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Synthesis of Phospholes and 1,1'-Biphospholes Mediated by Zirconacyclopentadienes and PBr_3

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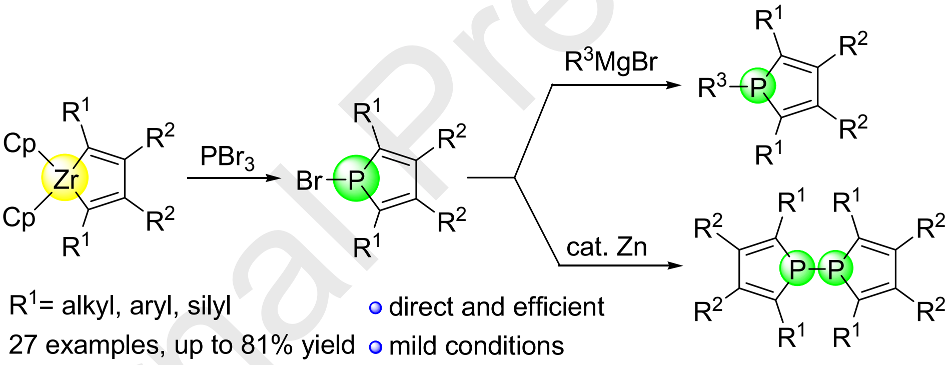
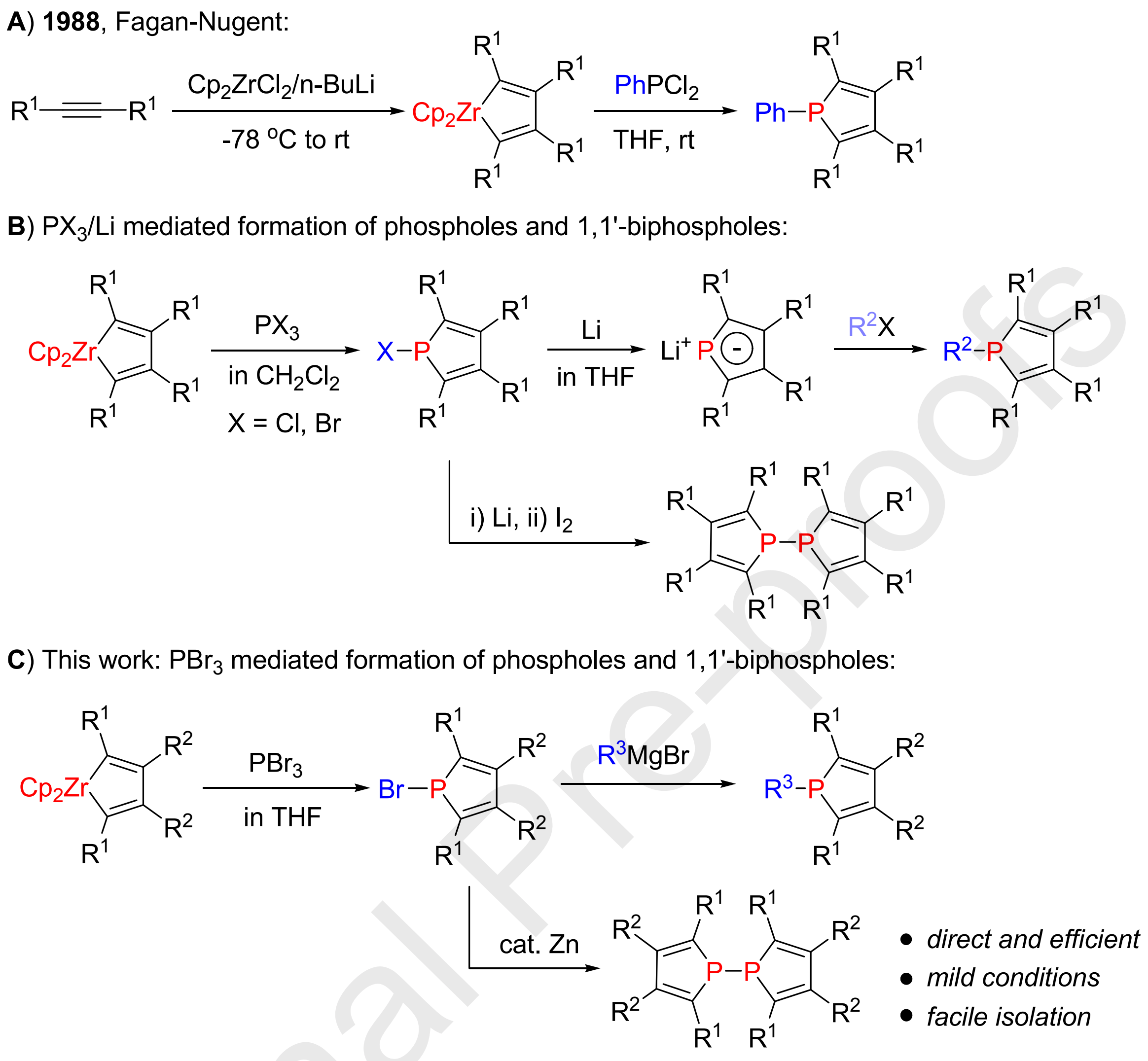


Abstract: The efficient synthesis of phospholes through the reactions of Grignard reagents with in situ-generated 1-bromophospholes has been developed. This method allows the easy substituent variation at the phosphorus atom of the phospholes. The 1,1'-biphospholes can also be conveniently prepared through Zn-promoted debromo-dimerization of 1-bromophospholes. The gold-phosphole complexes of LAuCl were also synthesized, which were found to act as efficient catalysts in gold-catalyzed [3+2] cycloaddition of ynamides with 4,5-dihydro-1,2,4-oxadiazoles.

Key words: Zirconacycle; metallacycle transfer; phospholes; 1,1’-biphospholes

Phosphole derivatives represent one of the most important classes of the phosphine-containing heterocycles, which have received much attention in organic functional materials and coordination chemistry, such as organic light-emitting diodes (OLEDs),[1] nonlinear optical devices,[2] sensory materials,[3] chiral metal-bis(azahelicene phosphole) assemblies,[4] and coordination-driven supramolecular assembly[5] etc. They have also been used as the ligands in transition metal catalysis such as hydro-formylation,[6] hydrogenation,[7] allylic substitution,[8] hydrosilylation,[9] olefin/CO copolymerization[10] and gold-catalyzed cycloisomerization[11] etc. Up to now, many synthetically useful methods for phospholes have been developed. Among them, Fagan-Nugent route[12] involving metallacycle transfer from zirconacyclopentadienes to various main group heteroles including phospholes is one of the most developed and significant tools, which allows the assembly of mono- or fused phospholes with a wide structural diversity and in one-pot operation (Scheme 1**A**). It is known that the nature of P-substituents in phospholes plays an important role in the stability and aromaticity of phospholes due to the hyperconjugation of the exocyclic P-R σ-bond and the dienic π-system,[13] which is also important in tuning the electronic properties and steric hindrance of the whole molecule. Although the P-substituents can be modified by Fagan-Nugent method through the use of different dichlorophosphines ($RPCl_2$), usually, only 1-P-phenyl-phospholes were prepared with $PhPCl_2$. This is possibly due to the low stability and less availability of other dihalophosphines. Except for this route, there are only limited methods for variation of P-substituents in Fagan-Nugent route, mainly including reductive cleavage of the P-R bond (R = aryl, halide) by lithium metal to give a phospholyl anion followed by reaction with electrophiles[14](Scheme 1**B**). However, this method usually suffers from the use of highly reactive lithium metal and/or restricted to special substrates. Early works by Douglas[15] and Mathey[14b] indicated that the reactions of zirconacyclopentadienes with PX_3 (X = Cl or Br) in CH_2Cl_2 afforded 1-halophospholes. The straightforward way for introducing of different P-substituents would be through the nucleophilic substitution of 1-halophospholes. However, in most reports, the resulted 1-halophospholes were transferred to phospholyl anions, and then were used for the preparation of P-R phospholes[14b-e] or 1,1'-biphospholes.[16] It was known that 1-halophospholes generated through other methods such as the reaction of dilithium derivative with phosphorus halides[17] could react with organolithium or Grignard reagents,[18] to our surprise, direct substitution of 1-halophospholes in Fagan-Nugent route is quite rare. To the best of our knowledge, when Grignard reagent was used as the nucleophile, there is only one report concerning the reaction of alkynyl Grignard reagents with 1-chlorotetraethylphosphole derived from zirconacycles leading to alkynylphospholes (two examples).[19] However, the reaction required tedious procedure involving two times of solvent-change. In this paper, we describe a convenient method for the synthesis of phospholes through the reactions of 1-halophospholes with Grignard reagents, which allows the facile substituent variation at the phosphorus atom of the phospholes (Scheme 1**C**). A zinc promoted formation of 1,1'-biphospholes is also described.

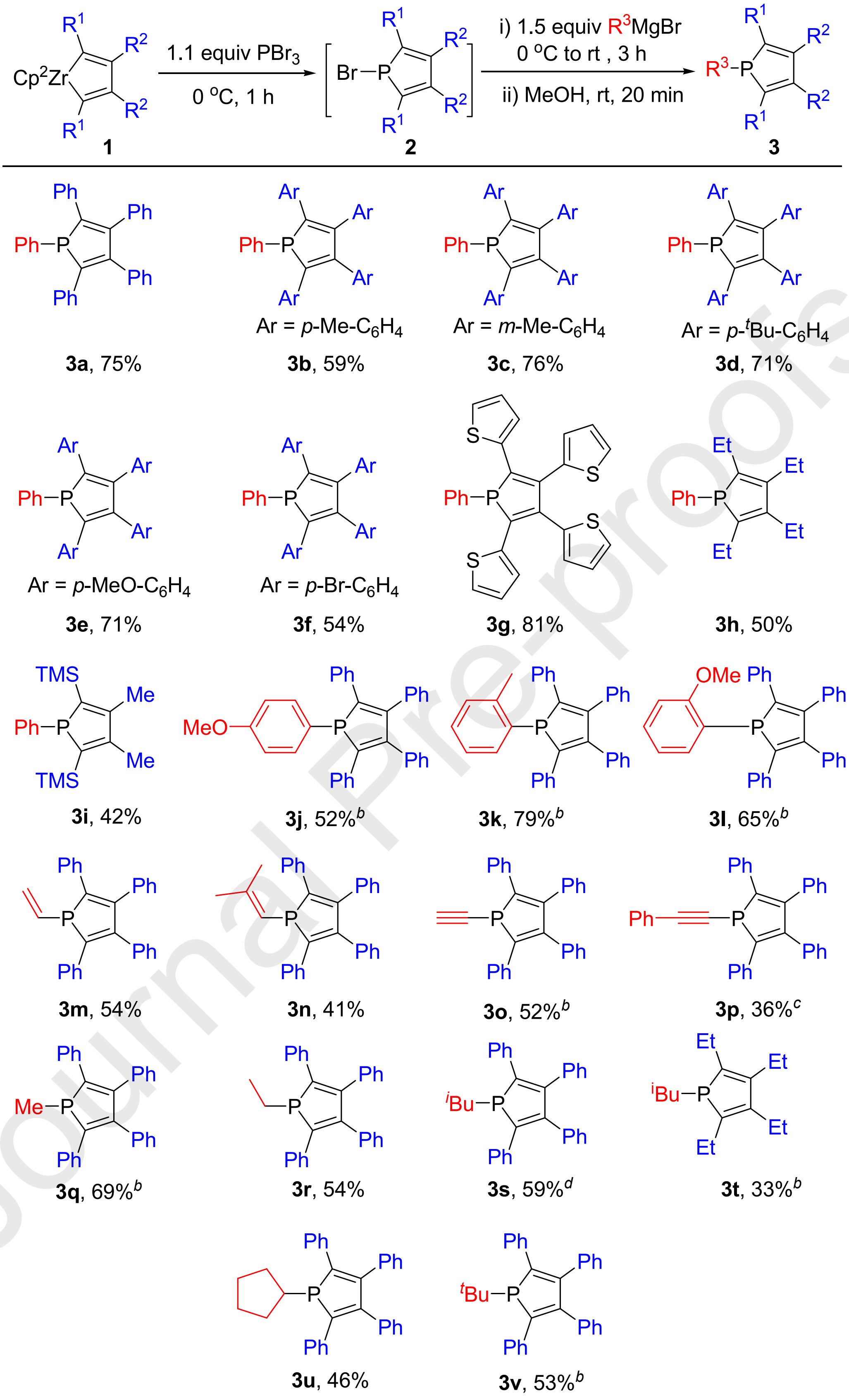
Scheme 1. Synthesis of phospholes and 1,1'-biphospholes



Zirconacyclopentadienes, which were easily prepared by reduction of Cp_2ZrCl_2 with n-BuLi followed by addition of two equiv of alkynes,[20] were chosen for the metallacycle transfer reaction with PBr_3. As illustrated in Scheme 2, treatment of zirconacyclopentadiene **1a** with 1.1 equiv of PBr_3 at 0 °C resulted in the color change from red to orange during the reaction going on. After the reaction mixture was stirred at 0 °C for 1 h, 1.5 equiv of PhMgBr was added. The color of the reaction mixture turned to light yellow immediately, and a large amount of precipitate could be observed as the reaction proceeded. After the workup, 1-phenylphosphole **3a** was obtained in 75% yield. The results suggested that the 1-bromophosphole **2a** was formed as an intermediate.[14b] Interestingly, a trace amount of 1,1'-biphosphole **4a** was also observed in this reaction. Usually, 1-halophospholes were prepared in CH_2Cl_2 from the pre-synthesized zirconacyclopentadienes,[14b-d] or through a one-pot procedure which required the change of the solvent from THF to CH_2Cl_2 after the generation of zirconacyclopentadiene.[14e,19] The synthesis described here does not need the solvent change in most cases, thus providing a convenient route to phospholes while avoiding the tedious operation.

With the optimized reaction conditions in hand, the scope of the substrates including both alkynes and Grignard reagents were examined. For aryl alkynes, electron-donating groups such as *p*-Me, *m*-Me, *p*-^{t}Bu and *p*-MeO on the aryl rings were well compatible, leading to **3b**-**3e** in 59-76% yields. An electron-withdrawing *p*-Br group, which is usually not tolerated in transition-metal catalyzed reactions, was suited for this reaction, leading to **3f** in 54% yield. A heterocycle ring such as 2-thienyl group could also be efficiently introduced at the C2~C5 positions of the phosphole ring, giving **3g** in 81% yield. The use of zirconacyclopentadienes derived from alkyl alkynes such as 3-hexyne resulted in 50% yield of the product **3h**. In the case of trimethyl(prop-1-ynyl)silane, the product **3i** was also formed smoothly in 42% yield as a single regioisomer. Next, the effects of various Grignard reagents were investigated. Aromatic Grignard reagents such as *p*-methoxyphenylmagnesium bromide provided **3j** in 52% yield. Sterically hindered Grignard reagents such as *o*-methyl- or *o*-methoxyphenylmagnesium bromides also reacted well in the reaction to furnish **3k**-**3l** in 65-79% yields. The results indicated that the steric effect of the Grignard reagents has little influence on the reaction. Vinyl and alkynylmagnesium bromides proved to be also suitable, leading to **3m**-**3p** in 36-54% yields. The reactivity of alkyl Grignard reagents were also tested. Methyl-, ethyl-, and sterically encumbered isobutyl, cyclopentyl or even *tert*-butyl-substituted Grignard reagents were all compatible with the reaction, giving **3q**-**3v** in 33-69% yields. The structure of **3q** was confirmed by X-ray crystallography.[21]

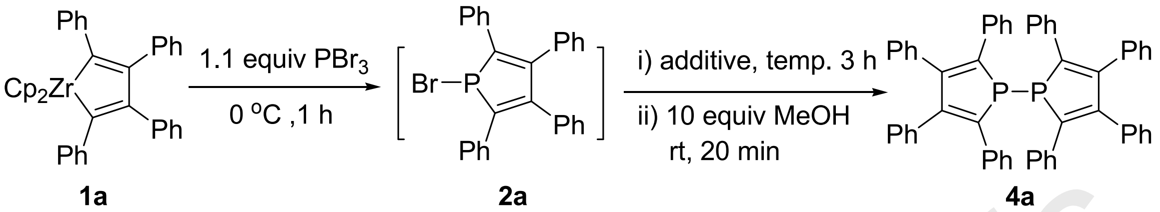
Scheme 2. Synthesis of mono-phospholes[a]



[a] Isolated yields. [b] 3 equiv of R^{3}MgBr was used. [c] Phenylethynylmagnesium bromide was prepared by the reaction of 2.4 equiv of phenylacetylene and 2.2 equiv of ethylmagnesium bromide. [d] After formation of zirconacycle, the solvent was removed, and DCM was added.

As mentioned above, a small amount of 1,1'-biphosphole could be observed during the process of PBr_3-mediated phosphole formation. 1,1'-Biphospholes were usually prepared through the reaction of 1-halophosphole with a large excess of metallic lithium followed by oxidation with I_2[16d] or by the reaction of 1-phenylphosphole with excess Li followed by the treatment with $AlCl_3$ and I_2.[16a] Nyulászi and Réau et al. found that treatment with zirconacyclopentadiene with an excess PBr_3 (ca. 2.7 equiv) resulted in the formation of 1,1'-biphospholes after stirring the reaction mixture for a long time (4 d).[16d] Inspired by our results, we next wish to develop a more efficient procedure for the synthesis of 1,1'-biphospholes. The results are shown in Table 1. Interestingly, when MeLi was added to the reaction mixture after formation of 1-bromophosphole, 1,1'-biphosphole **4a** was formed as the major product (50%, Table 1, entry 1). To our delight, addition of 1.0 equiv of zinc also delivered **4a** in 41% yield at 50 ^oC (entry 2). Decreasing the amount of zinc to 0.4 equiv afforded a slightly higher yield (entry 4 vs. 2 and 3). Other reductants such as Mg, Fe or Mn gave **4a** in lower yields (entries 5-7). Increasing the reaction temperature to 65°C improved the yield of **4a** significantly (entry 8). A 77% yield could be achieved at 65 ^oC by using only 20 mol% of Zn (entry 10). Without Zn, the reaction could also proceed, and a lower yield of 61% was observed (entry 12). The reaction mechanism is not clear yet. Possibly a P-centered radical is formed under thermal conditions through homolysis of the P-Br bond of 1-bromophosphole intermediate which dimerizes to give 1,1'-biphosphole. Zinc may play a role in accelerating the formation of the radical species.

Table 1. **Optimization of the Reaction Conditions for 1,1'-Biphospholes**[a]

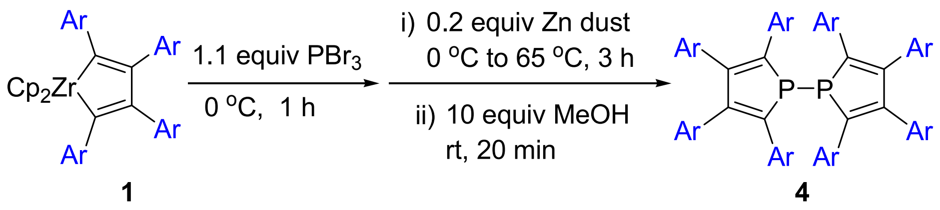


Entry	Additive (equiv)	Temp. (°C)	Yield (%)
1	MeLi (1.0)	rt	50
2	Zn (1.0)	50	41
3	Zn (0.5)	50	47
4	Zn (0.4)	50	50
5	Mg (0.4)	50	16
6	Fe (0.4)	50	35
7	Mn (0.4)	50	30
8	Zn (0.4)	65	78
9	Zn (1.0)	65	76
10	Zn (0.2)	65	77
11	Zn (0.1)	65	71
12	-	65	61
13	-	rt	12

[a]Isolated yields.

Under the optimized reaction conditions (Table 1, entry 10), a series of 1,1'-biphospholes were synthesized (Scheme 3). The functionalities such as *p*-Me, *m*-Me, *p*-^{t}Bu and *p*-OMe groups on the aryl rings were well tolerated (**4b**-**4e**). However, this method is not compatible with alkyl-substituted zirconacyclopentadienes.

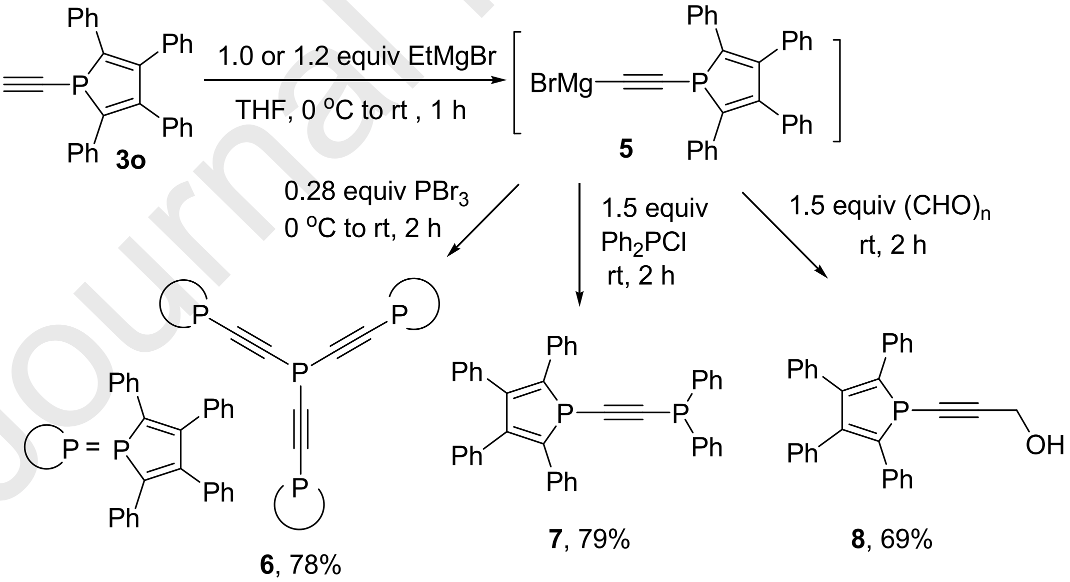
Scheme 3. Synthesis of 1,1'-Biphospholes



4a, Ar = Ph, 77%
4b, Ar = *p*-MeC$_6$H$_4$, 76%
4c, Ar = *m*-MeC$_6$H$_4$, 65%
4d, Ar =*p*-^{t}BuC$_6$H$_4$, 46%
4e, Ar = *p*-MeOC$_6$H$_4$, 51%

To demonstrate the synthetic utility of the phospholes obtained by the present method, transformations of the alkynylphosphole **3o** were performed. Treatment of **3o** with EtMgBr generated alkynyl Grignard reagent **5**. This intermediate was transferred to internal alkynes **6~8** through the reactions with various electrophiles such as PBr$_3$ PPh$_2$Cl and (CHO)$_n$, respectively. All these products were obtained in good yields.

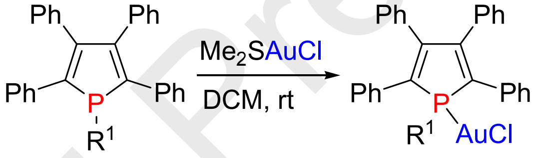
Scheme 4. **Transformations of the alkynylphosphole 3o**



Phospholes are potentially useful as ligands in transition-metal-catalyzed reactions. As our continuing interests in gold catalysis, we therefore attempted to synthesize

Au(I)-phosphole complexes and test its catalytic activity. As shown in Scheme 5, LAuCl complex derived from P-phenyl (**9a**) or P-^{t}Bu (**9b**) phospholes were readily prepared through their reactions with Me_2SAuCl. These complexes were isolated as air-stable solids in high yields.[21] Next, to evaluate the catalytic performance of phosphole-gold(I) complexes **9**, the gold-catalyzed [3+2] cycloaddition of ynamides with 4,5-dihydro-1,2,4-oxadiazoles[22] was chosen as a model reaction. To our delight, although these phosphole ligands are highly sterically hindered, their corresponding gold complexes showed good catalytic reactivity for this [3+2] cyclization (Scheme 6).

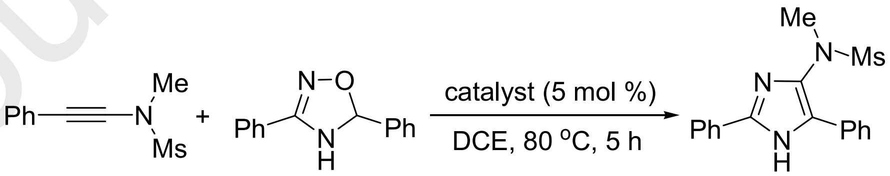
Scheme 5. **Synthesis of gold(I)-phosphole complex**



R^1 = Ph (**3a**)
R^1 = ^{t}Bu (**3v**)

9a, R^1 = Ph, 98%
9b, R^1 = ^{t}Bu, 87%

Scheme 6. **Gold(I)-phosphole complex-catalyzed reaction**



10 **11** (1.2 equiv) **12**

9a/$AgSbF_6$, 79%
9b/$AgSbF_6$, 82%
$PPh_3AuCl/AgSbF_6$, 64% (Ref. 20)

In summary, we have shown that phospholes could be synthesized through the reactions of Grignard reagents with in situ-generated 1-bromophospholes. Especially, the method provides a straightforward route for the introduction of different P-substituents in phospholes. The 1,1'-biphospholes can also be conveniently prepared through Zn-promoted debromo-dimerization of 1-bromophospholes. The gold-phosphole complexes of LAuCl were also synthesized, which were found to act as efficient catalysts in gold-catalyzed [3+2] cycloaddition of ynamides with 4,5-dihydro-1,2,4-oxadiazoles.

Acknowledgments

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Appendix A. Supplementary data

Experimental procedures, spectral data, X-ray crystallography of compounds CCDC-1952958 (**3q**), -1952959 (**4a**), -1952960 (**7**), and -1952957 (**9a**) are given in the Supporting Information.

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(21)CCDC-1952958 (**3q**), -1952959 (**4a**), -1952960 (**7**), and -1952957 (**9a**) contain the supplementary crystallographic data for this paper.

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Graphic Abstract for

Synthesis of Phospholes and 1,1’-Biphospholes Mediated by Zirconacyclopentadienes and PBr$_3$

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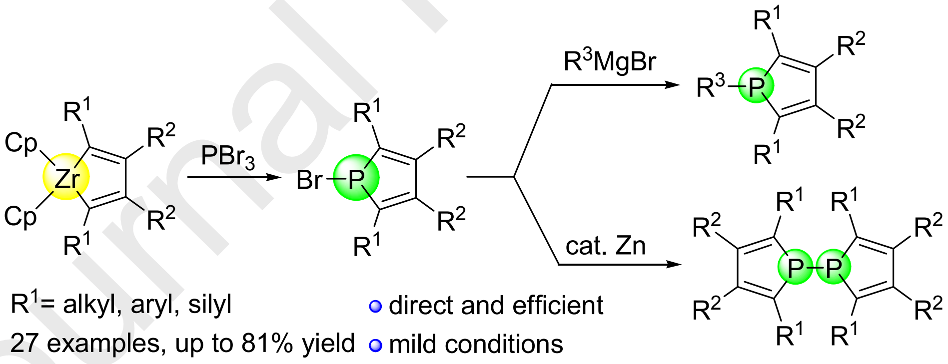

Hights

- Highly efficient synthesis of **phospholes through the reactions of Grignard reagents with in situ-generated 1-bromophospholes**

- **Easy substituent variation at the phosphorus atom of the phospholes**
- **Formation of 1,1'-biphospholes through Zn-promoted debromo-dimerization of 1-bromophospholes**
- **Gold-phosphole complexes serve as efficient catalysts in** [3+2] cycloaddition of ynamides with 4,5-dihydro-1,2,4-oxadiazoles

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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