** developed by the Cummins group has to be promoted by heating or catalyzed by TM catalysts.^[14, 16a, b]

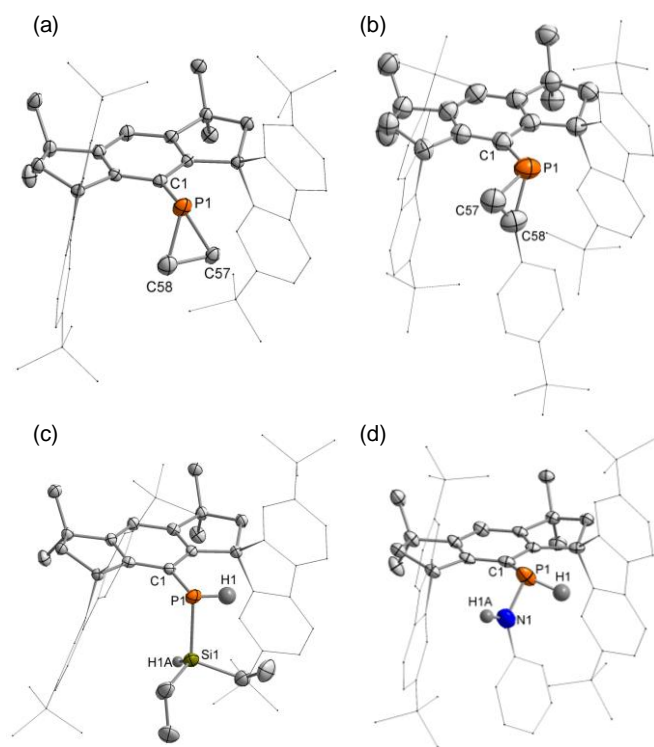
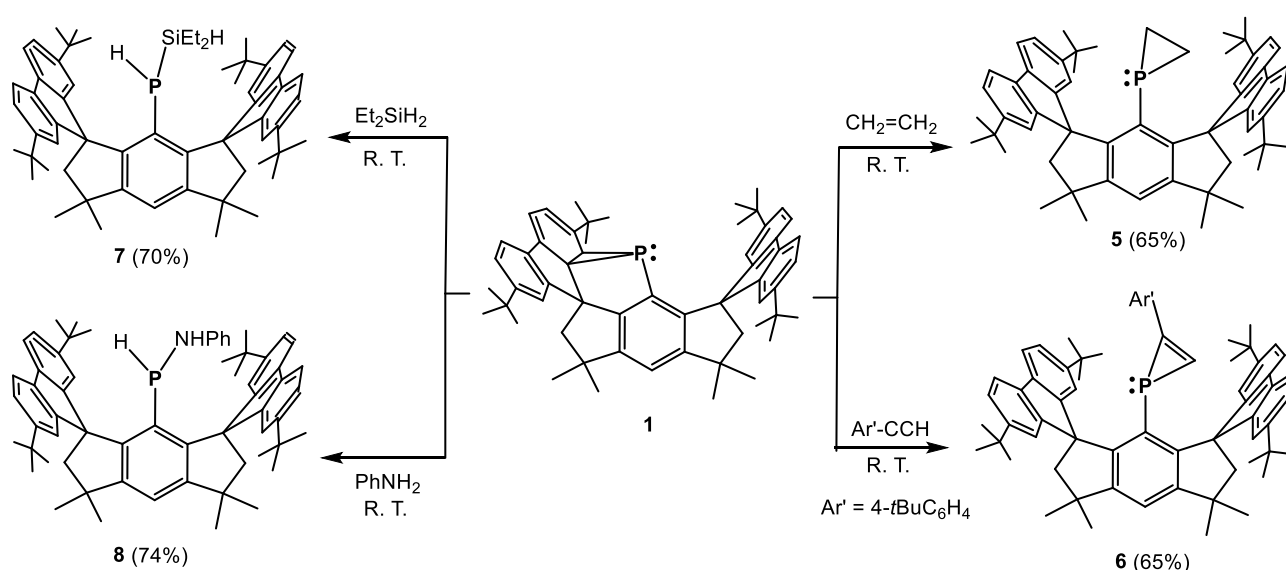


Figure 4. Thermal ellipsoid drawings of the molecular structures of **5-8**. All hydrogen atoms except those at the P, Si and N atoms in **7** and **8** are omitted, and the fluorenyl moieties, the Ar' and phenyl groups are shown in a wireframe style for clarity.

The molecular structures of **5** and **6** determined by SC-XRD analysis are shown in Figure 4. New three-membered PC₂ rings are shown in the structures. The C57–C58 distances are 1.513(4) and 1.308(5) Å, respectively, in accordance with their single and double bond nature. Moreover, the P–C bond lengths (1.847(3) and 1.848(3) Å for **5**; 1.779(4) and 1.808(4) Å for **6**) inside the PC₂ ring are shortened in comparison to those in **1**. In contrast to that of **1**, the P atoms in **5** and **6** are in the expected positions for atoms attached to a phenyl ring.

Interestingly, **1** could activate the Si–H and N–H bonds. The reactions of **1** with diethylsilane and phenylamine occurred smoothly at room temperature, and silylphosphine **7** and aminophosphine **8** were obtained in 70% and 74% yields, respectively (Scheme 3). Their structures were unambiguously determined by SC-XRD analysis (Figure 4). The activation of Si–H and N–H bonds represents rare examples of intermolecular inert bond activation with metal-free transient phosphinidenes. Oxidation cleavage of Si–H bonds with electrophilic metallophosphinidene complexes was reported by Sterenberg et al.^[36] Stephan and coworkers showed hydrosilylation of low-valent P₅Ph₅ mediated by the Lewis acid B(C₆F₅)₃.^[37] Hering-Junghans and coworkers recently revealed the first example of N–H activation at a metal-free P(I) center with phospho-Wittig reagents.^[31b]

In summary, we have described the synthesis and characterization of thermally robust phosphanorcaradiene **1** with high molecular-strain. It could react with Lewis bases to afford phosphinidene adducts. Strikingly, **1** was capable of activating C=C double and C≡C triple bonds, as well as Si–H and N–H bonds at room temperature. The driving force for these reactions is most likely the high ring-strain of the three-membered PC₂ ring and recovery of aromaticity of the benzene ring. This work represents the first demonstration of the great potential of phosphanorcaradiene as a synthetic equivalent of phosphinidene in small molecule activation. The use of **1** to synthesize more phosphorus compounds is under investigation in our laboratory.



Scheme 3. Activations of unactivated alkene, alkyne, silane and amine with **1**.

Acknowledgements

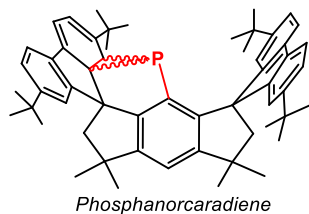
We thank the National Natural Science Foundation of China (Grants: 22322112 and 22071164), Fundamental Research Funds for the Central Universities, Sun Yat-sen University (23qnp35), and the Suzhou Science & Technology NOVA Program (Grant: ZXL2022445) for generous financial support. L.Z. thanks Guangxi University of Science and Technology (Grants: 03190227 and 03190228) and the Guangxi Department of Science and Technology (Grant: 2021GXNSFBA220021) for financial support.

Keywords: Phosphorus • Phosphanorcaradiene • Phosphinidene • Retro-Büchner reaction • Molecular-Strain

- [1] E. Buchner, T. Curtius, *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2377-2379.
- [2] E. Ciganek, *J. Am. Chem. Soc.* **1967**, *89*, 1454-1458.
- [3] a) C. R. Solorio-Alvarado, A. M. Echavarren, *J. Am. Chem. Soc.* **2010**, *132*, 11881-11883; b) Y. Guo, T. V. Nguyen, R. M. Koenigs, *Org. Lett.* **2019**, *21*, 8814-8818.
- [4] K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: the carbon copy*, John Wiley & Sons, New York, **1998**.
- [5] Selected reviews: a) S. C. Sau, P. K. Hota, S. K. Mandal, M. Soleilhavoup, G. Bertrand, *Chem. Soc. Rev.* **2020**, *49*, 1233-1252; b) A. Doddi, M. Peters, M. Tamm, *Chem. Rev.* **2019**, *119*, 6994-7112; c) Á. Vivancos, C. Segarra, M. Albrecht, *Chem. Rev.* **2018**, *118*, 9493-9586; d) E. Peris, *Chem. Rev.* **2017**, *118*, 9988-10031; e) M. Melaimi, R. Jazzar, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2017**, *56*, 10046-10068; f) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, S. Inoue, *Chem. Rev.* **2018**, *118*, 9678-9842.
- [6] Recent progress on carbene chemistry: a) Y. K. Loh, M. Melaimi, M. Gembicky, D. Munz, G. Bertrand, *Nature* **2023**, *623*, 66-70; b) C. Hu, X.-F. Wang, R. Wei, C. Hu, D. A. Ruiz, X.-Y. Chang, L. L. Liu, *Chem* **2022**, *8*, 2278-2289; c) R. Wei, X.-F. Wang, C. Hu, L. L. Liu, *Nat. Synth.* **2023**, *2*, 357-363; d) Y. K. Loh, M. Melaimi, D. Munz, G. Bertrand, *J. Am. Chem. Soc.* **2023**, *145*, 2064-2069; e) C. Hu, X.-F. Wang, J. Li, X.-Y. Chang, L. L. Liu, *Science* **2024**, *383*, 81-85.
- [7] Selected review on tetrylenes: a) S. Yao, A. Saddington, Y. Xiong, M. Driess, *Acc. Chem. Res.* **2023**, *56*, 475-488; b) C. Shan, S. Yao, M. Driess, *Chem. Soc. Rev.* **2020**, *49*, 6733-6754; c) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354-396; d) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479-3511.
- [8] a) H.-F. Grützmacher, W. Silhan, U. Schmidt, *Chem. Ber.* **1969**, *102*, 3230-3232; b) U. Schmidt, *Angew. Chem. Int. Ed.* **1975**, *14*, 523-528; c) H. Bock, M. Bankmann, *J. Chem. Soc. Chem. Commun.* **1989**, 1130-1132; d) A. H. Cowley, F. Gabbai, R. Schluter, D. Atwood, *J. Am. Chem. Soc.* **1992**, *114*, 3142-3144; e) X. Li, D. Lei, M. Y. Chiang, P. P. Gaspar, *J. Am. Chem. Soc.* **1992**, *114*, 8526-8531.
- [9] L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, *1*, 147-153.
- [10] a) G. Märkl, W. Burger, *Angew. Chem. Int. Ed.* **1984**, *23*, 894-895; b) G. Märkl, W. Burger, *Tetrahedron Lett.* **1983**, *24*, 2545-2548.
- [11] a) J. Kurita, S. Shiratori, S. Yasuike, T. Tsuchiya, *J. Chem. Soc. Chem. Commun.* **1991**, 1227-1228; b) S. Yasuike, H. Ohta, S. Shiratori, J. Kurita, T. Tsuchiya, *J. Chem. Soc. Chem. Commun.* **1993**, 1817-1819.
- [12] V. Lyaskovskyy, R. J. A. van Dijk-Moes, S. Burck, W. I. Dzik, M. Lutz, A. W. Ehlers, J. C. Slootweg, B. de Bruin, K. Lammertsma, *Organometallics* **2013**, *32*, 363-373.
- [13] a) H. Jansen, M. C. Samuels, E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, P. Chen, K. Lammertsma, *Chem. Eur. J.* **2010**, *16*, 1454-1458; b) H. Aktaş, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2010**, *49*, 2102-2113; c) M. L. G. Borst, R. E. Buló, C. W. Winkler, D. J. Gibney, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 5800-5801; d) M. L. G. Borst, R. E. Buló, D. J. Gibney, Y. Alem, F. J. J. de Kanter, A. W. Ehlers, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2005**, *127*, 16985-16999.
- [14] M.-L. Y. Riu, A. K. Eckhardt, C. C. Cummins, *J. Am. Chem. Soc.* **2022**, *144*, 7578-7582.
- [15] M. J. van Eis, H. Zappey, F. J. J. de Kanter, W. H. de Wolf, K. Lammertsma, F. Bickelhaupt, *J. Am. Chem. Soc.* **2000**, *122*, 3386-3390.
- [16] a) T. Xin, M. B. Geeson, H. Zhu, Z.-W. Qu, S. Grimme, C. C. Cummins, *Chem. Sci.* **2022**, *13*, 12696-12702; b) A. Velian, C. C. Cummins, *J. Am. Chem. Soc.* **2012**, *134*, 13978-13981; c) T. Xin, C. C. Cummins, *J. Am. Chem. Soc.* **2023**, *145*, 25989-25994.
- [17] a) M. Wang, T. Yang, R. Tian, D. Wei, Z. Duan, F. Mathey, *Chem. Commun.* **2020**, 56, 9707-9710; b) J. B. M. Wit, G. B. de Jong, M. Schakel, M. Lutz, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *Organometallics* **2016**, *35*, 1170-1176; c) M. Wang, Y. Xu, D. Wei, R. Tian, Z. Duan, F. Mathey, *Chem. Eur. J.* **2019**, *25*, 15036-15039; d) J. Wong, Y. Li, Y. Hao, R. Tian, F. Mathey, *Angew. Chem. Int. Ed.* **2015**, *54*, 12891-12893; e) Y. Hao, C. Zhang, Y. Mei, R. Tian, Z. Duan, F. Mathey, *Dalton Trans.* **2016**, 45, 8284-8290.
- [18] L. L. Liu, J. Zhou, R. Andrews, D. W. Stephan, *J. Am. Chem. Soc.* **2018**, *140*, 7466-7470.
- [19] a) D. Wang, C. Zhai, Y. Chen, Y. He, X.-d. Chen, S. Wang, L. Zhao, G. Frenking, X. Wang, G. Tan, *Nat. Chem.* **2023**, *15*, 200-205; b) D. Wang, W. Chen, C. Zhai, L. Zhao, S. Ye, G. Tan, *J. Am. Chem. Soc.* **2023**, *145*, 6914-6920; c) D. Wang, H. Chen, Y. He, X. Chen, L. Zhang, G. Tan, *Chin. J. Chem.* **2023**, DOI: 10.1002/cjoc.202300581.
- [20] a) M. Wu, H. Li, W. Chen, D. Wang, Y. He, L. Xu, S. Ye, G. Tan, *Chem* **2023**, *9*, 2573-2584; b) M. Wu, W. Chen, D. Wang, Y. Chen, S. Ye, G. Tan, *Nat. Sci. Rev.* **2023**, *10*, nwad169; c) The same bismuthinidene was reported during the same period: Y. Pang, N. Nöthling, M. Leutzsch, L. Kang, E. Bill, M. van Gastel, E. Reijerse, R. Goddard, L. Wagner, D. SantaLucia, S. DeBeer, F. Neese, J. Cornella, *Science* **2023**, *380*, 1043-1048.
- [21] a) T. Li, L. Zhang, Y. He, Y. Chen, D. Wang, J. Liu, G. Tan, *Chem. Commun.* **2023**, 59, 1533-1536; b) Y. Chen, M. Wu, D. Wang, N. Yuan, L. Xu, G. Tan, *Organometallics* **2023**, *42*, 538-542; c) H. Chen, Y. Chen, T. Li, D. Wang, L. Xu, G. Tan, *Inorg. Chem.* **2023**, *62*, 20906-20912; d) Y. He, C. Dai, D. Wang, J. Zhu, G. Tan, *J. Am. Chem. Soc.* **2022**, *144*, 5126-5135.
- [22] T. Matsuo, K. Suzuki, T. Fukawa, B. Li, M. Ito, Y. Shoji, T. Otani, L. Li, M. Kobayashi, M. Hachiya, Y. Tahara, D. Hashizume, T. Fukunaga, A. Fukazawa, Y. Li, H. Tsuji, K. Tamao, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1178-1191.
- [23] a) M. Soleilhavoup, G. Bertrand, *Chem* **2020**, *6*, 1275-1282; b) L. Dostál, *Coord. Chem. Rev.* **2017**, *353*, 142-158.
- [24] a) M. Tang, Y. Liang, J. Liu, L. Bian, Z. Liu, *CCS Chemistry* **2022**, *4*, 3230-3237; b) M. Tang, Y. Liang, X. Lu, X. Miao, L. Jiang, J. Liu, L. Bian, S. Wang, L. Wu, Z. Liu, *Chem* **2021**, *7*, 2160-2174.
- [25] J. Liedtke, S. Loss, G. Alcaraz, V. Gramlich, H. Grützmacher, *Angew. Chem. Int. Ed.* **1999**, *38*, 1623-1626.
- [26] a) G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8; b) X-ray crystallographic data sets of **1-8** are available free of charge from the Cambridge crystallographic Data Centre under reference numbers CCDC 2323602-2323609.
- [27] a) G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834-4843; b) G. Knizia, J. E. M. N. Klein, *Angew. Chem. Int. Ed.* **2015**, *54*, 5518-5522.
- [28] a) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, **1990**; b) T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580-592; c) A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397-5403; d) A. Savin, R. Nesper, S. Wengert, T. F. Fässler, *Angew. Chem. Int. Ed.* **1997**, *36*, 1808-1832.
- [29] a) L. Qiu, Q. Zhang, D. Wei, R. Tian, Z. Duan, *Dalton Trans.* **2022**, 51, 3046-3050; b) E. Y. Misochko, A. V. Akimov, D. V. Korchagin, Y. S. Ganushevich, E. A. Melnikov, V. A. Miluykov, *Phys. Chem. Chem. Phys.* **2020**, *22*, 27626-27631; c) A. Mardyukov, D. Niedek, *Chem. Commun.* **2018**, 54, 13694-13697; d) A. Mardyukov, D. Niedek, P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 5019-5022; e) A. V. Akimov, Y. S. Ganushevich, D. V. Korchagin, V. A. Miluykov, E. Y. Misochko, *Angew. Chem. Int. Ed.* **2017**, *56*, 7944-7947.

- [30] a) E. Urnėžius, S. Shah, J. D. Protasiewicz, *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *144*, 137-139; b) B. A. Surgenor, M. Bühl, A. M. Z. Slawin, J. D. Woollins, P. Kilian, *Angew. Chem. Int. Ed.* **2012**, *51*, 10150-10153.
- [31] a) S. Shah, J. D. Protasiewicz, *Chem. Commun.* **1998**, 1585-1586; b) F. Dankert, J.-E. Siewert, P. Gupta, F. Weigend, C. Hering-Junghans, *Angew. Chem. Int. Ed.* **2022**, *61*, e202207064; c) S. Shah, J. D. Protasiewicz, *Coord. Chem. Rev.* **2000**, *210*, 181-201.
- [32] M. R. Booth, S. G. Frankiss, *Spectrochim. Acta, Part A* **1970**, *26*, 859-869.
- [33] K. Takeuchi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2008**, *130*, 16848-16849.
- [34] S. Shah, G. P. A. Yap, J. D. Protasiewicz, *J. Organomet. Chem.* **2000**, *608*, 12-20.
- [35] M. M. Hansmann, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 15885-15888.
- [36] a) K. Vaheesar, T. M. Bolton, A. L. L. East, B. T. Sterenberg, *Organometallics* **2010**, *29*, 484-490; b) R. A. Rajagopalan, B. T. Sterenberg, *Organometallics* **2011**, *30*, 2933-2938.
- [37] S. J. Geier, D. W. Stephan, *Chem. Commun.* **2010**, *46*, 1026-1028.

Entry for the Table of Contents



As a synthon of phosphinidene

- * Coordination with Lewis bases
- * Activation of alkenes and alkynes
- * Activation of Si-H and N-H bonds

A thermally robust phosphanorcaradiene with a high molecular-strain was synthesized, which serves as a phosphinidene synthon. It coordinates with Lewis bases to form phosphinidene adducts. Moreover, it can activate unsaturated C=C double and C≡C triple bonds, as well as Si-H and N-H bonds, at room temperature.

Institute and/or researcher Twitter usernames: G. Tan Group @gengwentan