C–H Activation

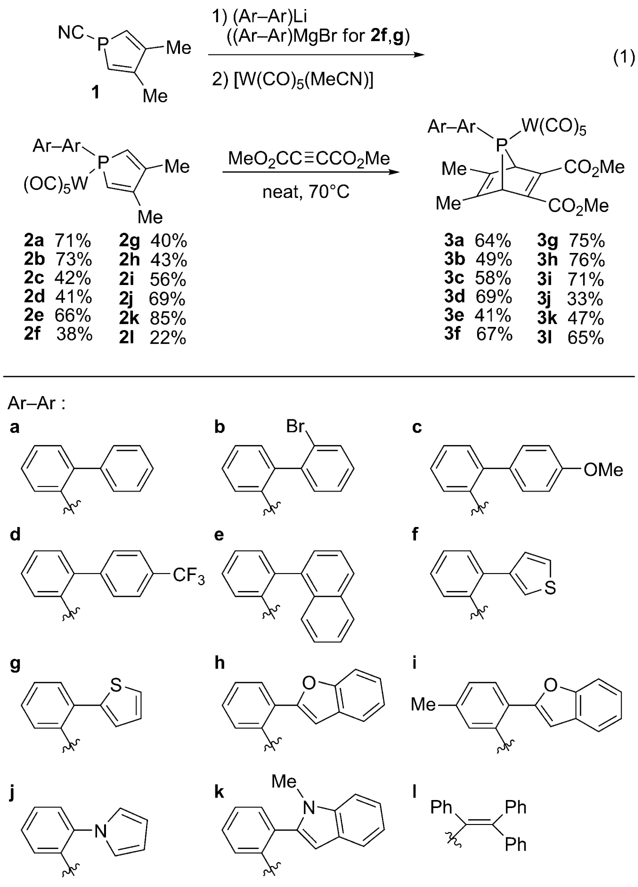
DOI: 10.1002/anie.201410603

Synthesis of Annelated Phospholes through Intramolecular C–H Activation by Monovalent Phosphorus[**]

Xinda Wei, Zongming Lu, Xu Zhao, Zheng Duan, and Francois Mathey**

Abstract: *Electrophilic terminal phosphinidene complexes [Ar-Ar-P-W(CO)$_5$] (Ar-Ar: biaryl or an analogue thereof) undergo a spontaneous insertion of the phosphorus atom into the vicinal C–H bonds to give annelated phospholes. Twelve examples are described, including biphenyl, thienyl, pyrrolyl, and benzofuryl groups as biaryl moieties. The activation energy of the insertion reaction is quite low (about 2 kcal mol^{-1}).*

Annelated phospholes are recognized as valuable precursors for the preparation of a variety of optoelectronic devices, which explains the upsurge of interest in the synthesis of these species in the recent literature.[1] A wide range of annelated phospholes, including some species that were never described before, were now prepared following a new methodology. The carbene-like chemistry of electrophilic terminal phosphinidene complexes [R-P-M(CO)$_n$] (M = Cr, Mo, W, Fe; n = 4,5) is well developed,[2] but so far the formation of single P–C bonds by insertion of phosphinidenes into C–H bonds remains scarce.[3] Champion and Cowley described the intramolecular insertion of P^{I} into the C–H bond of the vicinal *tert*-butyl group of the transient [Fe(CO)$_4$]/supermesitylphosphinidene complex.[3a] This report led us to consider the possibility that such insertions may be favored by proximity effects. A logical testing ground for this idea was the family of 1,1′-biaryl-2-phosphinidene complexes [1,1′-Ar-Ar-2-P-W(CO)$_5$]. Thus, we decided to investigate this family of phosphinidenes using the classical 7-phosphanorbornadiene route.[4] These precursors were synthesized as shown in Equation (1). Because of the bulkiness of the biaryl substituent, the synthesis of these 7-phosphanorbornadienes must be performed in neat acetylenedicarboxylate for extended periods of time. The cycloaddition takes place on the tungsten side of the phosphole ring, contrary to what happens with phenyl or methyl substituents.



(1)

The thermolysis of **3a** gives the complex of the parent dibenzophosphole **4a**, whose P–H bond is immediately visible on the ^{31}P NMR spectrum: δ^{31}P(**4a**) −43.3 (CDCl$_3$), $^{1}J_{\mathrm{PH}} = 341$ Hz. Similar thermolyses were carried out with **3b–l** to give **4b–l** with satisfactory yields, as shown in Equation (2). This result highlights the potential of this strictly neutral approach to annelated phospholes.

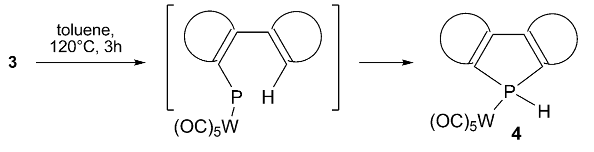
In biaryl analogues with a thiophene moiety, C–H activation can either take place at the α or β position (see products **4f** and **4g**). However, when both positions are available, there is a 100% preference for the α position [Equation (3)], as demonstrated by the synthesis of **4f**. Compounds related to **4f** have been reported recently,[5]

---

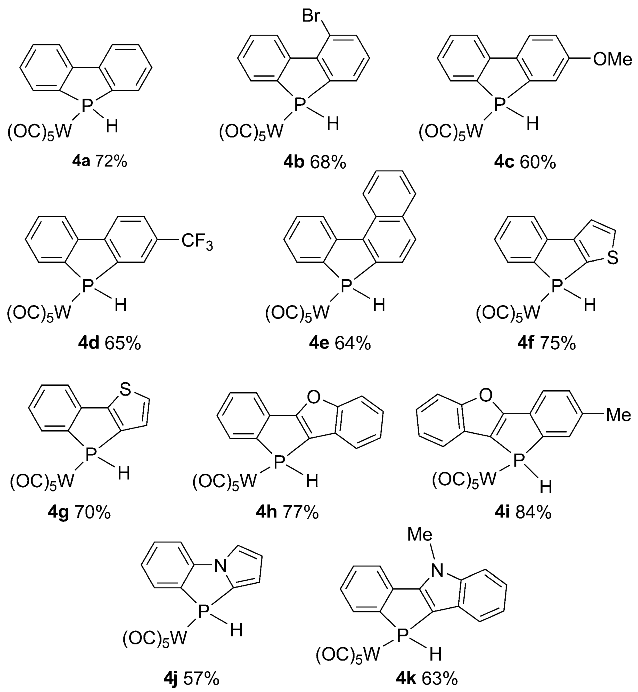
[*] X. Wei, Z. Lu, X. Zhao, Prof. Dr. Z. Duan, Prof. Dr. F. Mathey
College of Chemistry and Molecular Engineering
International Phosphorus Laboratory, Joint Research Laboratory for Functional Organophosphorus Materials of Henan Province
Zhengzhou University
Zhengzhou 450001 (P.R. China)
and
Division of Chemistry and Biological Chemistry
Nanyang Technological University
21 Nanyang Link, Singapore 637371 (Singapore)
E-mail: duanzheng@zzu.edu.cn
fmathey@ntu.edu.sg

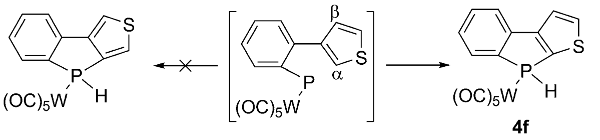
[**] This work was supported by the National Natural Science Foundation (21272218), Specialized Research Fund for the Doctoral Program of Higher Education (20134101110004), and Zhengzhou Science and Technology Department (131PYSGZ204) of China.

Supporting information for this article (including the experimental section, NMR and UV-Vis data, emission spectra, and the X-ray crystal structure of compound **4f**) is available on the WWW under http://dx.doi.org/10.1002/anie.201410603.



(2)





(3)

and the structure of **4f** has been confirmed by X-ray crystal analysis (Figure 1).[9]

The synthesis of previously unknown annelated heterophospholes such as **4j** is also quite noteworthy. The most significant NMR data of **4a–k** are collected in Table 1. The NMR data of the dibenzophospholes **4a–e** are quite homogeneous. Only the CF_3-substituted compound, **4d**, displays significant differences. According to reported data,[6] the higher $^1J_{PW}$ coupling of **4d** indicates its stronger acceptor properties in comparison to the other compounds. On the same basis, the α-connected phosphole **4f** has stronger acceptor properties than the β-connected thiophene derivative **4g**. The other compounds **4h–k** display significantly different NMR parameters. The heterophosphole **4j** appears to be the most powerful acceptor of the group.

In order to test the limits of the method, we investigated whether simpler structures, such as phosphindoles, could also be obtained by this approach. This is indeed the case, as shown by Equation (4).

To gain information on the insertion reaction, we computed the structure of the biphenylphosphinidene complex obtained from **3a** by DFT at the B3LYP/6-31G(d)-Lanl2dz

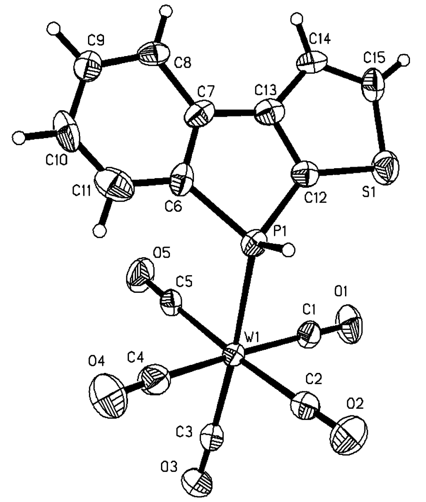
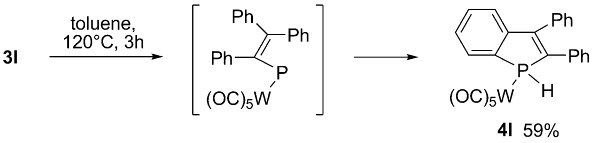


Figure 1. X-ray crystal structure of **4f**. Main bond lengths (Å) and angles (°): P1–W1 2.4845(14), P1–C6 1.817(5), P1–C12 1.811(5), C6–C7 1.380(7), C12–C13 1.384(6), C7–C13 1.456(7), C12–S1 1.743(5), S1–C15 1.710(11), C13–C14 1.479(11), C14–C15 1.343(11); C6-P1-C12 89.4(2), C12-S1-C15 93.0(4).

Table 1: NMR data of **4a–k** in $CDCl_3$.

	δ ^{31}P	δ ^1H (PH)	$^1J_{HP}$ [Hz]	$^1J_{PW}$ [Hz]
4a	−43.3	6.79	341	225
4b	−41.4	6.78	341	227.8
4c	−42.7	6.78	341	224.8
4d	−48.3	6.87	343.7	228.2
4e	−41.84	6.84	339.6	224.6
4f	−48.9	6.92	349	229.3
4g	−52.9	6.76	346	225
4h	−62.8	6.79	343.5	228.3
4i	−63.4	6.75	350.4	228.5
4j	−67.7	6.97	347.5	235.4
4k	−62.2	6.74	343.6	225.5



(4)

(W) level (Figure 2a).[7] The two aryl rings form an angle of 44°. The separation between P and H29 is relatively small at 2.73 Å. This proximity favors the insertion, which proceeds through a transition state that is shown in Figure 2b. In this transition state, the phosphole ring is already formed, but the migrating hydrogen atom is still closer to the carbon than to the phosphorus atom. The transition state lies only 2.0 kcal mol^{-1} above the starting phosphinidene (corrected for zero-point energy). The corresponding reaction profile is shown in Figure 2c. The insertion of the P atom into the C–H bond appears to be very easy. It is clear from these data that the relatively high temperature that is needed to perform the synthesis of these annelated phospholes **4** results in the collapse of the 7-phosphanorbornadiene **3**. Once the phosphinidene is generated, its cyclization is instantaneous.

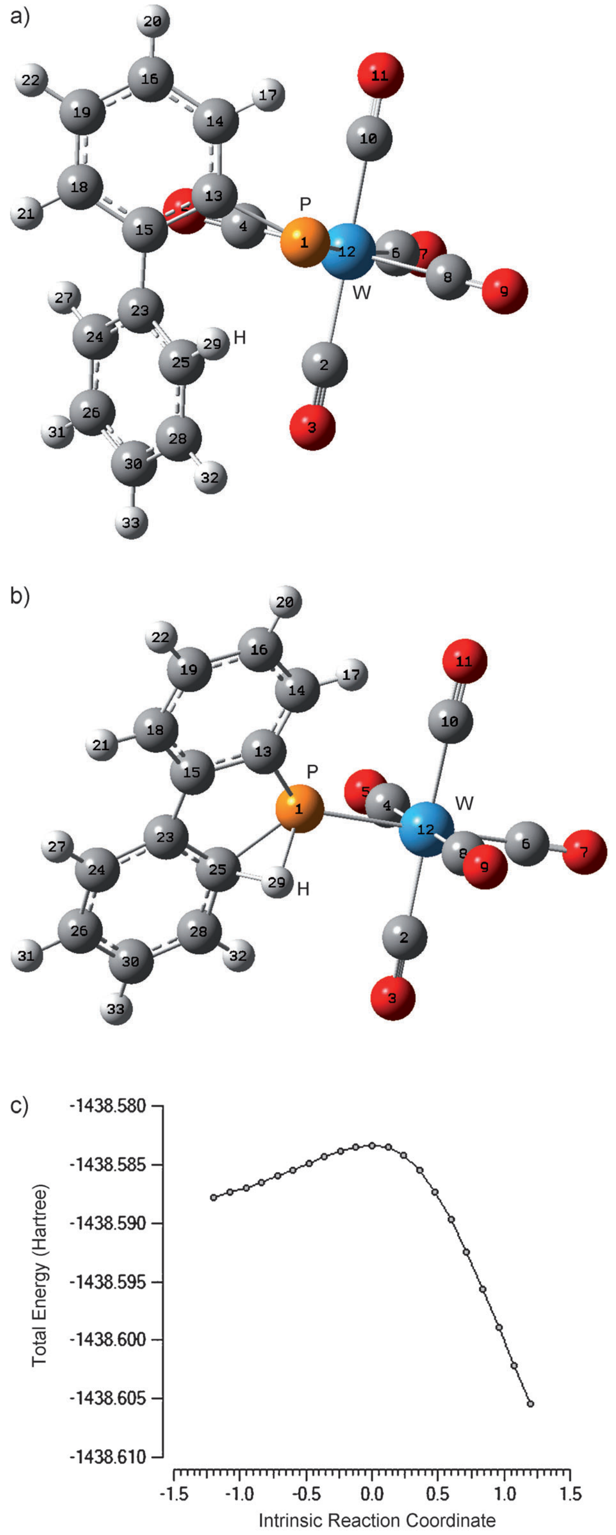
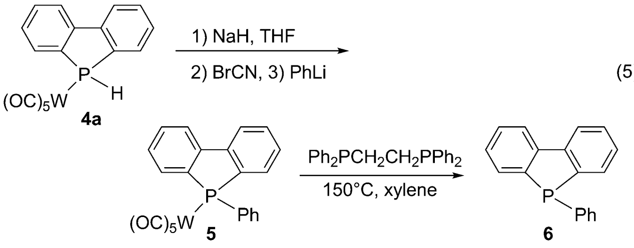


Figure 2. a) Computed structure of the biphenylphosphinidene P-W(CO)$_5$ complex and b) computed transition state (one negative frequency) leading to **4a**. Main bond lengths (Å) and angles (°): a) P1–W12 2.442, P1–C13 1.837, C13–C15 1.417, C15–C23 1.484, C23–C25 1.408, C25–H29 1.088, H29–P1 2.731; C13-P1-W12 112.77, C13-C15-C23-C25 44.03. b) P1–W12 2.555, P1–C13 1.785, P1–C25 1.878, P1–H29 1.638, C25–H29 1.302; C13-P1-C25 90.00, P1-H29-C25 78.50. c) Calculated profile for the reaction leading to **4a**.

In order to explain the specific formation of **4f** [see Eq. (3)], we also computed the electronic structure of the 3-thienylphenylphosphinidene complex. It appears that the cyclization occurs under charge control. The electrophilic phosphorus atom (Mulliken charge +0.323) preferably interacts with Cα (−0.383) rather than Cβ (−0.135).

The ability of monovalent phosphorus to easily activate vicinal C–H bonds (comparable with that of transition metals)[8] opens quite exciting perspectives. The only question that remains is whether it is possible to decomplex the annelated phospholes or not. This reaction is indeed possible, as shown in Equation (5), although the conditions have not been optimized.



(5)

Obviously, this new approach toward annelated phospholes has huge potential and supplements the existing routes[1] to these species whose potential as conjugated materials for optoelectronic applications is now well established. The emission spectra of several phospholes (see the Supporting Information) suggest that these species deserve further attention.

Received: October 30, 2014

Keywords: biaryls · C–H activation · insertion · phosphinidenes · phospholes

---

[1] Review: Y. Matano, H. Imahori, *Org. Biomol. Chem.* **2009**, *7*, 1258; Some recent references: W. Ma, L. Ackerman, *Synthesis* **2014**, *46*, 2297; B. Wu, M. Santra, N. Yoshikai, *Angew. Chem. Int. Ed.* **2014**, *53*, 7543; *Angew. Chem.* **2014**, *126*, 7673; Y. Unoh, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2013**, *52*, 12975; *Angew. Chem.* **2013**, *125*, 13213; H. Chen, W. Delaunay, J. Li, Z. Wang, P.-A. Bouit, D. Tondelier, B. Geffroy, F. Mathey, Z. Duan, R. Réau, M. Hissler, *Org. Lett.* **2013**, *15*, 330; K. Baba, M. Tobisu, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 11892; *Angew. Chem.* **2013**, *125*, 12108; Y.-R. Chen, W.-L. Duan, *J. Am. Chem. Soc.* **2013**, *135*, 16754; Y. Hayashi, Y. Matano, K. Suda, Y. Kimura, Y. Nakao, H. Imahori, *Chem. Eur. J.* **2012**, *18*, 15972; Y. Dienes, S. Durben, T. Karpati, T. Neumann, U. Englert, L. Nyulaszi, T. Baumgartner, *Chem. Eur. J.* **2007**, *13*, 7487; J. G. Cordaro, D. Stein, H. Grützmacher, *J. Am. Chem. Soc.* **2006**, *128*, 14962.

[2] Recent reviews: J. C. Slootweg, K. Lammertsma, *Sci. Synth.* **2009**, *42*, 15; R. Waterman, *Dalton Trans.* **2009**, 18; M. Rani, *Synlett* **2008**, 2078; F. Mathey, *Dalton Trans.* **2007**, 1861; K. Lammertsma, *Top. Curr. Chem.* **2003**, *229*, 95; K. Lammertsma, M. J. M. Vlaar, *Eur. J. Org. Chem.* **2002**, 1127; F. Mathey, N. H. Tran Huy, A. Marinetti, *Helv. Chim. Acta* **2001**, *84*, 2938.

[3] D. H. Champion, A. H. Cowley, *Polyhedron* **1985**, *4*, 1791; J. Svara, F. Mathey, *Organometallics* **1986**, *5*, 1159; N. H. Tran Huy, L. Ricard, F. Mathey, *New J. Chem.* **1998**, *22*, 75; R. E. Bulo, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, B. Wang, *Chem. Eur. J.* **2004**, *10*, 2732.

[4] A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667.

[5] Y. Kuninobu, T. Yoshida, K. Takai, *J. Org. Chem.* **2011**, *76*, 7370.

[6] F. Mercier, F. Mathey, C. Afiong-Akpan, J.-F. Nixon, *J. Organomet. Chem.* **1988**, *348*, 361.

[7] Gaussian 03 (Revision B.05), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **2003**.

[8] Review on synthetic aspects: G. Rouquet, N. Chatani, *Angew. Chem. Int. Ed.* **2013**, *52*, 11726; *Angew. Chem.* **2013**, *125*, 11942; Theoretical aspects: M. Lein, *Coord. Chem. Rev.* **2009**, *253*, 625.

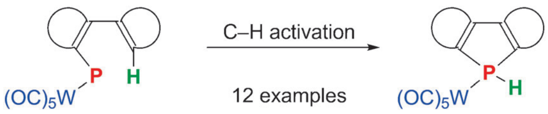
[9] CCDC 1012807 (**4 f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Communications

C–H Activation

X. Wei, Z. Lu, X. Zhao, Z. Duan,*
F. Mathey* ______________ ■■■■–■■■■

Synthesis of Annelated Phospholes through Intramolecular C–H Activation by Monovalent Phosphorus



Proximity matters: Electrophilic terminal phosphinidene complexes (left, with Ar-Ar being biaryl or an analogue thereof) undergo a spontaneous insertion of the P atom into the vicinal C–H bond to give annelated phospholes. The latter compounds are valuable precursors for the preparation of a variety of optoelectronic devices.