

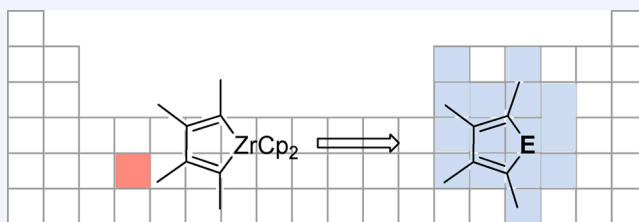
# Conversion of Zirconacyclopentadienes into Metalloles: Fagan–Nugent Reaction and Beyond

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**CONSPECTUS:** Metalloles are derivatives of cyclopentadiene in which the methylene unit is replaced by a heteroatom, such as S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, B, Al, Ga, and so on. Many metallole derivatives have been widely used as photovoltaic cells, organic light emitting diodes (OLEDs), chemical sensors, electrochromic devices, microelectronic actuators, and organic field effect transistors (OFETs). In the meantime, many of them showed promising biological activities. Due to the similarity to cyclopentadiene, the anionic forms of metalloles were also widely explored in coordination chemistry. As a result, development of a general method for the formation of metalloles from available starting materials is highly desired.



In this Account, we outline formation of various p-block element metalloles from zirconacyclopentadienes. The zirconacyclopentadienes can be easily prepared from two molecules of alkynes and a low-valent zirconocene species “Cp<sub>2</sub>Zr(II)” (Cp = cyclopentadienyl). Fagan and Nugent first reported the formation of main group metalloles from zirconacyclopentadiene, which provided a versatile approach for the construction of metalloles, especially for the formation of metalloles in heavier p-block elements. To further expand the substrate scope, a number of stepwise conversions were developed, which involve 1,4-dimetallo- or dihalo-1,3-butadiene as intermediates from zirconacyclopentadienes.

Here, four processes are classified based on direct and indirect conversion of zirconacyclopentadienes into metalloles. Direct reaction of zirconacyclopentadienes with element halides afforded heterocycles of main group elements, which provided a versatile method for the synthesis of metalloles. Nonetheless, the reaction scope was restricted to heavier p-block elements such as S, Se, P, As, Sb, Bi, Ge, Sn, Ga, and In. And these reactions usually suffered low yields and long reaction time. Transmetalation of zirconacyclopentadiene with copper chloride greatly enriched the zirconacyclopentadiene chemistry. The synthesis of stannoles and pyrroles from zirconacyclopentadienes has been developed in the presence of CuCl. The direct reaction of the zirconacyclopentadienes with SiCl<sub>4</sub> or R<sub>2</sub>SiCl<sub>2</sub> does not give the desired silacyclopentadiene derivatives, even in the presence of CuCl. It can be circumvented by using dilithiated dienes from diiododienes, which are easily prepared by the iodination of zirconacyclopentadienes using CuCl as an additive. Finally, an umpolung strategy, reaction of electrophilic 1,4-diiodo-1,3-butadiene with nucleophilic amine or sulfide reagents, was successfully used in the formation of pyrroles and thiophenes.

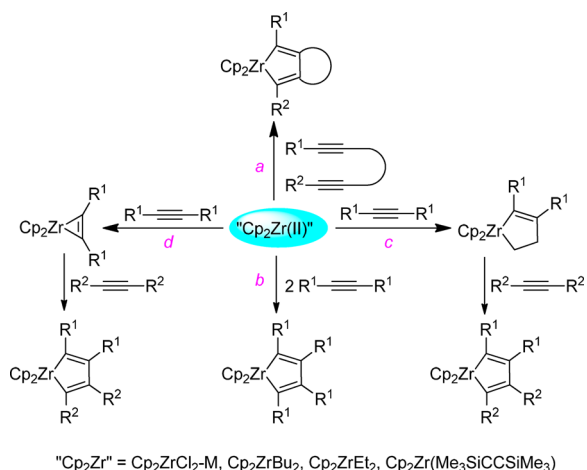
## 1. INTRODUCTION

Since the first synthesis of tetraphenylzirconacyclopentadiene in 1961,<sup>1</sup> a large number of zirconacyclopentadiene derivatives have been reported.<sup>2</sup> The zirconacyclopentadienes were usually prepared from two molecules of alkynes and a low-valent zirconocene species “Cp<sub>2</sub>Zr(II)”.<sup>3</sup> There are several systems for generation of low-valent zirconocene species *in situ*, such as Cp<sub>2</sub>ZrCl<sub>2</sub>–Na,<sup>3a</sup> Cp<sub>2</sub>ZrCl<sub>2</sub>–Mg,<sup>3b</sup> Cp<sub>2</sub>ZrCl<sub>2</sub>–Ln,<sup>3c</sup> Negishi reagent (Cp<sub>2</sub>ZrBu<sub>2</sub>),<sup>3d,e</sup> Takahashi reagent (Cp<sub>2</sub>ZrEt<sub>2</sub>),<sup>3f</sup> and Rosenthal’s reagent (Cp<sub>2</sub>Zr(Me<sub>3</sub>SiCCSiMe<sub>3</sub>)).<sup>3g</sup> Symmetrical zirconacyclopentadienes and bicyclic zirconacyclopentadienes were easily prepared by the reaction of 2 equiv of alkynes or diynes with Cp<sub>2</sub>Zr(II) species (Scheme 1, path a and path b). Unsymmetrical zirconacyclopentadienes were prepared by stepwise addition of two different alkynes through zirconacyclopentenes (Scheme 1, path c) or zirconacycloprenes (Scheme 1, path d).

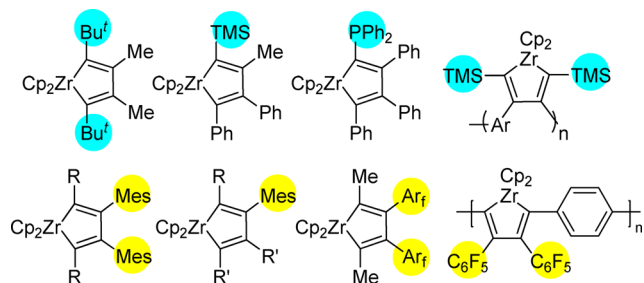
When unsymmetrical alkynes are employed, the reaction suffers from a regioselectivity problem leading to the formation of zirconacyclopentadienes in a mixture. In general, coupling of two unsymmetrical alkynes by the low-valent zirconocene could afford three kinds of isomers (*αα*, *αβ*, *ββ*). The regiochemistry of zirconacyclopentadienes can be controlled by the nature of the substituents (Figure 1). The most effective *α*-directing groups are often sterically demanding (e.g., trialkylsilyl, *tert*-butyl, and phosphino).<sup>4</sup> This strategy was applied by Tilley and other groups for the synthesis of a number of macrocyclic zirconacyclopentadienes.<sup>5</sup> However, when relatively bulky mesityl substituted alkynes were employed, the mesityl group exhibited a kinetic preference for coupling into the *β*-position of the zirconacyclopentadienes.<sup>6</sup> Tilley and co-workers also

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Scheme 1. Formation of Zirconacyclopentadienes<sup>a</sup>

<sup>a</sup>Path a, coupling of tethered diynes with zirconocene; path b, coupling of two identical alkynes with zirconocene; path c, coupling of two different alkynes through zirconacyclopentenes; path d, coupling of two different alkynes through zirconacycloprenenes.

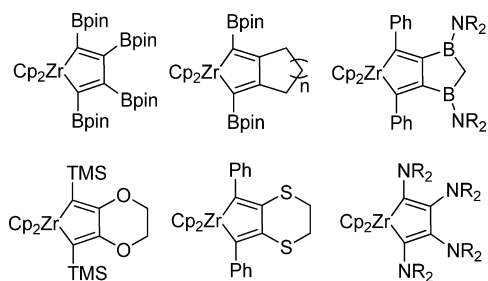


**Figure 1.** Regiochemistry of formation of zirconacyclopentadienes (TMS = trimethylsilyl, Ar = aromatic group, Mes = mesityl, Ar<sub>f</sub> = *p*-C<sub>6</sub>H<sub>4</sub>).

reported the influence of electronic factors on the regioselectivity of zirconacyclopentadienes, which showed that electron-withdrawing substituents (C<sub>6</sub>F<sub>5</sub>) preferentially adopt the  $\beta$ -position of the resultant zirconacyclopentadienes. This strategy has been employed in the syntheses of pentafluorophenyl-substituted polymers.<sup>7</sup>

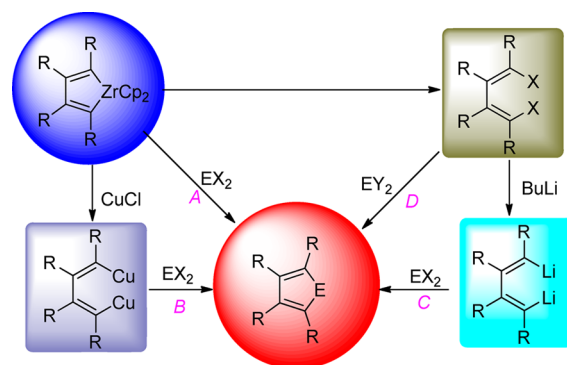
Heteroatom substituted zirconacyclopentadienes could also be prepared by the reaction of the corresponding heteroatom substituted alkynes with Cp<sub>2</sub>Zr(II) species. The typical examples are listed in Figure 2.<sup>8</sup>

The resulting zirconacyclopentadienes could react with various electrophiles to form acyclic and cyclic organic compounds such as multisubstituted 1,3-butadienes, benzenes,



**Figure 2.** Heteroatom substituted zirconacyclopentadienes (Bpin = 4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl).

cyclopentadienes, and cyclooctatetraenes, which are extensively employed in synthetic chemistry.<sup>2</sup> Among them, an important area of this progress in zirconacyclopentadiene chemistry is the construction of five-membered heterocycles. Fagan, Nugent, and co-workers first reported a direct reaction of the zirconacyclopentadienes with element halides to afford heterocycles of main group elements in 1988, which provided a versatile method for the synthesis of metalloles (Scheme 2,

Scheme 2. Four Processes for Formation of Metalloles from Zirconacyclopentadienes<sup>a</sup>

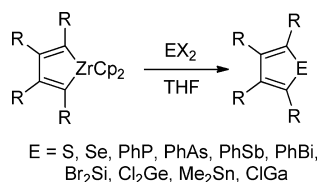
<sup>a</sup>(A) Direct transformation; (B) copper-mediated transformation; (C) transformation via iodination/lithiation; (D) coupling reaction via 1,4-diiodo-1,3-butadiene.

route A).<sup>9</sup> Nonetheless, the reaction scope was restricted to some p-block element halides, and some of the reactions suffered from low yields and long reaction time. That may be attributed to the low nucleophilicity of zirconacyclopentadienes to react with some p-block element halides. Transmetalation of the zirconacyclopentadiene with other transition metals greatly enriched zirconacyclopentadiene chemistry. For example, transmetalation of the zirconacyclopentadienes with copper chloride and subsequent carbon–carbon bond formation represents a milestone in the zirconacyclopentadiene chemistry.<sup>10</sup> Recently, the structures of 1,4-dicopper-1,3-butadienes were characterized by the Xi group.<sup>11</sup> The synthesis of stannoles and pyrroles from zirconacyclopentadienes has been developed in the presence of CuCl (Scheme 2, route B). It is known that the direct reaction of the zirconacyclopentadienes with SiCl<sub>4</sub> or R<sub>2</sub>SiCl<sub>2</sub> does not give the desired silole derivatives, even in the presence of CuCl. This can be circumvented by using dilithiated dienes from diiododienes, which are easily prepared by iodination of the zirconacyclopentadienes in the presence of CuCl (Scheme 2, route C).<sup>12</sup> Alternatively, an umpolung strategy, reaction of electrophilic 1,4-diiodo-1,3-butadiene with nucleophilic heteroatom reagents, was successfully used in the preparation of thiophenes and pyrroles with high efficiency (Scheme 2, route D). In this Account, we will summarize formation of various p-block metalloles from the zirconacyclopentadienes. Four processes are classified based on the direct transfer and indirect transfer via 1,4-dimetallo-1,3-butadienes or dihalo-1,3-butadienes as intermediates for the conversion of the zirconacyclopentadienes into metalloles (Scheme 2).

## 2. DIRECT TRANSFORMATION OF ZIRCONACYCLOPENTADIENES TO METALLOLES (ROUTE A)

Since Fagan, Nugent, and co-workers first reported a direct reaction of the zirconacyclopentadienes with element halides to afford heterocycles of main group elements (Scheme 3),<sup>9</sup> many developments and applications of this chemistry have been studied.

### Scheme 3. Fagan–Nugent Reaction: Synthesis of Heterocycles from Zirconacyclopentadienes by Metallacycle Transfer



### 2.1. Conversion of Zirconacyclopentadienes into Thiophenes, Selenophenes, and Tellurophenes

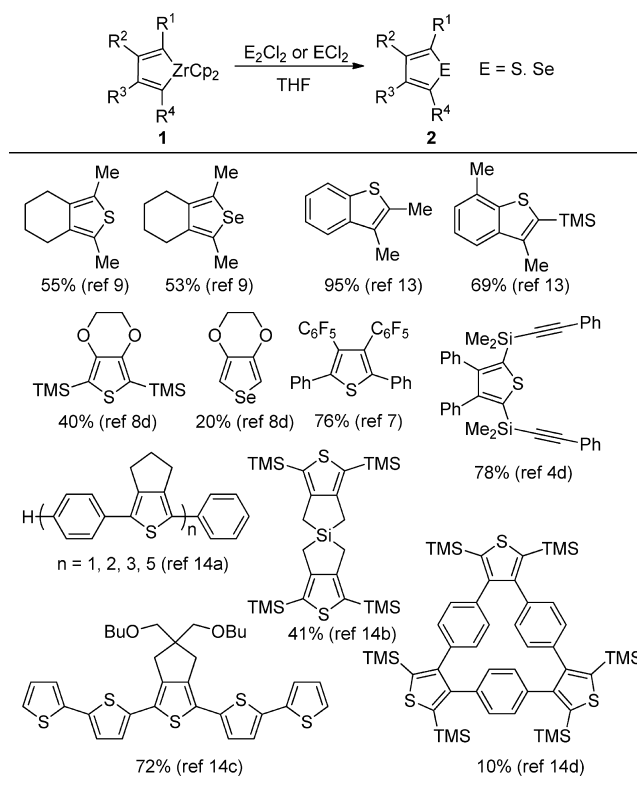
Fagan and Nugent found that reaction of zirconacyclopentadienes with S<sub>2</sub>Cl<sub>2</sub> and Se<sub>2</sub>Cl<sub>2</sub> afforded the corresponding thiophenes and selenophenes in moderate yields.<sup>9</sup> Buchwald developed this reaction, in which higher yields of polysubstituted benzo[*b*]thiophenes can be obtained from zirconaindenes by treatment with SCl<sub>2</sub> as sulfur source.<sup>13</sup> Furthermore, using SeCl<sub>2</sub> instead of Se<sub>2</sub>Cl<sub>2</sub> was also found to be more efficient in the formation of selenophenes. This strategy was applied in the synthesis of a large number of polysubstituted thiophenes and selenophenes, such as heteroatom-substituted thiophenes, oligomeric thiophenes, and macrocyclic thiophenes.<sup>14</sup> The representative thiophenes and selenophenes are listed in Scheme 4. Related to this reaction, a synthesis of thiophene or selenophene units from titanacyclopentadienes has been developed.<sup>15</sup>

Thiophene-based conjugated polymers have been most studied as electronic materials. Zade and co-workers have reported the preparation of cyclopenta[*c*]thiophene and cyclopenta[*c*]selenophene, which were converted into diverse polymers such as polythiophene, polyselenophene, poly(cyclopenta[*c*]selenylvinylene), and other donor–acceptor (D–A) type copolymers via cross-coupling reactions or electrochemical polymerization (Scheme 5).<sup>16</sup> In 2013, Rivard and co-workers developed a versatile and general synthetic route for the synthesis of pinacolboranyl substituted chalcogenophenes, which can be easily converted to related conjugated polymers by coupling with diiodoarenes (Scheme 6).<sup>8c</sup> Recently, we developed a two-step approach to thieno[3,4-*c*]pyrrole-4,6-dione (TPD) via metallacycle transfer and copper catalyzed oxidation (Scheme 7).<sup>17</sup>

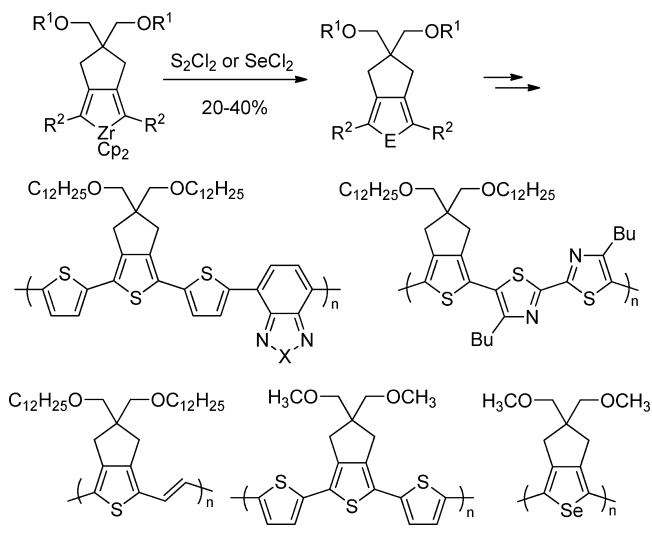
Reaction of tetraphenylzirconacyclopentadiene with thionyl chloride has been shown to give tetraphenylthiophene-1-oxide **3a** in 52% yield.<sup>9</sup> However, this method lacks generality. A general and efficient route was developed by Jiang and Tilley using SO<sub>2</sub> as an electrophile. Various functionalized thiophene-1-oxide derivatives and mixed thiophene–thiophene-1-oxide oligomers were prepared in high yields (Scheme 8).<sup>18</sup>

Reaction of the zirconacyclopentadienes with tellurium halide TeCl<sub>2</sub> failed to produce tellurophenes due to the poor solubility of TeCl<sub>2</sub>. Rivard and co-workers found that the

### Scheme 4. Typical Examples of Direct Transfer into Thiophenes and Selenophenes

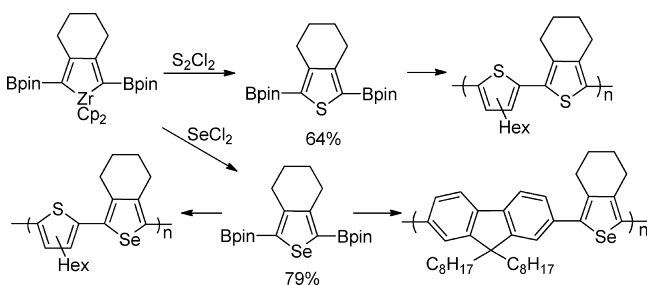


### Scheme 5. Synthesis of Cyclopenta[*c*]chalcogenophenes and Related Polymers

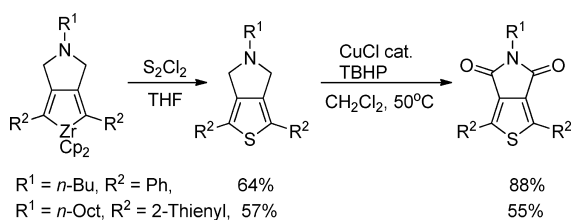


soluble 2,2'-bipyridyl-sequestered tellurium dichloride adduct (bipy-TeCl<sub>2</sub>) could react with the zirconacyclopentadienes to afford the tellurophenes **4** in moderate yields (Scheme 9).<sup>8c,19</sup> Moreover, tellurophenes with pinacolboronate (BPin) groups exhibited efficient green phosphorescence in the solid state and under ambient conditions. They also found that these tellurophenes could act as a solid-state on/off sensor for organic vapor. Similarly, benzo[*b*]tellurophenes were obtained from zirconaindenes.<sup>19b</sup> Benzo[*b*]tellurophenes showed weaker phosphorescence than above-mentioned tellurophenes.

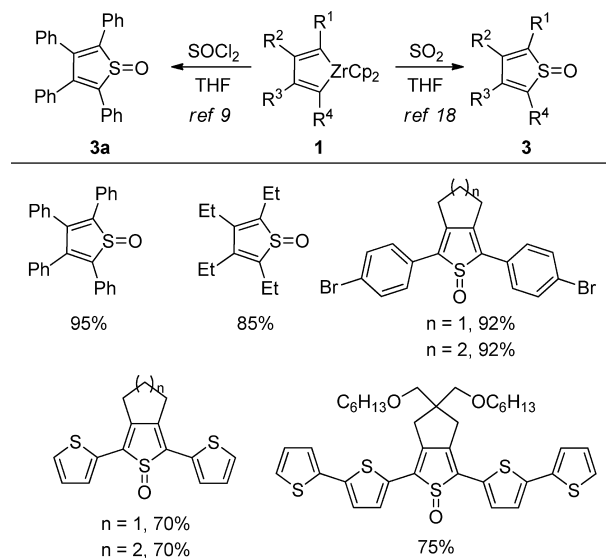
### Scheme 6. Synthesis of Boryl-Substituted Chalcogenophenes and Related Polymers



### Scheme 7. Two-Step Transfer into Thieno[3,4-c]pyrrole-4,6-dione



### Scheme 8. Transfer into Functionalized Thiophene-1-oxides

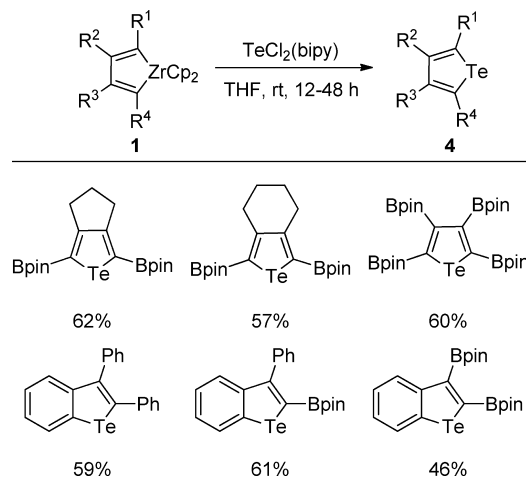


## 2.2. Conversion of Zirconacyclopentadienes into Phospholes, Arsoles, Stiboles, and Bismoles

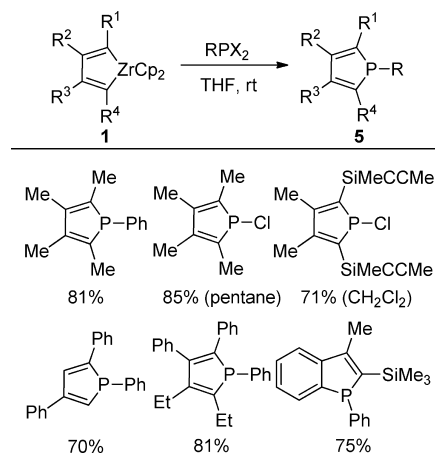
Treatment of the zirconacyclopentadienes with dichlorophosphine afforded phospholes in high yields (Scheme 10).<sup>9,20</sup> This transformation is one of the most versatile methods for the preparation of phospholes to date. With the development of various regio- and chemoselective methods of preparing multisubstituted zirconacyclopentadienes, the transfer process allows access to diverse substituted phospholes, which became important building blocks in the fields of catalysis, coordination chemistry, material sciences, and medicinal chemistry.<sup>21</sup> Some examples of phospholes and their derivatives synthesized by the Fagan–Nugent reaction are listed in Figure 3.<sup>22</sup> In addition, preparation of phospholes from titanacyclopentadienes has been reported.<sup>23</sup>

Arsoles, stiboles, and bismoles can be prepared by a similar method with substituted zirconacyclopentadienes. Reaction of

### Scheme 9. Direct Transfer into Tellurophenes



### Scheme 10. Direct Transfer into Phospholes<sup>a</sup>



<sup>a</sup>Other reaction solvents are indicated in parentheses.

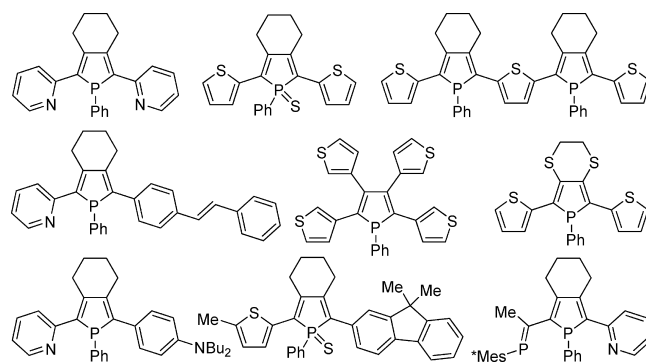
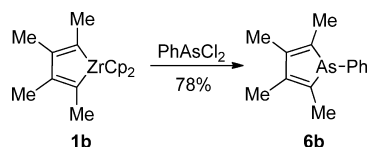


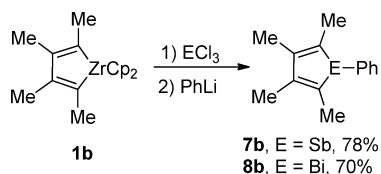
Figure 3. Typical Examples of Formation of Functionalized Phospholes.

tetramethylzirconacyclopentadiene **1b** with dichlorophenylarsine afforded the corresponding arsole **6b** in 78% yield (Scheme 11). The analogous stibole **7b** and bismole **8b** can be also prepared by treatment of the tetramethylzirconacyclopentadiene with  $SbCl_3$  or  $BiCl_3$  followed by arylation (Scheme 12).<sup>9</sup> Buchwald and co-workers further developed the formation stibaindoles from zirconaindenes (Scheme 13).<sup>24</sup>

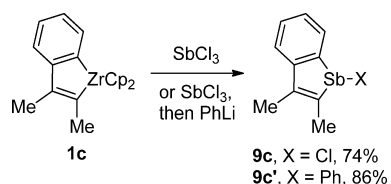
## Scheme 11. Direct Transfer into Arsole



## Scheme 12. Direct Transfer into Stibole and Bismole



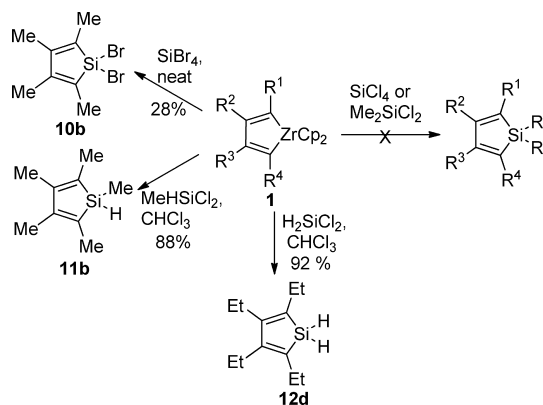
## Scheme 13. Direct Transfer into Stibaindoles



## 2.3. Conversion of Zirconacyclopentadienes into Siloles, Germoles, and Stannoies

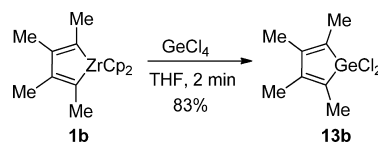
Reaction of the zirconacyclopentadienes with silicon halides ( $\text{Me}_2\text{SiCl}_2$  or  $\text{SiCl}_4$ ) failed to produce siloles. The reaction of zirconacyclopentadiene with  $\text{SiBr}_4$  afforded 1,1-dibromo-2,3,4,5-tetramethylsilole **10b** in low yield.<sup>9</sup> This may be attributed to steric constraints and size-mismatching of silicon halides and the zirconacyclopentadienes. Indeed, when less steric halosilanes, such as  $\text{MeHSiCl}_2$  and  $\text{H}_2\text{SiCl}_2$ , were employed, the desired siloles **11b** and **12d** were obtained in high yields (Scheme 14).<sup>25</sup> Remarkable solvent effects were found in this transformation. The reaction proceeded quickly only in chloroform and dichloromethane.

## Scheme 14. Direct Transfer into Siloles

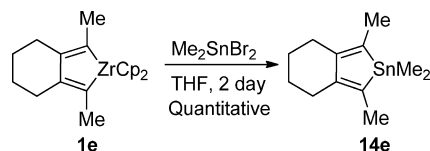


Reaction of tetramethylzirconacyclopentadiene with  $\text{GeCl}_4$  proceeded quite readily at room temperature and afforded germole **13b** in high yield (Scheme 15). In contrast, transmetalation with  $\text{Me}_2\text{SnBr}_2$  was quite slow; it needed long reaction time to complete the reaction to form stannole **14e** (Scheme 16).<sup>9</sup>

## Scheme 15. Transfer into Germole



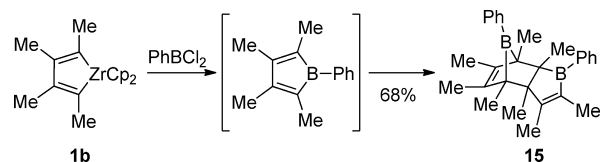
## Scheme 16. Transfer into Stannole



## 2.4. Conversion of Zirconacyclopentadienes into Boroles and Galloles

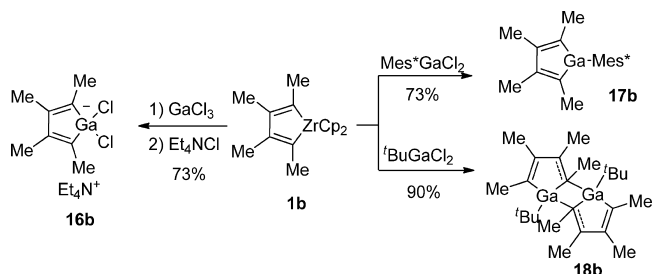
Boroles are unsaturated boron-containing five-membered cyclic molecules that have long been of interest due to their  $4\pi$  antiaromatic nature. The strategy of the zirconacyclopentadiene transfer was adopted in borole chemistry in 1988 by Fagan and co-workers.<sup>9b</sup> Reaction of  $\text{Cp}_2\text{ZrC}_4\text{Me}_4$  with  $\text{PhBCl}_2$  resulted in the formation of  $[\text{PhBC}_4\text{Me}_4]$ . However, this compound proved to be too reactive and only its Diels–Alder dimer **15** has been isolated (Scheme 17).

## Scheme 17. Transfer into Borole and Its Diels–Alder Dimer



Fagan and co-workers further found that reaction of tetramethylzirconacyclopentadiene with  $\text{GaCl}_3$  followed by addition of  $\text{Et}_4\text{NCl}$  allowed the isolation of the anionic gallole **16b**.<sup>9</sup> The free gallole **17b** was later reported by Cowley and co-workers by using a bulky aryl group substituent (2,4,6- $(t\text{Bu})_3\text{C}_6\text{H}_2$ ,  $\text{Mes}^*$ ) on the gallium atom.<sup>26</sup> When  $t\text{Bu}$  was employed on gallium, the reaction afforded the gallole dimer **18b** in 90% yield (Scheme 18).<sup>27</sup>

## Scheme 18. Transfer into Galloles and Gallole Dimer

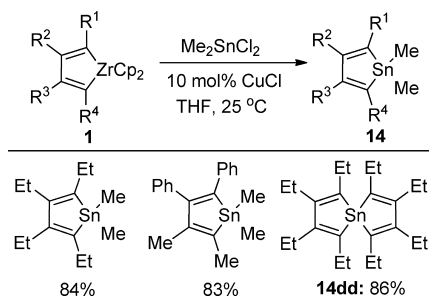


## 3. COPPER-MEDIATED CONVERSION OF ZIRCONACYCLOPENTADIENES INTO STANNOLES, BOROLES, AND PYRROLES (ROUTE B)

Although the Fagan–Nugent reaction provided a versatile method for the synthesis of heterocycles of main group elements from zirconacyclopentadienes, the reactions often had

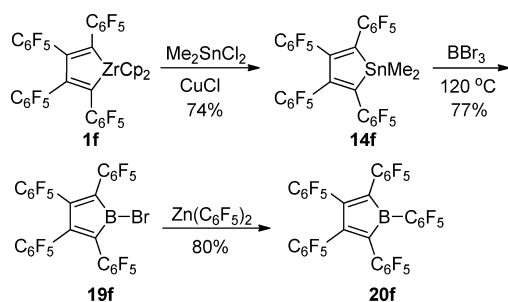
limitations, such as long reaction time, low yields, and limited scope of substituents. And also, the reactions were still not suitable for conversion of zirconacyclopentadienes into furans and pyrroles. Transmetalation of zirconacyclopentadiene to copper complexes represents a milestone in zirconacyclopentadiene chemistry. Many reactions have been developed in this area. Takahashi and co-workers found that transfer of zirconacyclopentadienes to stannoles proceeded more efficiently in the presence of a catalytic amount of CuCl (Scheme 19).<sup>28</sup> Treatment zirconacyclopentadiene with half an equivalent of SnCl<sub>4</sub> lead to the formation of spiro stannole **14dd**.

### Scheme 19. CuCl-Catalyzed Transfer into Stannoles



In 2009, Piers and co-workers reported a new synthetic route to a perfluoropentaphenylborole **20f** by tandem Zr/Sn and Sn/B transmetalation of tetra(pentafluorophenyl)-zirconacyclopentadiene **1f**.<sup>29</sup> This strategy is based on the construction of the metallole framework through the coupling of perfluorodiphenylacetylene with Rosenthal's reagent. The conversion of tetra(pentafluorophenyl)zirconacyclopentadiene to stannole **14f** was first developed in the presence of CuCl. The resulting stannole was then treated with BBr<sub>3</sub> to give borole, which was then arylated by Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> to afford the perfluoropentaphenylborole **20f** (Scheme 20). Perfluoropenta-

### Scheme 20. CuCl-Mediated Transfer into Stannole and Borole

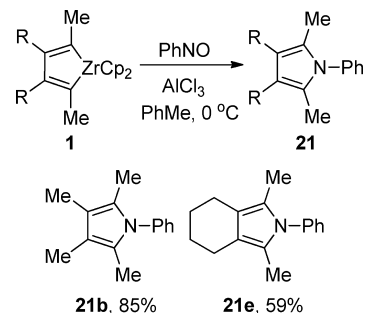


phenylborole showed unique properties of both antiaromaticity and tremendous Lewis acidity, which could activate dihydrogen<sup>30</sup> and form a stable adduct with CO.<sup>31</sup> Piers and co-workers also reported perfluorinated triphenylboraindene with a similar procedure, which has essentially equal Lewis acidic strength but is substantially more soluble.<sup>32</sup>

Direct synthesis of pyrroles by the Fagan–Nugent reaction has not been successfully achieved. Nakamoto and Tilley have reported that the reaction of zirconacyclopentadienes with nitrosobenzene gave pyrroles in the presence of AlCl<sub>3</sub>.<sup>33</sup> This reaction has a strict substrate limitation. Only two examples of pyrroles, that is, tetramethyl-*N*-phenylpyrrole (**21b**) and 1,3-

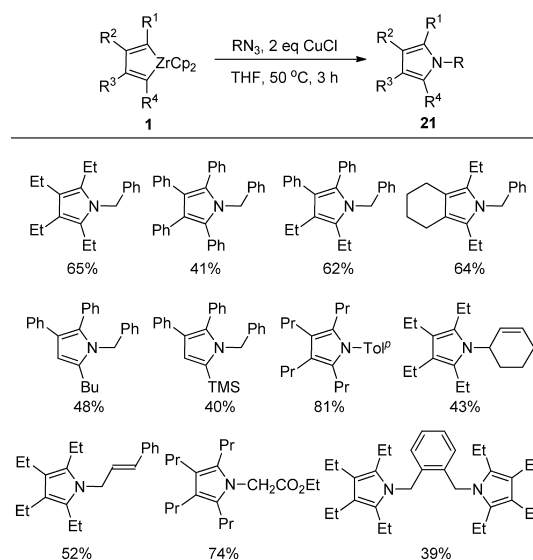
dimethyl-2-phenyl-4,5,6,7-tetrahydro-isoindole (**21e**), were obtained (Scheme 21).

### Scheme 21. AlCl<sub>3</sub>-Mediated Transfer into Pyrroles



During our study of copper-catalyzed or mediated amination with zirconocene complexes,<sup>34</sup> we found that reaction of zirconacyclopentadienes with azides afforded the corresponding pyrroles **21** in the presence of CuCl (Scheme 22). The reaction tolerated various substituents including alkyl, aryl, and trimethylsilyl group on zirconacyclopentadienes and alkyl, aryl, and allyl group on azides.<sup>34d</sup>

### Scheme 22. Typical Examples of CuCl-Mediated Transfer into Pyrroles

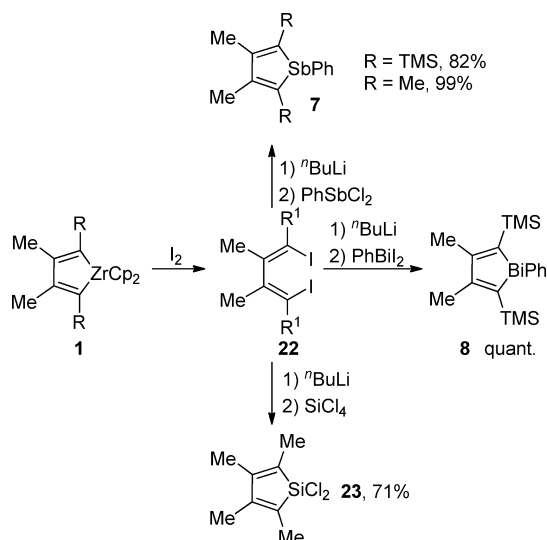


## 4. CONVERSION OF ZIRCONACYCLOPENTADIENES INTO STIBOLES, BISMOLES, SILOLES, PYRROLES, BOROLES, AND ALUMOLES BY THE AID OF IODINATION/LITHIATION PROCESSES (ROUTE C)

The traditional approach to metalloles was started from 1,4-dithio-1,3-butadienes, which were prepared by lithium mediated reductive dimerization of alkynes.<sup>35</sup> However, only limited 1,4-dithio-1,3-butadienes were readily available with this method. It is known that zirconacyclopentadienes can be converted to the 1,4-dithio-1,3-butadienes in two-step. This method afforded diverse 1,4-dithio-1,3-butadienes with different alkyl, aryl, and silyl substituents. Ashe and co-workers developed a two-step approach to stiboles **7**<sup>36</sup> and bismoles **8**:<sup>37</sup> (1) conversion of zirconacyclopentadienes to 1,4-diiodo-1,3-butadienes **22** and (2) lithiation of 1,4-diiodo-1,3-butadienes

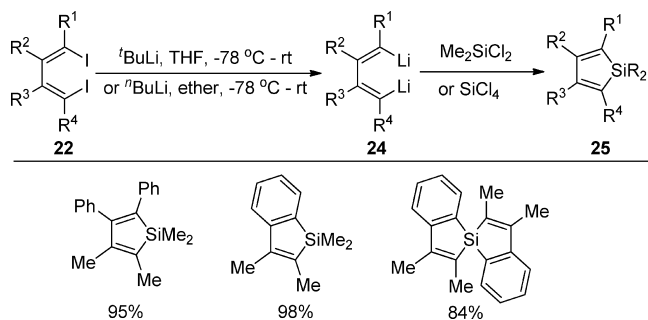
and then treatment with element halides (Scheme 23). Compared with the Fagan–Nugent reaction, the indirect

**Scheme 23. Two-Step Transfer into Stiboles, Bismoles, and Siloles**



approach afforded the product in higher yields and better purity as well as reaction universality. The direct transmetalation of zirconacyclopentadienes to siloles has high substrate limitation. West and co-workers extended this two-step approach for the synthesis of silole **23** (Scheme 23).<sup>38</sup> We also reported the two-step approach to prepare the siloles or spiro compounds (Scheme 24).<sup>12</sup> Tamao and co-workers

**Scheme 24. Transfer into Siloles through Iodination/Lithiation Processes**

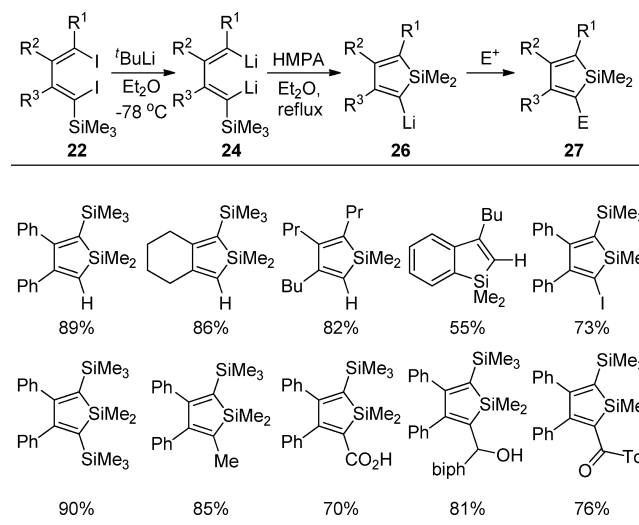


reported a procedure for the preparation of siloles from 1,4-dihalobutadienes. In this case, the 1,4-dihalobutadienes were prepared by the halogenolysis of titanacyclopentadienes.<sup>39</sup>

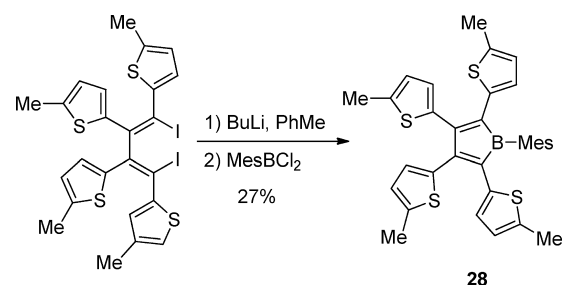
Xi and co-workers found that 1-silyl-1,4-dithio-1,3-butadienes **24** underwent novel intramolecular skeletal rearrangements affording 1-lithiosiloles, **26**, in the presence of hexamethylphosphoramide (HMPA). The 1-lithiosiloles could be further applied for the synthesis of a variety of functionalized siloles **27** with electrophiles (Scheme 25).<sup>40</sup>

The electron-donating tetrathienyl-substituted borole was recently prepared by Yamaguchi and co-workers.<sup>41</sup> With bis(5-methyl-2-thienyl)acetylene as starting material, 1-mesityl-2,3,4,5-tetrakis(5-methyl-2-thienyl)borole, **28**, was successfully obtained by a straightforward two-step approach (Scheme 26). The tetrathienylborole had a particularly small HOMO–

**Scheme 25. Intramolecular Transfer into 1-Lithiosiloles**



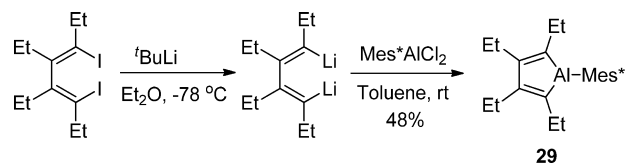
**Scheme 26. Transfer into Borole through Iodination/Lithiation Processes**



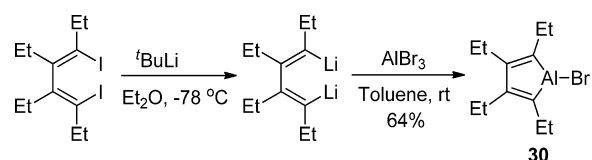
LUMO gap, which is reflected in the UV–vis absorption maxima ( $\lambda_{\text{max}} = 735 \text{ nm}$ ) at long wavelength that is significantly red-shifted compared with pentaphenylborole ( $\lambda_{\text{max}} = 560 \text{ nm}$ ).

Alumole was proposed as intermediate in  $\text{AlCl}_3$  mediated reaction of zirconacyclopentadienes.<sup>42</sup> The Lewis-base-free alumole was isolated by Tokitoh and co-workers in 2013. Treatment of  $\text{Mes}^*\text{AlCl}_2$  with 1,4-dithio-1,3-butadiene in toluene afforded alumole, **29**, as a colorless solid (Scheme 27).<sup>43</sup> Reaction of 1,4-dithio-1,3-butadiene with  $\text{AlBr}_3$  afforded 1-bromoalumole, **30**, which was found to exist as a dimeric structure in the crystalline state (Scheme 28).<sup>44</sup>

**Scheme 27. Transfer into Alumole through Iodination/Lithiation Processes**

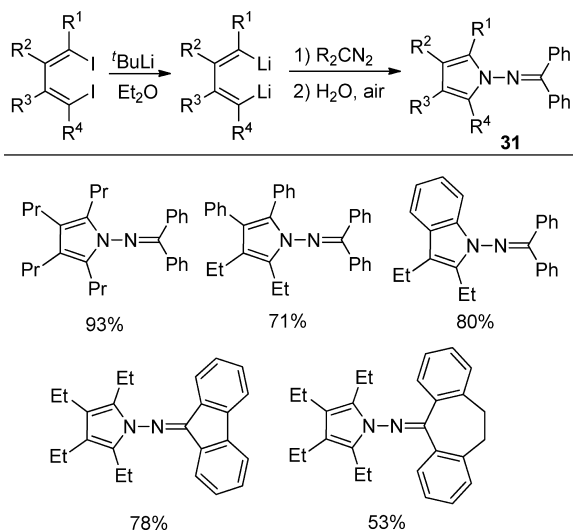


**Scheme 28. Transfer into 1-Bromoalumole through Iodination/Lithiation Processes**



In 2013, Xi and co-workers reported an efficient synthesis of 1-imino-pyrrole derivatives **31** in high yields from the reaction of diaryl diazomethanes with *in situ* generated 1,4-dilithio-1,3-butadienes (Scheme 29).<sup>45</sup>

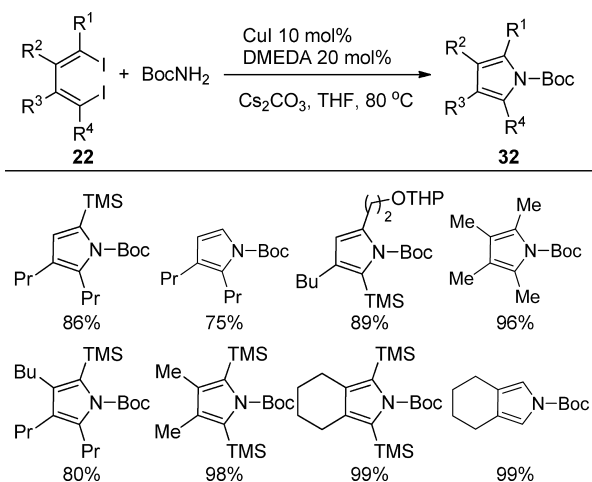
**Scheme 29. Transfer into 1-Imino-pyrroles through Iodination/Lithiation Processes**



## 5. ZIRCONACYCLOPENTADIENES TO PYRROLES AND THIOPHENES BY THE AID OF A 1,4-DIHALO-1,3-BUTADIENES (ROUTE D)

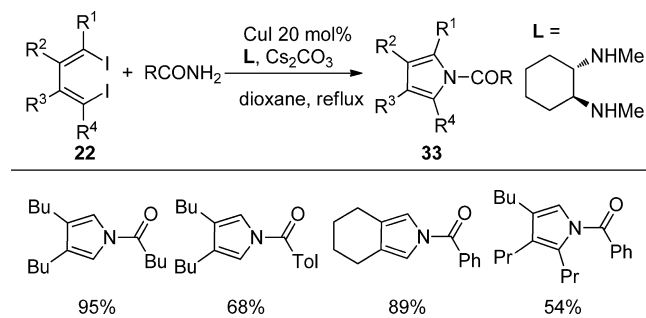
Since nucleophilic nitrogen sources (amines) are more common than electrophilic nitrogen sources, reaction of 1,4-dihalo-1,3-butadienes with amines/amides would provide a versatile method for the preparation of pyrroles. In 2007, Buchwald and co-workers reported synthesis of pyrroles **32** via copper-catalyzed coupling reaction of 1,4-dihalo-1,3-butadienes with  $\text{BocNH}_2$  (Scheme 30).<sup>46</sup> The transformation allows the synthesis of pyrroles with a wide variety of functional groups and substitution patterns. At the same time, Li and co-workers also reported a relevant procedure for the synthesis of pyrroles **33**, in which the substrate scope was extended to alkyl and aryl

**Scheme 30. Transfer into *N*-Boc-pyrroles via 1,4-Diiodo-1,3-butadienes**



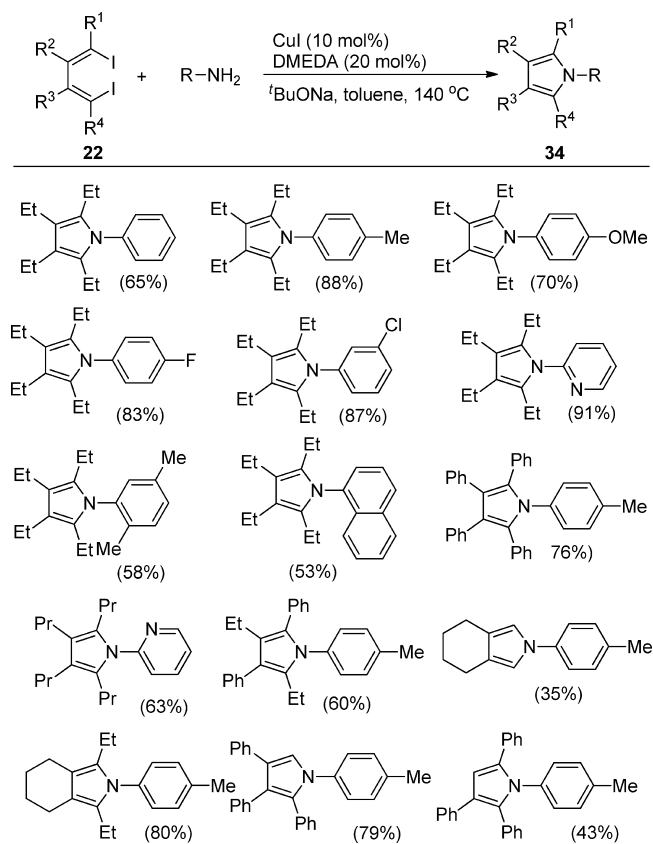
amides (Scheme 31).<sup>47</sup> We further developed this transformation to the synthesis of *N*-arylpyrroles **34** by using

**Scheme 31. Transfer into *N*-Acylpyrroles via 1,4-Diiodo-1,3-butadienes**



primary amines (Scheme 32).<sup>48</sup> Anilines with electron-donating and electron-withdrawing substituents as well as a hetero-aromatic amine performed very well under the conditions.

**Scheme 32. Transfer into *N*-Arylpyrroles via 1,4-Diiodo-1,3-butadienes**

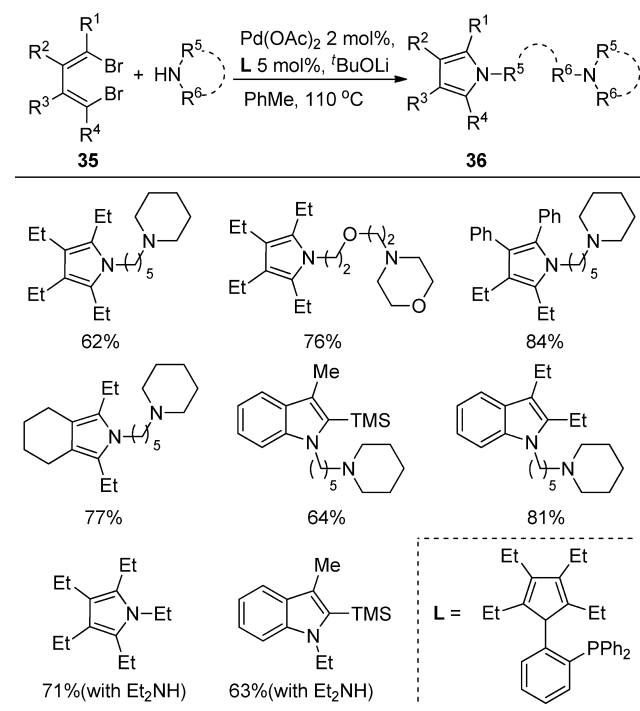


Xi and co-workers recently reported palladium-catalyzed reaction of 1,4-dibromo-1,3-butadienes **35** with secondary amines afforded pyrroles **36** with cleavage of one C–N bond (Scheme 33).<sup>49</sup>

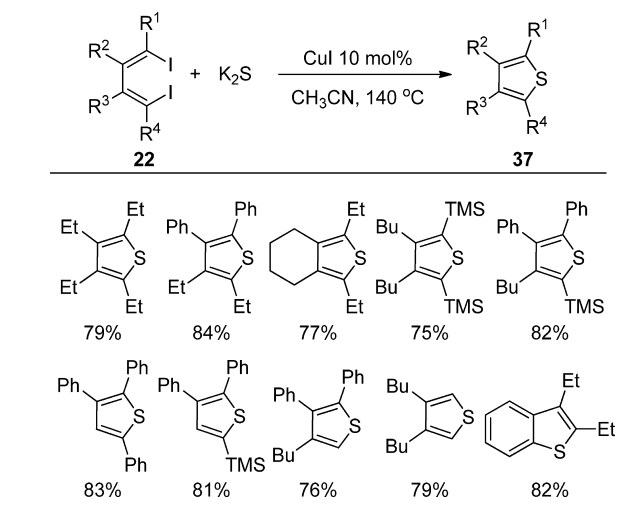
Recently, we developed copper-catalyzed coupling reactions of 1,4-diiodo-1,3-butadienes with potassium sulfide, which afforded di-, tri-, and tetra-substituted thiophenes **37** in 72–93% yield (Scheme 34).<sup>50</sup>



Scheme 33. Coupling of 1,4-Dibromo-1,3-butadienes with Secondary Amines Leading to Pyrroles



Scheme 34. Copper-Catalyzed Transfer into Thiophenes via 1,4-Diiodo-1,3-butadienes

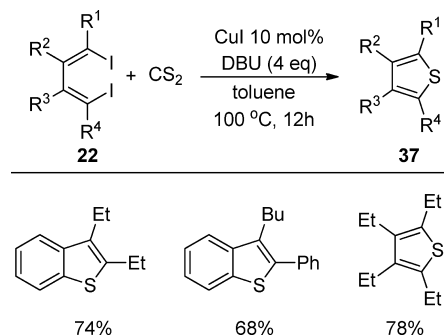


During the course of formation of heterocycles using carbon disulfide, we explored the CS<sub>2</sub>-DBU system as sulfuric source, which coupled with 1,4-diiodo-1,3-butadiene to afford thiophenes and benzothiophenes (Scheme 35).<sup>51</sup>

## 6. SUMMARY AND OUTLOOK

The Fagan–Nugent reaction, involving a direct reaction of zirconacyclopentadienes with element halides, provided a straightforward pathway for the preparation of variously substituted thiophenes, selenophenes, tellurophenes, phospholes, arsoles, stiboles, bismoles, gerroles, stannoles, and galloles. The zirconacyclopentadienes could transfer into stannoles, pyrroles, and boroles with satisfactory results in the presence of CuCl. For less reactive element reagents, the zirconacyclopentadienes transfer into pyrroles, stiboles, bis-

Scheme 35. Copper-Catalyzed Transfer into Thiophenes



moles, siloles, boroles, and aluoles by the aid of an iodination/lithiation processes in satisfactory yields. Alternatively, an umpolung strategy, reaction of electrophilic 1,4-diiodo-1,3-butadiene with nucleophilic heteroatom reagents, was successfully used in the preparation of thiophenes and pyrroles from the zirconacyclopentadienes. The Fagan–Nugent reaction together with the supplemental reactions affords a convenient method for the synthesis of p-block element metalloles from simple starting materials via zirconacyclopentadienes. The synthetic methodology to phosphole-, thiophene-, and selenophene modified with longer conjugated systems is widely developed. The extension of this versatile methodology to other p-block element metalloles such as arsoles, boroles, siloles, and gerroles, as well as their applications, are under active investigation. It can be anticipated that synthesis and application of p-block element metalloles will be an interest field in synthetic chemistry as well as optic and electronic materials chemistry.

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### Notes

The authors declare no competing financial interest.

### Biographies

**Xiaoyu Yan** was born in Nanyang, China. He obtained his B.Sc. (2008) and Ph.D. degree (2013) in Tsinghua University under the supervision of Prof. Chanjuan Xi. Since 2014, he has been a postdoctoral researcher in the group of Prof. Holger Braunschweig (University of Würzburg) supported by the *Alexander von Humboldt Foundation*.

**Chanjuan Xi** was born in Jingyang, China. After receiving her B.Sc. degree from Lanzhou University in 1986, she worked at Lanzhou Institute of Chemical Physics, CAS (1986–1995). In course of her work, she earned a Master's degree in 1994. In 1996, she joined Hokkaido University and earned her Ph.D. in 1999 and spent one year as a postdoctoral fellow in Catalysis Research Center, Hokkaido University, with Prof. Tamotsu Takahashi. In 2000, she joined Tsinghua University as Associate Professor, and then she was promoted to a Professor in 2005.

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