Synthetic Methods

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Synthesis of Phosphabenzenes by an Iron-Catalyzed [2+2+2] Cycloaddition Reaction of Diynes with Phosphaalkynes**

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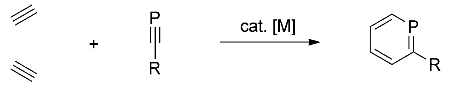
Abstract: *A method for the synthesis of phosphabenzenes under iron catalysis is described. Thus, the* FeI_2*-catalyzed [2+2+2] cycloaddition of diynes with phosphaalkynes in m-xylene gave a variety of phosphabenzenes in good to high yields (up to 87 % yield).*

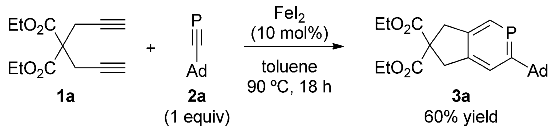
The development of novel methods for the construction of aromatic rings is important in enabling access to new drugs, materials, and other useful molecules.[1] In sharp contrast to benzenes and pyridines, which have been synthesized by a broad range of organic reactions, the synthesis of phosphabenzenes has received relatively little attention.[2–6] Phosphabenzenes are attractive motifs as heavier-atom-containing benzene analogues, and have been utilized as ligands for transition-metal complexes.[2,3] Since the first synthesis of phosphabenzenes by the treatment of pyrylium salts with phosphine equivalents,[4] a number of other synthetic methods have been investigated.[2,5,6] However, to the best of our knowledge, no transition-metal-catalyzed reactions have been reported for the synthesis of phosphabenzenes.

Transition-metal-catalyzed [2+2+2] cycloaddition has been studied extensively as a powerful strategy for the selective preparation of benzenes and pyridines.[7] Recently, a variety of transition-metal catalysts have been applied to [2+2+2] cycloaddition reactions of two alkynes with nitriles to produce pyridines with high selectivity. Against this background, we envisaged the use of phosphaalkynes[8,9] as substrates for [2+2+2] cycloaddition reactions catalyzed by transition-metal complexes as a novel synthetic method toward phosphabenzenes (Scheme 1). Herein we disclose our preliminary results on the use of iron-catalyzed[10,11] [2+2+2] cycloaddition reactions of diynes with phosphaalkynes to synthesize the corresponding phosphabenzenes in good to high yields.



Scheme 1. Strategy for the synthesis of phosphabenzenes by a transition-metal-catalyzed [2+2+2] cycloaddition reaction.

At first, we carried out reactions of 4,4-bis(ethoxycarbonyl)hepta-1,6-diyne (**1a**) with 1-adamantylphosphaethyne (**2a**) in the presence of a variety of transition-metal complexes, such as cobalt, nickel, ruthenium, rhodium, and iridium complexes, which were previously reported to function as effective catalysts of various [2+2+2] cycloaddition reactions.[7] Unfortunately, these transition-metal complexes did not act as effective catalysts (see Table S1 in the Supporting Information for details). However, when FeI_2 was used as a catalyst in toluene at 90 °C for 18 h, the desired phosphabenzene **3a** was obtained in 60 % yield (Scheme 2). This result prompted us to investigate the iron-catalyzed reaction in detail.



Scheme 2. Initial investigation of the transition-metal-catalyzed [2+2+2] cycloaddition reaction. Ad = adamantyl.

The reaction of **1a** with **2a** (2 equiv) in the presence of FeI_2 (10 mol %) in *m*-xylene at 140 °C (bath temperature) for 18 h gave **3a** in 83 % yield (Table 1, entry 1). In this reaction system, no formation of benzene derivatives by the trimerization of **1a** was observed. The use of $FeBr_2$ and $FeCl_2$ as catalysts, in place of FeI_2, gave **3a** in 16 and 17 % yield, respectively (Table 1, entries 2 and 3). No reaction occurred in the presence of iron(II) trifluoromethanesulfonate ($Fe(OTf)_2$; Table 1, entry 4); however, the addition of KI (20 mol %) led to the formation of **3a** (Table 1, entry 5). These results indicate that the iodide ligand at the iron center plays an important role in promoting the present reaction.

When *o*- and *p*-xylene were used as solvents, **3a** was obtained in slightly lower yield (Table 1, entries 6 and 7). The reaction did not proceed smoothly in the solvents anisole and *ortho*-dichlorobenzene (Table 1, entries 8 and 9). When 1,3-bis(diphenylphosphino)propane (dppp) and 2,2′-bipyridyl (bpy) were added as ligands to the iron complex, the yield of **3a** decreased dramatically (Table 1, entries 10 and 11). Reduced iron complexes generated in situ by the reduction of

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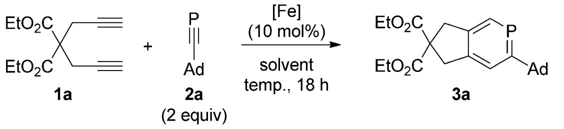
Table 1: Optimization of the reaction conditions with substrates **1a** and **2a**.[a]



Entry	[Fe]	Additive	Solvent	*T*	Yield [%][b]
1	FeI_2	–	*m*-xylene	140 °C	83
2	$FeBr_2$	–	*m*-xylene	140 °C	16
3	$FeCl_2$	–	*m*-xylene	140 °C	17
4	$Fe(OTf)_2$	–	*m*-xylene	140 °C	0
5	$Fe(OTf)_2$	KI[c]	*m*-xylene	140 °C	50
6	FeI_2	–	*o*-xylene	140 °C	71
7	FeI_2	–	*p*-xylene	140 °C	74
8	FeI_2	–	anisole	140 °C	0
9	FeI_2	–	*o*-$C_6H_4Cl_2$	140 °C	3
10	FeI_2	dppp[c]	*m*-xylene	140 °C	12
11	FeI_2	bpy[c]	*m*-xylene	140 °C	0
12	FeI_2	Zn[c]	*m*-xylene	140 °C	0
13	FeI_2	–	*m*-xylene	90 °C	64
14	FeI_2	–	*m*-xylene	60 °C	42
15	FeI_2	–	*m*-xylene	RT	0
16	FeI_2[c]	–	*m*-xylene	140 °C	80
17	–	–	*m*-xylene	140 °C	0

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.30 mmol), iron catalyst (0.015 mmol), solvent (1.5 mL), 18 h. [b] Yield of the isolated product. [c] 20 mol %. Tf = trifluoromethanesulfonyl.

Fe^{II} salts with Zn have been reported to act as efficient catalysts in iron-catalyzed [2+2+2] cycloaddition reactions.[10-d,e,11c] However, no reaction took place when Zn was added to the present reaction system (Table 1, entry 12). As the reaction temperature was lowered, the product yield decreased (Table 1, entries 13–15). The use of 20 mol % of FeI_2 did not improve the yield of **3a**, but no formation of **3a** was observed at all in the absence of FeI_2 (Table 1, entries 16 and 17). These results clearly indicate that FeI_2 plays a critical role in promoting the [2+2+2] cycloaddition of the diyne with the phosphaalkyne.

The molecular structure of **3a** was determined unambiguously by X-ray crystallographic analysis (Figure 1). The bond lengths and angles of the phosphabenzene ring in **3a** are similar to those of phosphabenzene derivatives previously reported by other research groups.[12]

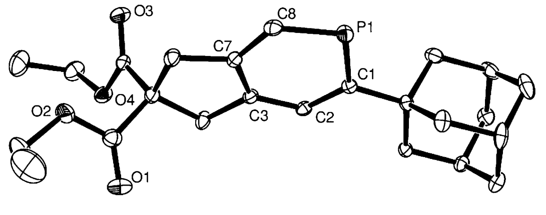
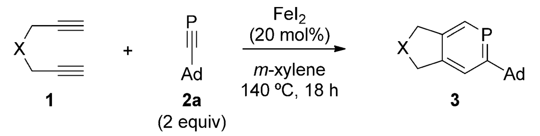
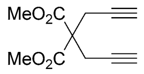
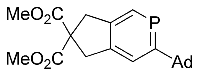
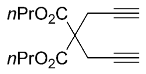
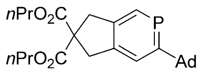
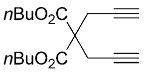
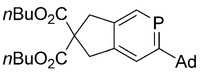
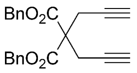
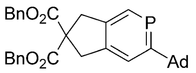
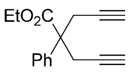
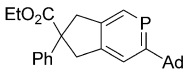
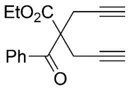
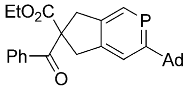
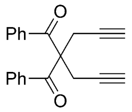
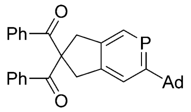
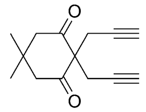
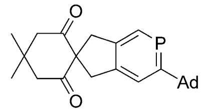
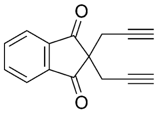
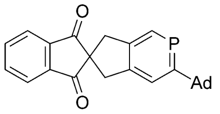
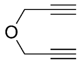
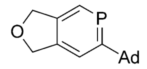
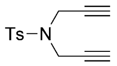
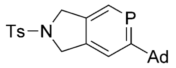
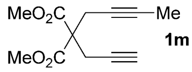
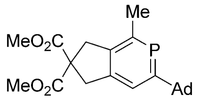
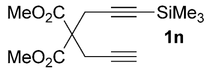
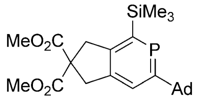
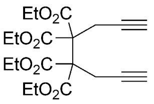
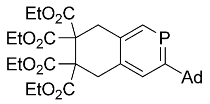


Figure 1. ORTEP drawing of **3a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.7588(15), C1–C2 1.388(3), C2–C3 1.397(3), C3–C7 1.396(2), C7–C8 1.394(3), P1–C8 1.7159(19); C1-P1-C8 102.60(8), P1-C1-C2 122.04(13), C1-C2-C3 124.54(14), C2-C3-C7 123.36(15), C3-C7-C8 122.42(16), P1-C8-C7 124.84(13).

We investigated the reactions of a variety of diynes **1** with **2a** (Table 2). The use of 20 mol % of FeI_2 was necessary to

Table 2: Reactions of diynes **1** with 1-adamantylphosphaethyne (**2a**).[a]

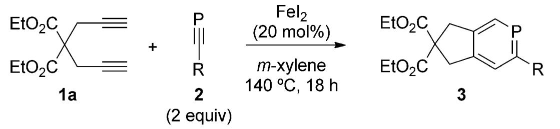


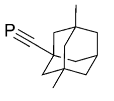
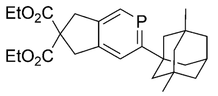
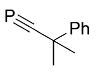
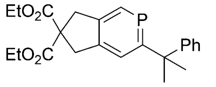
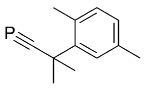
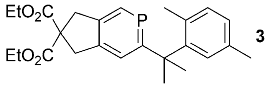
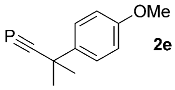
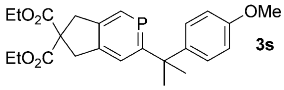
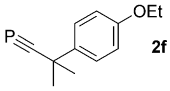
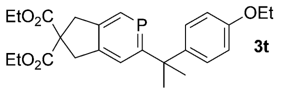
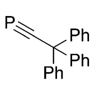
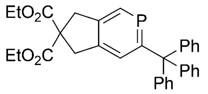
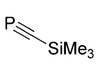
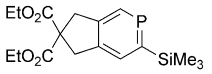
Entry	Diyne **1**		Phosphabenzene **3**		Yield [%][b]
1		**1b**		**3b**	80
2		**1c**		**3c**	77
3		**1d**		**3d**	71
4		**1e**		**3e**	70
5		**1f**		**3f**	51
6		**1g**		**3g**	76
7		**1h**		**3h**	62
8		**1i**		**3i**	76
9		**1j**		**3j**	46
10[c]		**1k**		**3k**	53
11		**1l**		**3l**	52
12		**1m**		**3m**	22
13		**1n**		**3n**	26
14		**1o**		**3o**	15

[a] Reaction conditions: **1** (0.15 mmol), **2a** (0.30 mmol), FeI_2 (0.030 mmol), *m*-xylene (1.5 mL), 140 °C (bath temperature), 18 h. [b] Yield of the isolated product. [c] The reaction was carried out at 80 °C in toluene. Bn = benzyl, Ts = *p*-toluenesulfonyl.

obtain the corresponding phosphabenzenes **3** in high yields.[13] Diynes bearing methyl, *n*-propyl, *n*-butyl, and benzyl ester moieties were successfully converted into the corresponding phsophabenzenes **3b–e** in high yields (Table 2, entries 1–4). The presence of a phenyl group instead of an ester group in substrate **1f** enabled the synthesis of **3f** in 51 % yield (Table 2, entry 5). Diynes derived from a β-ketoester (substrate **1g**) and 1,3-diketones (substrates **1h–j**) were also applicable, and the desired phosphabenzenes **3g–j** were obtained in good yields (Table 2, entries 6–9). Phosphabenzenes **3k** and **3l** containing ether and sulfonamide moieties were also obtained in good yields (Table 2, entries 10 and 11). The use of diynes **1m** and **1n** with an internal alkyne moiety afforded **3m** and **3n** in only 22 and 26 % yield (Table 2, entries 12 and 13), thus indicating that only diynes with two terminal alkyne moieties can be transformed into the corresponding phosphabenzenes in good to high yields. When we used a 1,7-octadiyne derivative, the corresponding product **3o** with a fused six-membered ring was obtained in 15 % yield (Table 2, entry 14). Unfortunately, when 1,6-heptadiyne and 1,7-octadiyne were used as substrates, no formation of the corresponding phosphabenzenes was observed. These results indicate that the Thorpe–Ingold effect[14] plays an important role in the present reaction system.

Table 3: Reactions of 4,4-bis(ethoxycarbonyl)hepta-1,6-diyne (**1a**) with phosphaalkynes **2**.[a]



Entry	Phosphaalkyne **2**		Phosphabenzene **3**		Yield [%][b]
1		**2b**		**3p**	63
2		**2c**		**3q**	80
3		**2d**		**3r**	87
4		**2e**		**3s**	82
5		**2f**		**3t**	83
6		**2g**		**3u**	73
7		**2h**		**3v**	trace

[a] Reaction conditions: **1a** (0.15 mmol), **2** (0.30 mmol), FeI$_2$ (0.030 mmol), *m*-xylene (1.5 mL), 140 °C (bath temperature), 18 h. [b] Yield of the isolated product.

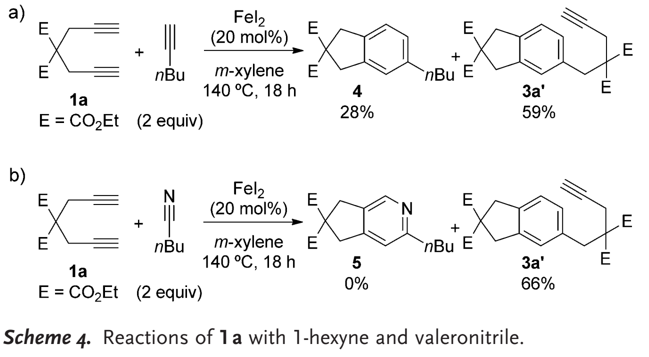
Next, we investigated reactions of **1a** with other phosphaalkynes **2** as substrates (Table 3). When (3,5-dimethyl-1-adamantyl)phosphaethyne (**2b**) was used under the standard reaction conditions, the corresponding phosphabenzene **3p** was obtained in 63 % yield (Table 3, entry 1). The use of phosphaalkyne **2c** bearing a 1-methyl-1-phenylethyl group gave **3q** in 80 % yield (Table 3, entry 2). The introduction of methyl and alkoxy groups on the benzene ring of **2c** was also possible, and the corresponding products **3r–t** were obtained in high yields (Table 3, entries 3–5). The reaction of phosphaalkyne **2g** bearing a very bulky trityl group gave **3u** in 73 % yield (Table 3, entry 6). However, trimethylsilylphosphaethyne (**2h**) was not applicable in this reaction system: only a trace amount of **3v** was obtained under the same reaction conditions (Table 3, entry 7). The decomposition of **2h** may occur under the catalytic reaction conditions at 140 °C, as **2h** has been reported to have low thermal stability.[15] These results suggest that the use of phosphaalkynes bearing a tertiary alkyl group is necessary for the synthesis of the corresponding phosphabenzenes in the present reaction system.

To evaluate the thermodynamic nature of the present reaction, we calculated the Gibbs free energy ($\Delta G^{298\mathrm{K}}$) of the reactions of 1,6-heptadiyne with phosphaethyne, hydrogen cyanide, and acetylene at the B3LYP/6-311G** level of theory (Scheme 3). The reaction free energy for the formation of phosphabenzenes is more exergonic than that for pyridines, but less exergonic than that for benzenes. Notably, the thermodynamic nature of the [2+2+2] cycloaddition for the formation of phosphabenzenes is similar to that of other [2+2+2] cycloaddition reactions, although the thermodynamic stability of phosphaalkynes is quite different from that of alkynes and nitriles.[8]

X	$\Delta G^{298\mathrm{K}}$ [kcal mol^{-1}]
P	–101.2
N	–83.6
CH	–119.4

Scheme 3. Calculated reaction free energies (B3LYP/6-311G**).

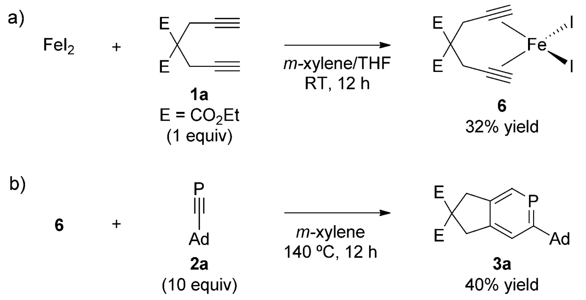
Next, we applied the present reaction conditions with FeI$_2$ (20 mol %) as a catalyst to [2+2+2] cycloaddition reactions for the formation of benzenes and pyridines (Scheme 4). When **1a** was treated with 1-hexyne in the presence of FeI$_2$,



Scheme 4. Reactions of **1a** with 1-hexyne and valeronitrile.

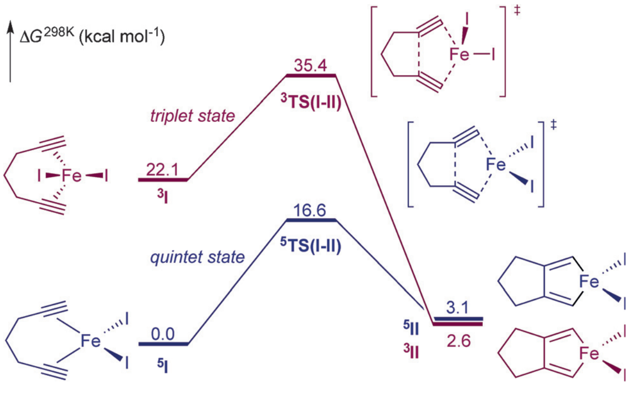
benzene derivatives **4** and **3a′** were formed in good yields (Scheme 4a). On the other hand, when we examined the reaction of **1a** with valeronitrile, the formation of **3a′** was observed, but no pyridine derivative **5** was detected at all (Scheme 4b). It is known that the electronic structure of phosphaalkynes is similar to that of alkynes rather than nitriles.[2b,8] Therefore, the present reaction system for the synthesis of phosphabenzenes might be related to [2+2+2] cycloaddition for the synthesis of benzenes. Moreover, the formation of benzene derivatives suggests the existence of ferracyclopentadiene species as key reactive intermediates[16] in the present reaction system, because ferracyclopentadiene intermediates have been proposed for iron-catalyzed [2+2+2] cycloaddition processes to form benzenes.[11c,d,f]

To obtain further information on the reaction pathway, we investigated the stoichiometric reactivity of FeI_2 toward **1a**. When FeI_2 was treated with **1a** in *m*-xylene/THF (1:1) at room temperature, the corresponding π-alkyne complex **6** was obtained in 32% yield (Scheme 5a). The treatment of **6** with **2a** at 140 °C for 12 h afforded the phosphabenzene **3a** in 40% yield (Scheme 5b). These results indicate that the π-alkyne–iron complex **6** may be involved in the present reaction system.

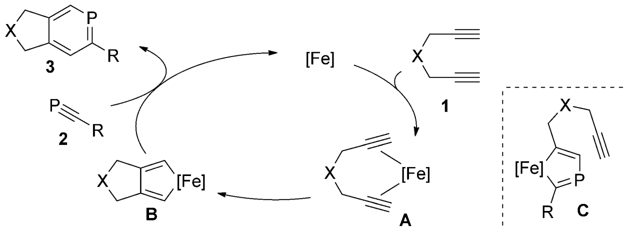


Scheme 5. Synthesis and reactivity of the π-alkyne complex **6**.

DFT calculations with the B3LYP* hybrid functional[17] support the oxidative cyclization of a π-alkyne–iron complex to give a ferracyclopentadiene complex (Scheme 6). The quintet state of the complex ^{5}**I**, in which 1,6-heptadiyne is coordinated to FeI_2, is much lower in Gibbs free energy than the triplet-state complex ^{3}**I**. The complex ^{5}**I** is transformed into the ferracyclopentadiene ^{5}**II** via the transition state ^{5}**TS(I-II)**. The activation free energy is 16.6 kcal mol^{-1}, and the reaction is slightly endergonic (3.1 kcal mol^{-1}). In the ferracyclopentadiene, the free energy of the triplet state ^{3}**II** is slightly lower than that of the quintet state ^{5}**II**. Thus, the following reaction with phosphaalkynes is considered to proceed from the triplet-state ferracyclopentadiene ^{3}**II**, which is formed through intersystem crossing, or the quintet state ^{5}**II**.



Scheme 6. Gibbs free energy diagram for oxidative cyclization.



Scheme 7. A plausible reaction pathway.

A plausible reaction pathway based on the experimental results and DFT calculations is shown in Scheme 7. First, an iron complex **A** containing **1** as a π-alkyne ligand is formed from FeI_2 and **1**. Next, oxidative cyclization of the diyne in **A** affords a ferracyclopentadiene intermediate **B**,[16] which reacts with the phosphaalkyne **2** to give the corresponding phosphabenzene **3**. At present, however, we cannot exclude another reaction pathway via a 3-phospha-1-ferracyclopentadiene species **C**[18] as a key reactive intermediate.

In summary, we have developed an efficient method for the synthesis of phosphabenzenes by the iron-catalyzed [2+2+2] cycloaddition of diynes with phosphaalkynes. With this reaction system, 2,4,5-trisubstituted phosphabenzenes can be obtained in high yields. We believe the method described herein provides a useful platform for the exploration of functional molecules containing a phosphabenzene moiety.

Keywords: [2+2+2] cycloaddition · homogeneous catalysis · iron · phosphaalkynes · phosphabenzenes

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