



Communication

Cycloadditions of 1-iminylphosphirane complexes with allenes

Juan Li, Mingyue Cui, Rongqiang Tian*, Zheng Duan*, François Mathey

College of Chemistry, Green Catalysis Center, International Phosphorus Laboratory, International Joint Research Laboratory for Functional Organophosphorus Materials of Henan Province, Zhengzhou University, Zhengzhou 450001, China



ARTICLE INFO

Article history:

Received 25 April 2020

Received in revised form 6 May 2020

Accepted 19 May 2020

Available online 28 May 2020

Keywords:

Phosphirane

Allene

Ring expansion

Cycloaddition

Carbonylative

Heterocycle

ABSTRACT

A cascade carbonylative ring expansion and [2 + 2]/[4 + 2] cycloaddition of strained 1-iminylphosphirane complexes with aryl allenes were reported. The carbonylative ring expansion of 1-iminylphosphirane complexes provides an azaphosphacyclohexone complex intermediate with a C=P double bond. The following [2 + 2] or dearomatic [4 + 2] cycloaddition of this intermediate with allenes is modulated by the aryl substituents on the imino carbon. The regioselective [2 + 2] cycloaddition with 1,1-diaryllallene provides an entry to bicyclo[4.2.0]octan-4-one skeletons featuring a four-membered phosphacyclobutane moiety. While dearomatic [4 + 2] cycloaddition was preferred with less aromatic naphthalene and yielded octahydrochrysene skeleton containing heteroatoms.

© 2020 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

Published by Elsevier B.V. All rights reserved.

Strained three-membered rings such as cyclopropanes, oxiranes and aziridines have been widely used as key building blocks for the synthesis of various high-value medium-sized rings or peri-fused ring systems [1]. However, the development of a similar chemistry with phosphiranes was somewhat hampered until now [2]. Based on our continuous interest on the phosphorus heterocycle chemistry [3], we demonstrated that 1-acylphosphirane tungsten complexes rearrange into 1,3-oxaphospholene complexes with a highly reactive P=C double bond, which is a phosphorus analogue of the Cloke-Wilson rearrangement (Scheme 1a) [4]. Recently, replacing the acyl group with an imino group led us to disclose a novel rearrangement of 1-iminylphosphirane complexes under a CO atmosphere. The successive cycloaddition with olefins yielded 7-aza-1-phosphanorbornane complexes (Scheme 1b) [5]. More interestingly, in the presence of $M(\text{CO})_6$ ($M = \text{W}, \text{Mo}$), the reactions of 1-iminylphosphirane complexes and alkenes provide annulated heterodecalins with high molecular complexity and skeletal diversity (Scheme 1c). The proposed mechanism includes the carbonylative ring expansion and dearomatic Diels-Alder reaction [6].

The carbonylative ring expansion of strained 1-iminylphosphirane complexes provides an azaphosphacyclohexone complex intermediate with a relatively stable C=P double bond. It is known that the highly reactive phosphalkenes can give head-to-head [2 + 2] dimers [7]. On the other hand, cumulated double bonds

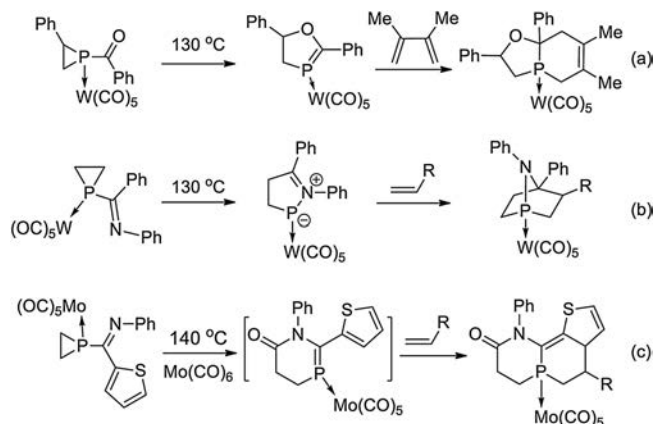
impart an extra reactivity to allene, making it a remarkably active component participating in a variety of cycloaddition reactions [8]. For example, the [2 + 2] cycloaddition reactions of allenes with imines afford azetidines, via a stepwise diradical mechanism rather than a concerted one-step mechanism [9]. This prompted us to investigate the reaction behavior of azaphosphacyclohexone complex with allenes.

We initiated our studies by investigating the reaction of 1-iminylphosphirane **1a** with 1,1-diphenylallene **2a** in the presence of $\text{Mo}(\text{CO})_6$. As shown in Scheme 2, three kinds of products were isolated. The structure of **3aa** was unambiguously established by the X-ray crystallographic analysis (Fig. 1). The phosphorus atom attached to the central carbon atom of the allene. The strain within the 4-membered ring is obvious when looking at the long P1-C9 bond at 1.91 Å. The structure of **4aa** was established by comparing the NMR data of similar structure depicted in Scheme 1c, and was identified by a characteristic =CH₂ resonance in the ¹³⁵dept NMR spectrum at $\delta = +131.7$ ($J_{\text{CP}} = 21.2$ Hz). Comparison of the NMR spectra of **4aa** and **5aa**, the disappearance of characteristic =CH₂ resonance and appearance of a new sp³ CH₂ resonance at high-field indicated the formation of **5aa**. Similarly, replacing the thienyl group in imino moiety (**1a**) by 2-naphthyl (**1b**) provided corresponding product **3ba** along with **6ba**.

To understand the reaction mechanism, the reaction was performed without 1,1-diphenylallene **2a**. The ³¹P NMR of crude reaction solution shows a new peak at +132 ppm which indicate the formation of intermediate **7** reference to the literature report [6]. Subsequent reaction of **7** with **2a** led to the formation of the expected **3ba** and **6ba**. Thus, a cascade mechanism for this reaction

* Corresponding authors.

E-mail addresses: tianrq@zzu.edu.cn (R. Tian), duanzheng@zzu.edu.cn (Z. Duan).



Scheme 1. Important ring expansions of phosphirane complexes.

was proposed (Scheme 3). The carbonylative ring expansion of 1-iminylphosphirane complexes results in the formation of a reactive azaphosphacyclohexone derivative **7**. When **7** undergoes [2 + 2] cycloaddition with the terminal double bond of allene **2a**, the phosphacyclobutane fused **3ba** is produced. The good regioselectivity of [2 + 2] cycloaddition to form **3ba** probably due to the steric hindrance of two phenyl groups inhibited the reactivity of the internal double bond of allene. While, the interesting dearomatic [4 + 2] cycloaddition [10] of **7** with **2a** gives peri-fused heterocycles **6ba**.

Replacing thiophene and naphthalene substituents with benzenoid resulted in the selective formation of the [2 + 2] cycloadducts **3** (Table 1). These results indicated that the selectivity between [2 + 2] and dearomatic [4 + 2] cycloaddition reactions might be tuned by the aryl substituent on imino carbon. The reaction with **1c** gave **3ca** as a sole product in moderate yield (Table 1, entry 1). The efficiency was found to be related to the electron richness of the aryl group on imino carbon, a general trend followed the order electron rich (**1d**, entry 2, 55%) > neutral (**1c**, entry 1, 48%) > electron deficient (**1e**, entry 3, 35%). Electron donating group increases the electron density of C=P double bond in the intermediates which promote the activities of the C=P double bond towards to allenes. Both electron-rich (Table 1, entry 4) and electron-deficient (Table 1, entry 5) aryl substituted allenes worked smoothly with **1c** and afford the corresponding [2 + 2]

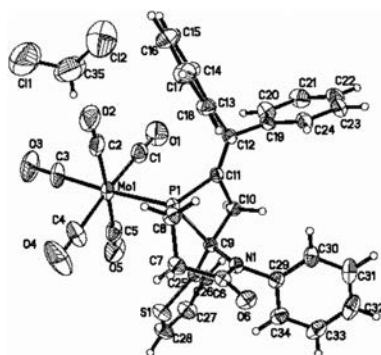
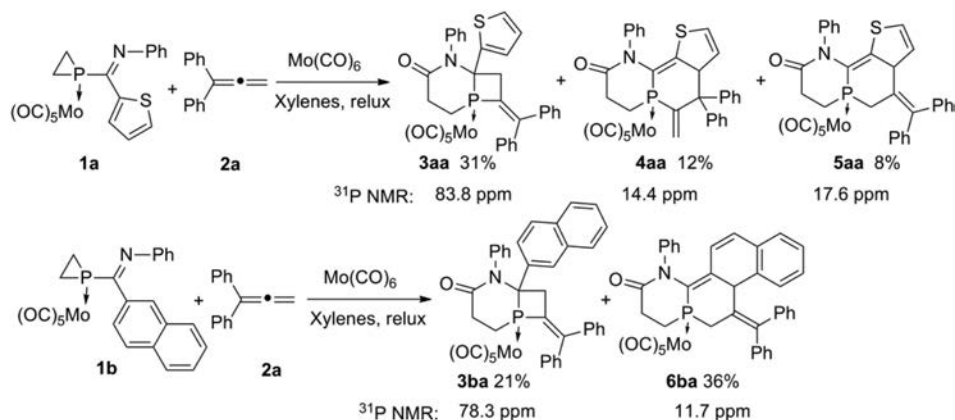


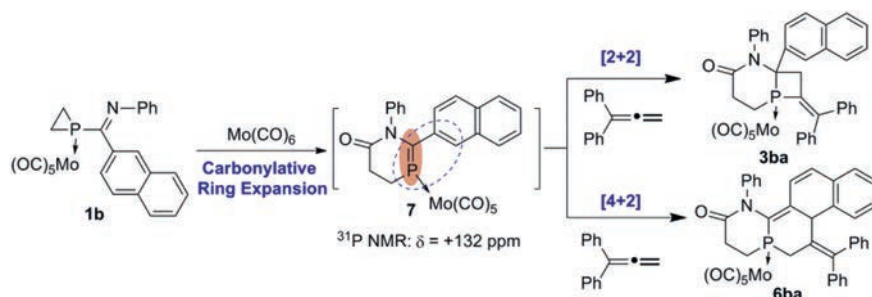
Fig. 1. Molecular structure of diphosphane **3aa**. Selected distances [Å] and angles [°]: P1-C8 1.833(4), P1-C9 1.909(3), P1-C11 1.822(2), C9-C10 1.564(4), C10-C11 1.511(5), C11-C12 1.330(5), P1-Mo1 2.4930(9), C8-P1-C9 103.55(16), C8-P1-C11 111.04(18), C9-P1-C11 76.51(15).

cycloadducts **3cb** and **3cc**. These [2 + 2] cycloadditions with 1,1-diaryllallenes proceeded exclusively at the less substituted double bond. When a less steric hindered 1-phenylallene **2d** was employed, both double bonds in allenes could participate in the [2 + 2] cycloaddition and yielded a pair of regio-isomers (Table 1, entries 6 and 7). All the new P—C bonds were selectively formed with the central carbon of allenes. Unfortunately, this reaction did not proceed with electron-poor allenolate (Table 1, entry 8).

The result with 1-phenylallene **2d** promoted us to revisit the reaction behaviors of thienyl and naphthyl substituted **1a** and **1b** with the less steric hindered allenes. To our delight, the decreased steric hindrance of allene improved both the chemical- and regioselectivities. The dearomatic [4 + 2] cycloadditions, which involving the less aromatic thienyl and naphthyl moieties, became more facile than the competing [2 + 2] cycloadditions (Scheme 4). Moreover, the [4 + 2] reaction with the internal C=C double bond is preferred over the terminal ones of the allene. In all these cases, the products were purified as a mixture of [4 + 2] cycloadducts and the ratios of two adducts were determined by ³¹P NMR. The structure of major product **6bd** was fully confirmed by single-crystal X-ray crystallography analysis (Fig. 2). The X-ray structure of **6bd** confirmed the correction of structure **4aa**. It is worth noting that the regioselectivity decreased with an electron-rich aryl-substituted allene **2g** (3:1), which indicated the regioselectivity was ascribed to the electronic and steric effects

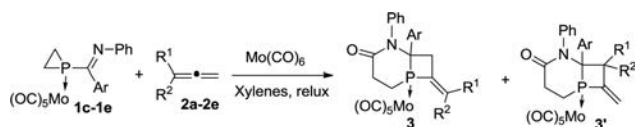


Scheme 2. Reactions of 1-iminylphosphirane complex **1a** and **1b** with 1,1-diphenylallene **2a**.



Scheme 3. Plausible reaction pathway.

Table 1

Reaction of phosphirane complexes **1c–1e** with allenes **2a–2e**.

Entry	Phosphirane		Allene			Product	Yield (%) ^a
	1	Ar	2	R ¹	R ²		
1	1c	Ph	2a	Ph	Ph	3ca	48
2	1d	<i>p</i> -MeOPh	2a	Ph	Ph	3da	55
3	1e	<i>p</i> -CF ₃ Ph	2a	Ph	Ph	3ea	35
4	1c	Ph	2b	<i>p</i> -MeOPh	<i>p</i> -MeOPh	3cb	61
5	1c	Ph	2c	<i>p</i> -FPh	<i>p</i> -FPh	3cc	53
6	1c	Ph	2d	Ph	H	3cd+3cd'	43 ^b
7	1d	<i>p</i> -MeOPh	2d	Ph	H	3dd+3dd'	61 ^b
8	1c	Ph	2e	CO ₂ Et	H		0

^a Yields of the isolated product.^b A mixture of **3** and **3'** in a ratio of 1:1, the ratios were determined by ³¹P NMR spectra.

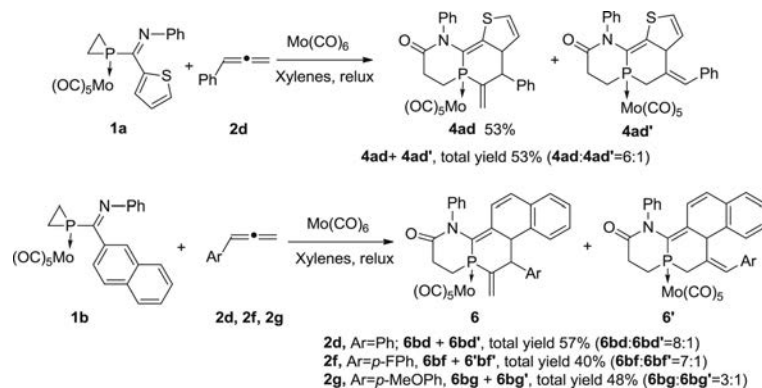
of allene, but the steric hindrance has a more pronounced impact. It should be noted that the reaction with naphthalene substituted **1b** provides an access to the phospho-hydrochrysenone skeleton [11].

In summary, we describe a cascade carbonylative ring expansion and [2+2]/[4+2] cycloaddition of 1-iminylphosphirane complexes with aryl allenes. Particularly, [2+2]/[4+2] cycloaddition in the second step could be modulated by the aryl substituents on the imino carbon of phosphirane complexes. High aromatic benzenoid improved the [2+2] cycloaddition

selectivity and providing a practical entry to a variety of bicyclo [4.2.0]octan-4-one skeletons featuring phosphacyclobutane rings. While dearomatic [4+2] cycloaddition was preferred with naphthalene and yielded octahydrochrysenone skeleton containing heteroatoms.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Scheme 4. Reactions of 1-iminylphosphirane complex **1a** and **1b** with 1-aryllallene **2**.

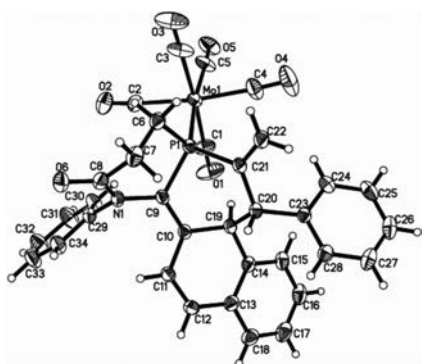


Fig. 2. Molecular structure of diphosphane **6bd**. Selected distances [Å] and angles [°]: P1–C6 1.839(4), P1–C9 1.820(3)(3), P1–C21 1.841(4), C21–C22 1.314(5), C8–O6 1.212(5), P1–Mo1 2.5104(12), C6–P1–C21 103.48(18), C6–P1–C9 98.04(19), C9–P1–C21 97.31(16).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21302174, 21672193 and 21272218), China Post-doctoral Science Foundation (No. 2017M622362), Ministry of Industry and Information Technology of the People's Republic of China (No. Z135060009002), Key Research Projects of Universities in Henan Province (No. 20A150040) and Zhengzhou University of China.

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.ccllet.2020.05.026>.

References

- [1] (a) T.F. Schneider, J. Kaschel, D.B. Werz, *Angew. Chem. Int. Ed.* 53 (2014) 5504–5523;
 (b) Y. Wang, Z.X. Yu, *Acc. Chem. Res.* 48 (2015) 2288–2296;
 (c) C. Ebner, E.M. Carreira, *Chem. Rev.* 117 (2017) 11651–11679;
 (d) G. Fumagalli, S. Stanton, J.F. Bower, *Chem. Rev.* 117 (2017) 9404–9432.
- [2] (a) F. Mathey, *Chem. Rev.* 90 (1990) 997–1025;
 (b) R.E. Buló, H. Jansen, A.W. Ehlers, et al., *Angew. Chem. Int. Ed.* 43 (2004) 714–717.
- [3] (a) J. Wong, Y.X. Li, Y.W. Hao, et al., *Angew. Chem. Int. Ed.* 54 (2015) 12891–12893;
 (b) Y.W. Hao, C.L. Zhang, Y.B. Mei, et al., *Dalton Trans.* 45 (2016) 8284–8290;
 (c) Z.S. Hu, Z.Y. Li, K. Zhao, et al., *Org. Lett.* 17 (2015) 3518–3520;
 (d) H.Y. Huang, G.Y. Tao, Z.B. Wei, et al., *Organometallics* 37 (2018) 464–468;
 (e) H.Y. Huang, H.Y. Luo, G.Y. Tao, et al., *Org. Lett.* 20 (2018) 1027–1030;
 (f) M. Wang, Y. Xu, D.H. Wei, et al., *Chem. Eur. J.* 25 (2019) 15036–15039;
 (g) Y.Y. Song, L.L. Wang, Z. Duan, F. Mathey, *Chin. Chem. Lett.* 31 (2020) 329–332.
- [4] R.Q. Tian, C.L. Zhang, Y. Xu, et al., *Chem. Eur. J.* 23 (2017) 13006–13009.
- [5] Y. Xu, M. Wang, D.H. Wei, et al., *Dalton Trans.* 48 (2019) 5523–5526.
- [6] Y. Xu, C.Y. Jiao, J. Li, et al., *Org. Lett.* 21 (2019) 9512–9515.
- [7] S. Wang, K. Samedov, S.C. Serin, et al., *Eur. J. Inorg. Chem.* 26 (2016) 4144–4151.
- [8] (a) N. Krause, A.S.K. Hashmi, *Modern Allene Chemistry*, Vols. 1–2, Wiley-VCH Verlag GmbH & Co., Weinheim, 2004;
 (b) M.R. Siebert, J.M. Osbourn, K.M. Brummond, et al., *J. Am. Chem. Soc.* 132 (2010) 11952–11966;
 (c) T. Iwata, F. Inagaki, C. Mukai, *Angew. Chem. Int. Ed.* 52 (2013) 11138–11142;
 (d) F. Lopez, J.L. Mascarenas, *Chem. Soc. Rev.* 43 (2014) 2904–2915;
 (e) W. Ding, N. Yoshikai, *Angew. Chem. Int. Ed.* 58 (2019) 2500–2504;
 (f) X.L. Han, P.P. Lin, Q.J. Li, *Chin. Chem. Lett.* 30 (2019) 1495–1502.
- [9] E. Schaumann, H. Mrotzek, *Tetrahedron* 35 (1979) 1965–1968.
- [10] (a) A.R. Pape, K.P. Kaliappan, E.P. Kündig, *Chem. Rev.* 100 (2000) 2917–2940;
 (b) S.H. Meiere, J.M. Keane, T.B. Gunnoe, et al., *J. Am. Chem. Soc.* 125 (2003) 2024–2025;
 (c) B.K. Liebov, W.D. Harman, *Chem. Rev.* 117 (2017) 13721–13755.
- [11] X.Q. Zhang, T. Guzi, L. Pettus, A.G. Schultz, *Tetrahedron Lett.* 43 (2002) 7605–7608 and references cited therein.