Regio-controlled intramolecular reductive cyclization of diynes

Kohei Tamao and Shigehiro Yamaguchi

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan
E-mail address: tamao@scl.kyoto-u.ac.jp

Abstract: Metal promoted intramolecular reductive cyclization of diynes, useful for construction of cyclic diene systems, is formally classified into three types with respect to the orientation of two acetylene moieties to the newly formed ring. While the *exo-exo* mode of reductive cyclization reactions have been well known to be promoted by transition metal two-electron reductants, the *exo-endo* mode has rarely been studied and the *endo-endo* mode had been virtually unknown. Presented herein are the first examples of the *endo-endo* mode cyclization of diynes promoted by lithium naphthalenide, in addition to some typical examples of nickel-catalyzed *exo-exo* mode cyclization of diynes and their applications to the synthesis of novel π-conjugated oligomers and polymers containing silacyclopentadiene ring. The unusual electronic structures of the silole-containing π-conjugated systems have been analyzed by molecular orbital calculations.

INTRODUCTION

The chemistry of π-conjugated polymers continues to flourish in the last few decades, for anticipated wide applicability in the field of molecular electronics. Current interests have especially been directed toward structure modifications of various homopolymers and copolymers by developing new cyclic conjugate monomer units (ref. 1). We have recently been interested in π-conjugated polymers containing silole (silacyclopentadiene) rings as a new monomer unit, in view of the unique electronic structure having unusually low-lying LUMO (vide infra). This review is concentrated on the synthesis and some properties of the following two types of polymeric compounds, i.e., silole-thiophene copolymers (ref. 2) and silole homo oligomers as models of polysiloles (ref. 3), as shown in Scheme 1.

Scheme 1
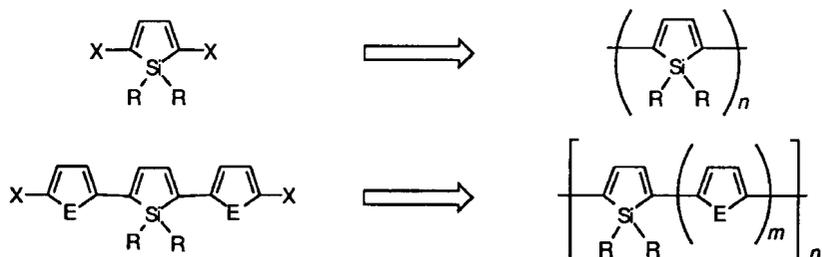
The most straight-forward strategy for the synthesis of these polymers and oligomers may be the transition-metal catalyzed or mediated coupling reactions of the appropriate α,ω-difunctionalized monomer units. There seemed no problem in this coupling step, since a variety of methodologies had been developed so far. The main problems in these projects were how to prepare the requisite monomer units. There had been no method for the synthesis of 2,5-bis(heteroaryl)-substituted siloles and 2,5-difunctionalized siloles (ref. 4), when we started this study a few year ago. We anticipated that intramolecular reductive cyclization of diynes would be most promising for construction of these monomer units.

REGIOSELECTIVITY OF INTRAMOLECULAR REDUCTIVE CYCLIZATION OF DIYNES

In principle, there are three modes for cyclization of diynes with respect to the orientation of the resulting olefins to the newly formed ring, as shown in Scheme 2 (refs. 3a, 5).

Scheme 2

[M]

exo - exo   *exo - endo*   *endo - endo*

The *exo-exo* mode cyclization is most common, as achieved with a variety of transition metal two-electron reductants such as Ti(II), Zr(II), Co(I), Rh(I), Ni(0), and Pd(0) complexes (ref. 6): almost all reductive intramolecular cyclizations so far developed fall into this category. We have used the Ni(0)-catalyzed cyclization (ref. 6c) for construction of 2,5-dithienylsilole systems, as will be mentioned later. The *exo-endo* mode cyclization has been very rare: the reductive cyclization of macrocyclic oligo-ynes with alkali metals may be regarded as only one example so far reported (ref. 7). The *endo-endo* mode reductive cyclization had been unknown, to our best knowledge, until we developed the reductive cyclization of diethynylsilanes with lithium naphthalenide, as the first example of this category last year (ref. 3a). Described herein are the *exo-exo* and the *endo-endo* mode reactions.

EXO-EXO MODE REDUCTIVE CYCLIZATION OF 1,6-HEPTADIYNES CATALYZED BY NICKEL(0) COMPLEXES

1,7-Dithienyl-1,6-heptadiyne is treated with hydrodisilane in the presence of a Ni(0) species to form 2,5-dithienylsilole derivative in moderate yields, the cyclization proceeding in the *exo-exo* mode as shown in Scheme 3 (ref. 2a). This cyclization is an intramolecular version of the intermolecular cyclization reported by Kumada and his co-workers (ref. 8). While the intermolecular cyclization of alkylarylacetylenes gives 3,4-diarylsilole regioselectively, the intramolecular cyclization can reverse the regioselectivity to give the fully conjugated 2,5-diarylsiloles. A possible catalytic cycle shown in Fig. 1 involves oxidative addition, α-elimination to a silylene-nickel species, cycloaddition, insertion of the remaining acetylene into the resulting Ni-C bond, and the final reductive elimination of the product, regenerating the Ni(0) catalyst.

Scheme 3

TBSO   OTBS   + $HMe_2SiSiMe_2H$ →   Ni(acac)$_2$ (x 0.05) PEt$_3$ (x 0.1) DIBAH (x 0.1)   THF, reflux, 11 h

TBSO   OTBS   Me   Me

77 %   yellow
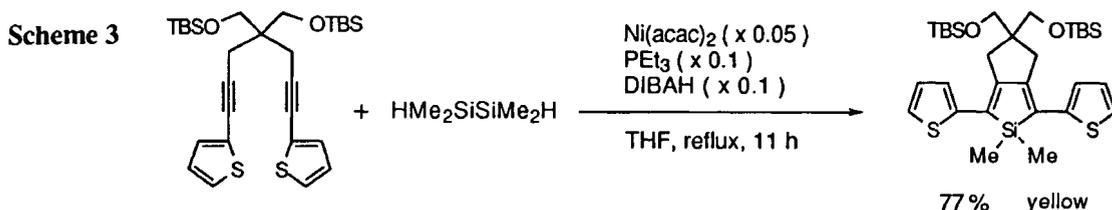
The cyclization can be applied to a thiophene-(1,6-heptadiyne) alternating cooligomer (ref. 2b). Thus, the "double" intramolecular cyclization is promoted in the presence of a stoichiometric amount of Ni(0) species to give a silole:thiophene 1:1 alternating cooligomer efficiently, as shown in Scheme 4.

Scheme 4

TBSO   OTBS   TBSO   OTBS   +   2 $HMe_2SiSiMe_2H$

Ni(acac)$_2$ (x1), PEt$_3$ (x2), DIBAH (x2)
————————————————————
THF, room temp., 12 h

TBSO   OTBS   TBSO   OTBS
Me Me   Me Me

34% λ_{max} = 490, 524 nm, deep red
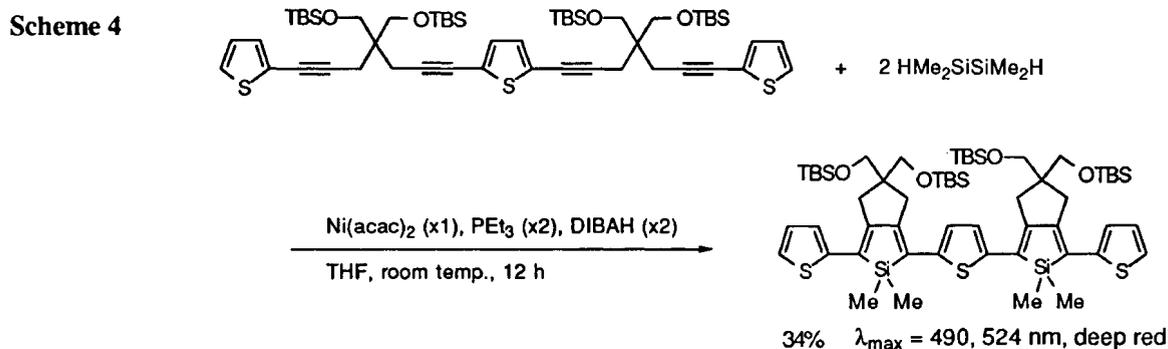
A series of copolymers, varying the silole:thiophene ratios from 1:2 to 1:4, have been prepared by palladium-catalyzed cross-coupling reactions of the appropriate halo- and stannyl-derivatives of monomer units, as exemplified by the formation of 1:2 copolymer (Scheme 5).
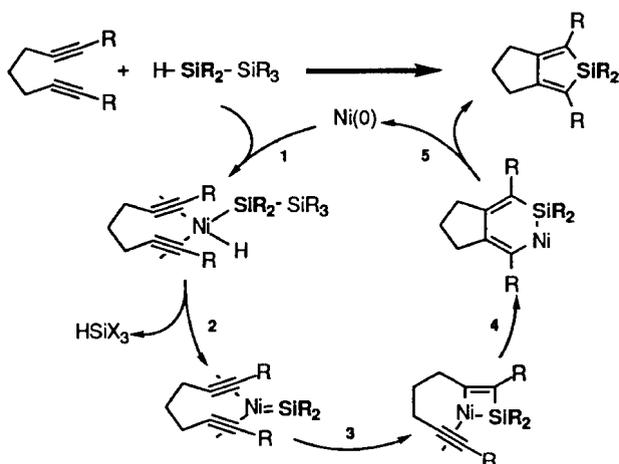
Fig. 1 Nickel-catalyzed *exo-exo* mode cyclization of diynes with silylene species to form silole.

Scheme 5

65% $n \approx 11$
λ_{max} = 594, 615 nm
Deep Red-Violet Solid
Deep Blue Solution
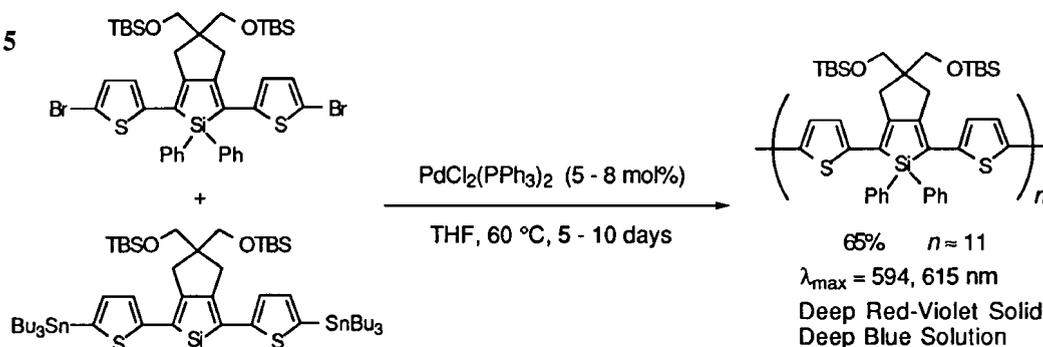
The polymers exhibit long λ_{max} in the UV-vis absorption spectra, having intense colors as shown for each polymer. The unique π-electronic structures of these silole-thiophene copolymers will be discussed later.

ENDO-ENDO MODE REDUCTIVE CYCLIZATION OF DIETHYNYLSILANES AND DIETHYNYLMETHANES

Di(phenyethynyl)silane is added to an excess amount of lithium naphthalenide in THF at room temperature to form 2,5-dilithiosilole in one step, as shown in Scheme 6 (ref. 3a). The key point to attain high yield is the dropwise addition of the diethynylsilane into an "electron pool" consisting of an excess amount of reductant, and thereby both acetylene moieties are reduced simultaneously to from a bis(anion radical) intermediate that undergoes radical coupling to form the 3,4-carbon-carbon bond leaving anions at the 2,5-positions. The use of a stoichiometric amount of reductant lowered the yield of dilithiosilole significantly, together with the formation of a lithium phenylacetylide as a byproduct via cleavage of the silicon-carbon bond. Thus, it appears that a mono(anion radical) arising from less efficient stepwise reduction under the electron deficiency is prone to undergo cleavage of the silicon-carbon bond prior to the formation of the di(anion radical). The phenyl group at the terminal position of acetylene is also essential for obtaining the dilithiosilole: A complex mixture was obtained in the case of an alkyl-, alkenyl- or silyl-substituted and a parent ethynyl group. The phenyl groups may thus act as a stabilizer of the crucial bis(anion radical) species.

Scheme 6

(R = Me, Et, *i*-Pr, Hex)
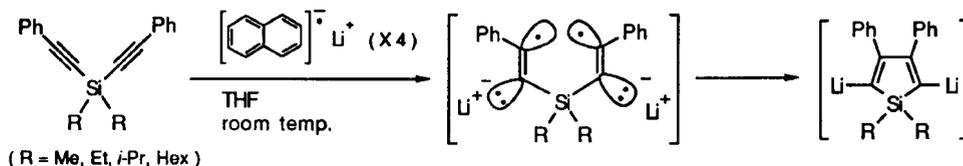
This reductive cyclization by use of the one-electron reductant is the first example of the *endo-endo* mode cyclization and may be regarded as an anion analogue of Bergman cyclization (ref. 9), a neutral thermal cyclization of enediynes in the *endo-endo* mode and also as an intramolecular version of intermolecular reductive coupling of diphenylacetylene with lithium to the corresponding 1,4-dilithio-1,3-butadiene (ref. 10).

The dilithiosiloles can be trapped with a variety of electrophiles to afford the corresponding 2,5-difuncitonalized silole derivatives, as shown in Scheme 7. The dibromosilole can be further converted into some unsymmetrically disubstituted siloles. Thus, the first general methodology for the synthesis of 2,5-difuncitonalized siloles has been developed.

Scheme 7

E = Br (72%), I (64%), Me₃Si (86%),
Bu₃Sn (49%), PhSe (73%)

E = H (82%), Me₃Si (79%),
Bu₃Sn (79%)
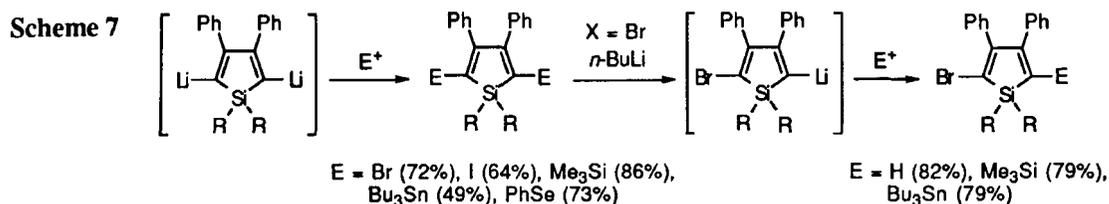
The *endo-endo* mode reductive cyclization of the carbon analog, diethynylmethane (1,4-pentadiyne), could be achieved by addition to an excess amount of lithium naphthalenide at −78 °C to form 1,4-dilithiocyclopentadiene, which was trapped immediately after the addition to give various 1,4-difunctionalized cyclopentadienes in up to 20% yields, as shown in Scheme 8 (ref. 3b). Cleavage of the central carbon-acetylene bond was one of the side reactions to give a lithioallene. The difference in reactivities between the silicon and the carbon counterparts may be ascribed to the stabilization of the bis(anion radical) intermediates by the silicon atom.

Scheme 8

E = H (20%), I (18%),
Me₃Si (13%)
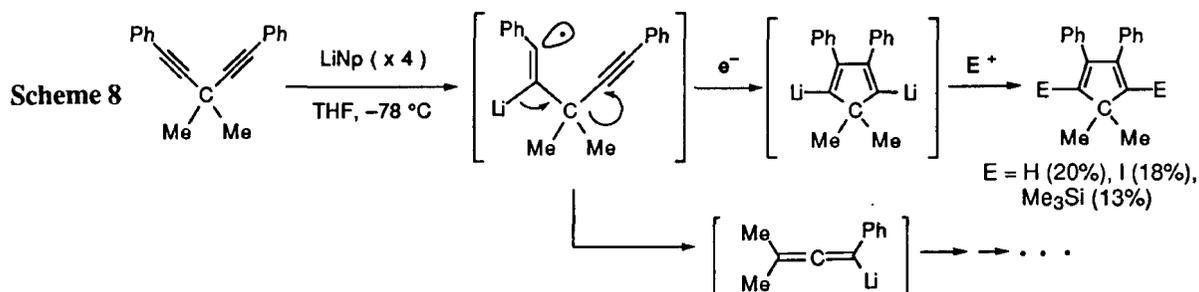
Synthesis of oligosiloles and bicyclopentadiene via oxidative coupling

With various kinds of 2,5-difunctionalized silole derivatives in our hand, we have tried to prepare oligomers and/or polymers of silole by applying a variety of conditions for nickel- and palladium-catalyzed cross and/or homo coupling reactions, but none of them afforded characterizable coupling products. However, we finally found that a two-step oxidative coupling of lithiosiloles via higher order cuprates, recently reported by Lipshutz (ref. 11), was most effective. The typical results are summarized in Scheme 9. By this method, bisilole and quatersilole have been prepared successfully for the first time. Similarly, the carbon analog, bicyclopentadiene, could be prepared efficiently from the 2,4-diiodocyclopentadiene derivative, as shown in Scheme 9. This is also the first member of the well-characterized 1,1'-bicyclopentadiene.

Scheme 9

69 % yellow X'al

orange powder

X = I or H: colorless X'al
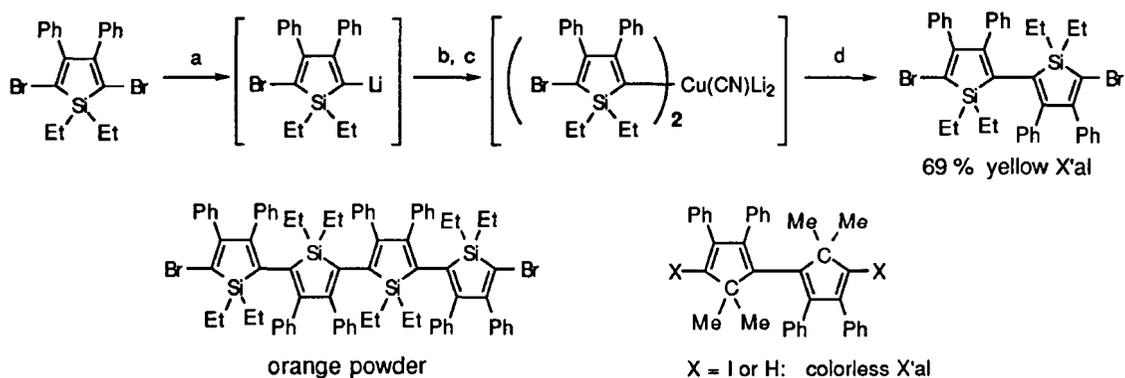
(a) *n*-BuLi (x 1.1), Et₂O, −78 °C ~ 0 °C, 3 h.   (b) − BuBr *in vacuo*.
(c) CuCN (x 0.5), TMEDA, THF, −78 °C ~ 0 °C.   (d) *p*-dinitrobenzene (x 5), −78 °C, 1 h.

X-RAY STRUCTURES, ABSORPTION SPECTRA, AND ELECTRONIC STRUCTURES OF OLIGOMERS

X-ray structures

X-ray structures of the thiophene-silole-thiophene oligomer and bisilole are shown in Fig. 2. While the thiophene-silole oligomer has the nearly coplanar arrangements of the three rings (ref. 2a), the bisilole has highly non-coplanar arrangement between two rings with large twist angles 62° from the anti conformation (ref. 3a). The structure of the bisilole is further deformed by folding of two rings from the connecting bond in the same direction with the folding angle ca. 15°. Highly twisted structures have been observed also for the bicyclopentadiene derivative (not shown here) (ref. 3b).
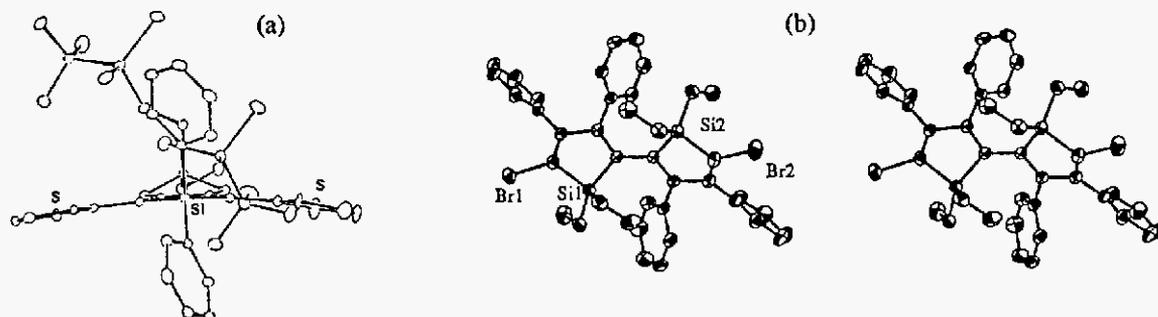
Fig. 2 X-ray structures of (a) thiophene-silole-thiophene monomer unit and (b) dibromobisilole (stereoview).

UV-vis absorption spectra

The silole-thiophene combination causes large red shifts compared with the thiophene homooligomers and polymers. For example, the thiophene-silole-thiophene monomer unit (λ_{max} 416 nm) displays about 60 nm red shifts compared with terthiophene (355 nm) (ref. 12a) and, remarkably, the absorption maxima of the silole:thiophene 1:2 polymer (594 and 615 nm) are about 150 nm longer than the absorptions of poly(3-alkylthiophene)s (435 - 450 nm) (ref. 12b). The data demonstrate a unique combination of these two heterocyclic diene systems.

It should be further noted that the bisilole is yellow in spite of the twisted conformation and has λ_{max} at 398 nm, which is 58 nm longer than the $\lambda_{max} = 340$ nm of the colorless bicyclopentadiene and the longest among the absorption maxima of some common conjugated dimers of five-membered cyclic dienes such as 2,2'-bithiophene 302 nm, 2,2'-bifuran 278 nm, and 2,2'-bipyrrole 276 nm (ref. 12c). These data clearly suggest a crucial role of the silicon atom in the silole-containing new π-conjugated systems.

Electronic structures of oligomers: an Important role of silicon atom

Molecular orbital calculations on the silole ring, as well as cyclopentadiene and thiophene, have demonstrated a unique π-electronic structures of silole and an important role of silicon atom therein. The results are summarized as follows. The silole ring has exceptionally low-lying LUMO level, as shown in Fig. 3. The origin of the low-lying LUMO is a lobe on silicon in-phase with lobes on the adjacent carbon atoms in the silole ring. The in-phase lobe on silicon is a part of σ^* orbital of the exocyclic Si-H bonds. It has been thus deduced that the low-lying LUMO of silole is ascribed to the efficient σ^*-π^* conjugation which makes possible a through conjugation involving the C-Si-C moiety, as visualized in Fig. 4. This is diagnostic of the silole ring, because no such orbital is available in other ring systems.
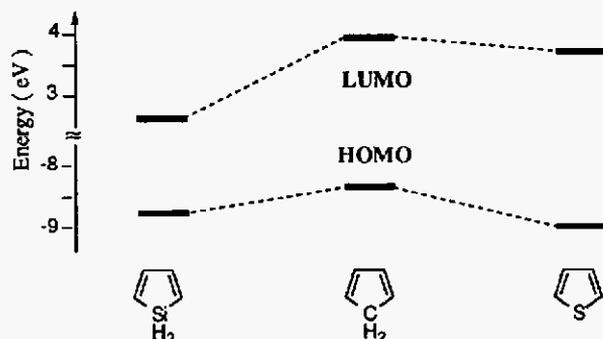
Fig. 3   HOMO and LUMO levels for silole, cyclopentadiene, and thiophene, based on HF/6-31G* calculations.
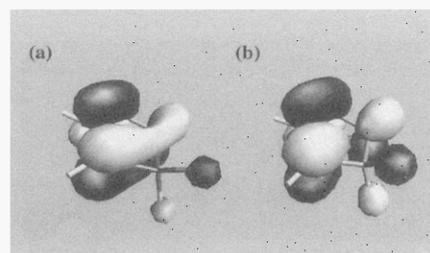
Fig. 4   LUMO levels of (a) silole and (b) cyclopentadiene.

As a result, in the silole-containing oligomers and polymers, the overall LUMO levels have been lowered by large contribution of the low-lying LUMO of silole ring(s) to the whole electronic structure. In the highly deformed bisilole, there seems to be an enhanced σ^*-π^* conjugation via spatial orbital interaction, resulting in the lowering of the LUMO level (ref. 3b). These low-lying LUMO levels must be the origin of the unusually long λ_{max} observed in these silole-containing π-conjugated oligomers and polymers.

CONCLUSION

We have developed a new *endo-endo* mode of intramolecular reductive cyclization of diynes, as well as the *exo-exo* mode of reaction, and have demonstrated that these regio-controlled cyclization of diynes are useful for construction of new cyclic π-conjugate systems, as exemplified by the silole rings. It is obviously anticipated that the *exo-endo* mode reductive cyclization also would provide us new π-conjugate ring systems. It is further stressed that a combination of these cyclization reactions and transition-metal catalyzed or mediated coupling reactions could be the most promising methodology for the synthesis of new π-conjugated polymers in the field of modern material sciences.

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