Phosphinidene Complexes

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Using Monovalent Phosphorus Compounds to Form P–C Bonds**

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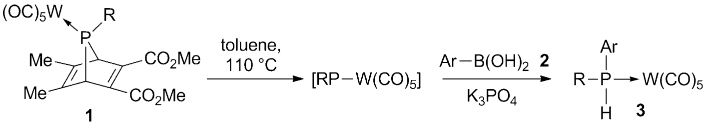
Since its inception in 1855 with the work of Hofmann on trialkyphosphines,[1] organophosphorus chemistry has relied on the tools available for forming P–C bonds. Not surprisingly, a lot of work has been done on this topic.[2] The most recent advances concern the use of catalysts.[3] Herein, we describe a new route to P–C bonds. The flourishing development of the chemistry of electrophilic terminal phosphinidene complexes[4] that derive from monovalent phosphorus offers the possibility of creating a new approach to P–C bonds, one that relies on the conversion of P^I into P^{III} just as the classical Arbuzov reaction relies on a P^{III}-to-P^V transformation. Unfortunately, to date, no reasonably general synthesis of P–C bonds from phosphinidenes is available, except for a range of versatile cycloaddition reactions with unsaturated hydrocarbons. The literature contains a few reports of phosphinidene insertions into special C–H bonds[5] and two examples of reactions with soft carbon nucleophiles, that is, malonate anions[6] and stabilized phosphorus ylids.[7] Based on these last results, it appeared that the key to success was the choice of an appropriate mild carbon nucleophile. This led us to consider the possible use of the organoborates widely used in the Suzuki cross-coupling reaction.[8]

Our preliminary experiments were carried out with the 7-phenyl-7-phosphanorbornadiene precursor **1a** (R = Ph),[9a] phenylboronic acid **2a** (Ar = Ph), and a variety of bases. The best conditions are given in Equation (1):



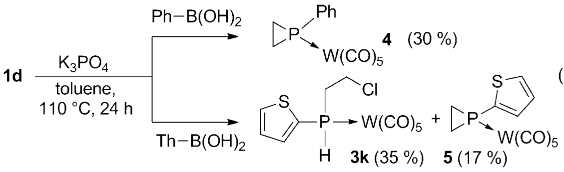
(1)

According to the ^{31}P monitoring of the reaction mixture, the reaction is extremely clean. The reaction must be run under strictly anhydrous conditions since terminal phosphinidene complexes readily insert into the O–H bond of water.[10] Potassium phosphate appears to be the best base; potassium carbonate and triethylamine are inefficient. Catalysts such as CuCl or [$Pd_2(dba)_3$] (dba = dibenzylidenacetone) lower the yields and induce the formation of by-products. We verified that the reaction is quite general as shown in Table 1. The X-ray crystal structure of **3b** is shown in Figure 1.

Table 1: Reaction of 7-phosphanorbornadienes **1** with arylboronic acids **2**. Th = thienyl, Fu = furyl.

1 R	**2** Ar	Reaction time [h]	**3** Yield [%]
1a Ph	**2a** Ph	17	**3a** 48
1a Ph	**2b** 2-Th	17	**3b** 76
1a Ph	**2c** 2-Fu	15	**3c** 37
1a Ph	**2d** 4-MeO-C_6H_4	17	**3d** 52
1b Me	**2a** Ph	24	**3e** 46
1b Me	**2b** 2-Th	24	**3f** 69
1b Me	**2c** 2-Fu	14	**3g** 20
1b Me	**2d** 4-MeO-C_6H_4	16	**3h** 45
1c Bn	**2a** Ph	18	**3i** 52
1c Bn	**2b** 2-Th	18	**3j** 65
1d CH_2CH_2Cl	**2b** 2-Th	24	**3k** 35
1e OMe	**2a** Ph	3	**3l** 10

The mechanism of this reaction is necessarily complex since the role of the base is to allow the transfer of the aryl group from the electrophilic boronic acid to the electrophilic phosphinidene complex. What is known is that a simple base such as an amine is totally inefficient because it gives a loose adduct with the phosphinidene, which becomes nucleophilic.[11] A possible explanation would be that a single anionic phosphate complexes both the phosphinidene and the boronic acid and thus allows the transfer of the aryl anion from boron to phosphorus to give a phosphido complex. To find evidence for this phosphido complex, we repeated the reaction with 7-β-chloroethyl-7-phosphanorbornadiene (**1d**)[9b] [Eq. (2)].



(2)

The formation of the phosphiranes **4** and **5** supports the intermediacy of a nucleophilic phosphido intermediate. Note that the nucleophilicity of this intermediate strongly depends on the nature of the aryl group since **3k** does not fully cyclize under the reaction conditions used.

The next step of our investigation concerned the possible use of alkylboronic acids. Surprisingly, we obtained the reduction product **6** [Eq. (3)].

In the Suzuki cross-coupling, the intermediate alkylpalladium species can undergo β or α-H elimination with formation of a palladium hydride, an observation that explains why the coupling reaction fails. This type of β or α-

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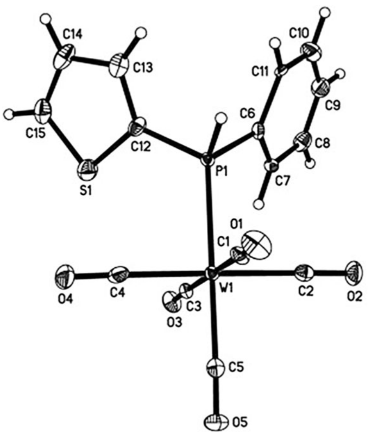
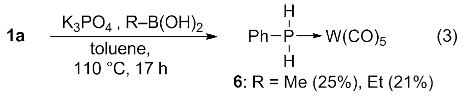


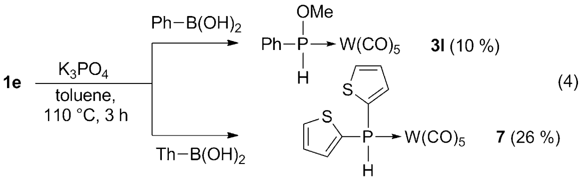
Figure 1. X-ray crystal structure of **3b**. Main bond lengths [Å] and angles [deg]: P–W 2.4940(10), P–C6 1.816(4), P–C12 1.799(15); C6-P-C12 100.0(4), C6-P-W 119.10(14), C12-P-W 120.0(6).[13]



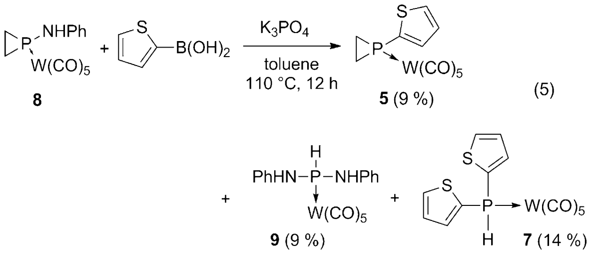
6: R = Me (25%), Et (21%)

H elimination cannot take place at phosphorus, so we have no simple explanation for why the coupling failed in this case.

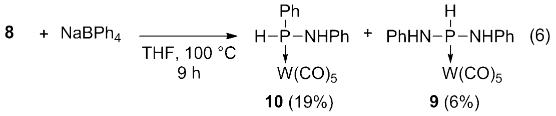
The final experiments concerned the possible use of alkoxy- and aminophosphinidenes in this kind of reaction. The reaction of methoxyphosphinidene, produced from the appropriate 7-phosphanorbornadiene precursor **1e**,[9c] proved to be less satisfactory than the use of P–Me or P–Ph derivatives owing to the reactivity of the P–OMe bond toward the boron reagent (boron is more oxophilic than phosphorus) [Eq. (4)].



Similarly, using the 1-phenylaminophosphirane complex **8** as the phosphinidene precursor,[12] we noticed the high reactivity of the P–N bond, an effect that can supersede the cycloreversion in the case of the reaction with 2-thienylboronic acid. This leads to a complex mixture of products [Eq. (5)].



Changing the conditions and using the milder sodium tetraphenylborate, more satisfactory but still insufficient results were obtained [Eq. (6)].



This new method for forming P–C bonds has great potential because it can use the wide array of aryl and heterocyclic boronic acids that has been developed for the popular Suzuki cross-coupling reaction and combine them with the numerous electrophilic phosphinidene complexes that have been reported. Furthermore, the final products incorporate a P–H bond that can be used for further transformations.

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[1] For a recent review of the work of A. W. Hofmann in organophosphorus chemistry, see: L. D. Quin, *Heteroat. Chem.* **2013**, *24*, 243.

[2] See, for example: a) A. Michaelis, R. Kaehne, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1048; b) B. A. Arbusov, *Pure Appl. Chem.* **1964**, *9*, 307; c) B. A. Trofimov, S. N. Arbuzova, N. K. Gusarova, *Russ. Chem. Rev.* **1999**, *68*, 215; d) D. Enders, A. Saint-Dizier, M. I. Lannou, A. Lenzen, *Eur. J. Org. Chem.* **2006**, 29; e) M. T. Honaker, J. M. Hovland, R. N. Salvatore, *Curr. Org. Chem.* **2007**, *11*, 31; f) P. A. Badkar, N. P. Rath, C. D. Spilling, *Org. Lett.* **2007**, *9*, 3619; g) Y. Zhu, J. P. Malerich, V. H. Rawal, *Angew. Chem.* **2010**, *122*, 157; *Angew. Chem. Int. Ed.* **2010**, *49*, 153; h) A. Perrier, V. Comte, C. Moise, P. Richard, P. Le Gendre, *Eur. J. Org. Chem.* **2010**, 1562; i) M. C. Lamas, A. Studer, *Org. Lett.* **2011**, *13*, 2236; j) C. S. Daeffler, R. Grubbs, *Org. Lett.* **2011**, *13*, 6429; k) F. J. Wang, M. L. Qu, F. Chen, Q. Xu; M. Shi, *Chem. Commun.* **2012**, *48*, 8580; M. Shi, *Chem. Commun.* **2012**, *48*, 8580; l) F. Alonso, Y. Moglie, G. Radivoy, M. Yus, *Green Chem.* **2012**, *14*, 2699.

[3] a) I. P. Beletskaya, M. A. Kazankova, *Russ. J. Org. Chem.* **2002**, *38*, 1391; b) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079; c) F. M. J. Tappe, V. T. Trepohl, M. Oestreich, *Synthesis* **2010**, 3037; d) Q. Xu, L. B. Han, *J. Organomet. Chem.* **2011**, *696*, 130; e) D. Zhao, R. Wang, *Chem. Soc. Rev.* **2012**, *41*, 2095; f) O. Berger, C. Petit, E. L. Deal, J.-L. Montchamp, *Adv. Synth. Catal.* **2013**, *355*, 1361.

[4] 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.

[5] 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.

[6] C. Compain, N. H. Tran Huy, F. Mathey, *Heteroat. Chem.* **2004**, *15*, 258.

[7] N. H. Tran Huy, C. Compain, L. Ricard, F. Mathey, *J. Organomet. Chem.* **2002**, *650*, 57; N. Hoffmann, C. Wismach, P. G. Jones, R. Streubel, N. H. Tran Huy, F. Mathey, *Chem. Commun.* **2002**, 454; N. H. Tran Huy, C. Compain, L. Ricard, F. Mathey, *Organometallics* **2002**, *21*, 4897.

[8] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; b) S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem.* **2004**, *116*, 1907; *Angew. Chem. Int. Ed.* **2004**, *43*, 1871; c) C. G. Blettner, W. A. Konig, W. Stenzel, T. Schotten, *J. Org. Chem.* **1999**, *64*, 3885; d) P. Appukkuttan, A. B. Orts, R. P. Chandran, J. L. Goeman, J. Van der Eycken, W. Dehan, E. Van der Eycken, *Eur. J. Org. Chem.* **2004**, 3277; e) W. Zhang, C. H.-T. Chen, Y. Lu, T. Nagashima, *Org. Lett.* **2004**, *6*, 1473; f) Y. Kabri, A. Gellis, P. Vanelle, *Eur. J. Org. Chem.* **2009**, 4059; g) Y. Kabri, M. D. Crozet, R. Szabo, P. Vanelle, *Synthesis* **2011**, 3115.

[9] a) A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Chem. Soc. Chem. Commun.* **1982**, 667; b) B. Deschamps, F. Mathey, *Tetrahedron Lett.* **1985**, *26*, 4595; c) J.-M. Alcaraz, J. Svara, F. Mathey, *New J. Chem.* **1986**, *10*, 321.

[10] A. Marinetti, F. Mathey, *Organometallics* **1982**, *1*, 1488.

[11] I. Kalinina, F. Mathey, *Organometallics* **2006**, *25*, 5031.

[12] B. Deschamps, L. Ricard, F. Mathey, *Polyhedron* **1989**, *8*, 2671.

[13] CCDC 969341 (**3b**) 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.