Metal mediated synthesis of substituted cyclooctatetraenes

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Substituted cyclooctatetraenes are a class of interesting and important compounds both theoretically and synthetically. Since Reppe first discovered the Ni-catalyzed tetramerization of ethyne affording cyclooctatetraene in 1948, transition metal mediated synthesis of this type of compounds has become a primary methodology. In this *Feature Article*, based on our own recent results and other groups' related reports, we describe major achievements on transition metal mediated or catalyzed synthetic methods for substituted cyclooctatetraenes, with focus on reaction patterns, mechanisms, and structural diversity of products.

1 Introduction

Cyclooctatetraene (COT) is a highly valuable organic intermediate[1] and at the same time, a very useful sterically demanding ligand for metals.[2] On the other hand, despite the same $(CH)_n$ formulation, benzene and COT have strikingly different properties which appear to forcefully substantiate the Hückel theory, making COT obtain its historical role in aromaticity concepts.[3] Hence, COT is one of the compounds of most fascination not only for organic synthesis and organometallic chemistry, but also for theoretical chemistry as well.

As mentioned above, unlike benzene, COT is a non-planar but tub-shaped molecule having the D_{2d} conformation which is more stable than the planar D_{4h} and the delocalized D_{8h}. In this molecule there exists a persistent dynamic equilibrium both for the ring inversion and the bond shift. The D_{8h} delocalized structure is considered as the crucial pathway for these fluxional changes (Scheme 1).[3c]

Under different conditions COT **1** is also able to undergo tautomerization and give its valence isomers. For example, *via* the intramolecular Diels–Alder reaction, COT can transform into bicyclo[4,2,0]octa-2,4,7-triene **2**; while by photolysis it will then change into another tautomer, semibullvalene **3** (SBV). All of these isomers are less stable than COT due to their highly strained structures. Thus these compounds are readily rearranged back into COT itself (Scheme 2).[3c]

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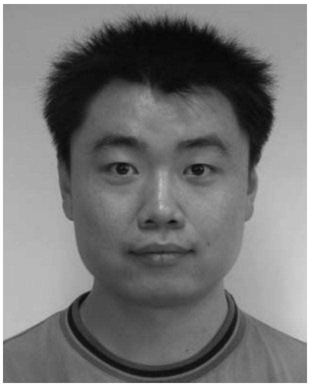
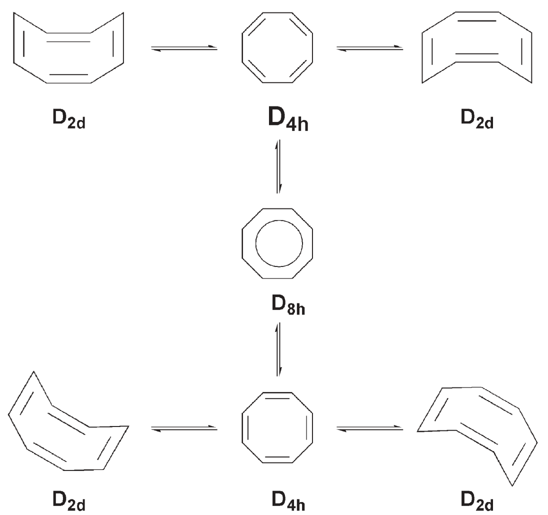


Chao Wang

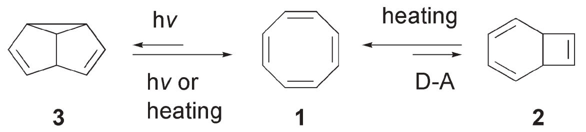
Chao Wang was born in Shaanxi province, China in 1981. He began his study on chemistry in Peking University (Beijing, China) since 1998 and received his BS degree in 2002. In the same year and the same university he joined Professor Zhenfeng Xi's group as a graduate student with the research topic of "development of new reactions of bismetallic reagents". He has received several awards during his PhD courses including "Roche Creative Chemistry Award" in 2006. He obtained his PhD degree in June 2007 and is currently a postdoctoral fellow in Professor Ei-ichi Negishi's group in Purdue University. His research interests include organic synthesis and development of synthetic methods using organometallic compounds.

Zhenfeng Xi

Zhenfeng Xi was born in 1963 in Henan Province, China. He received his BS degree from Xiamen University in 1983, and his MS degree from Nanjing University, Zhengzhou University and the Henan Institute of Chemistry in 1989. He joined Professor Tamotsu Takahashi's group at the Institute for Molecular Sciences, Japan, as a PhD course student in 1993 and obtained a PhD degree in 1996. He took an Assistant Professor position at Hokkaido University, Japan, in 1997, after he worked as a postdoctoral research fellow with Professor Takahashi at CRC. In 1998, he joined the College of Chemistry at Peking University, where he is now a Professor. He received several awards including Outstanding Young Investigator award from Qiu Shi Science & Technologies Foundation in 2000 and Yaozeng Huang Organometallic Chemistry Award in 2004. He has been the holder of Cheung Kong Professorship since 2002. Professor Xi's research interests include development of synthetic methodologies based on selective cleavage of C–H, C–C and C–X bonds mediated by organometallic compounds, development of organometallic reagents, study on mechanisms of reactions involving reactive organometallic intermediates, and synthesis of functional structures.



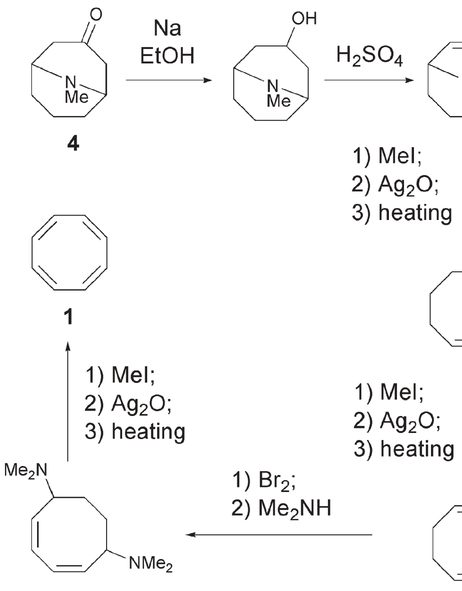
Scheme 1



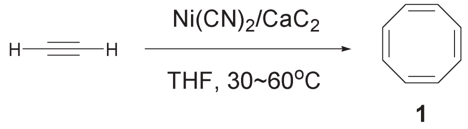
Scheme 2

The first synthesis of COT was described by Willstätter and co-workers in 1911. This is a multi-step transformation starting with pseudo-pelletierine **4**.[4] An extensive series of Hoffmann eliminations were used to form the double bonds and only a small amount of COT was finally obtained (Scheme 3).

A practically useful approach for synthesis of COT was reported by Reppe *et al.* in 1948, which is a one-step procedure from easily available ethyne with a $Ni(CN)_2/CaC_2$ precatalyst in THF at 30–60 °C (Scheme 4).[5] This pioneering synthetic method for the eight-membered carbocycle allowed COT to become one of the mass commercially available chemicals, which was in fact inaccessible by conventional routes at that time.



Scheme 3



Scheme 4

During the following decades after Reppe's invention, metal-mediated protocols have gradually taken the dominating position among various preparative methods for COT. This article is a mini-review on development of the scopes of metal-mediated synthesis of COT. Some valence isomers of COT, which are closely related to this topic, will be also briefly introduced. Much effort has been focused on transition metal mediated reaction patterns, mechanisms, and structural diversity of products.

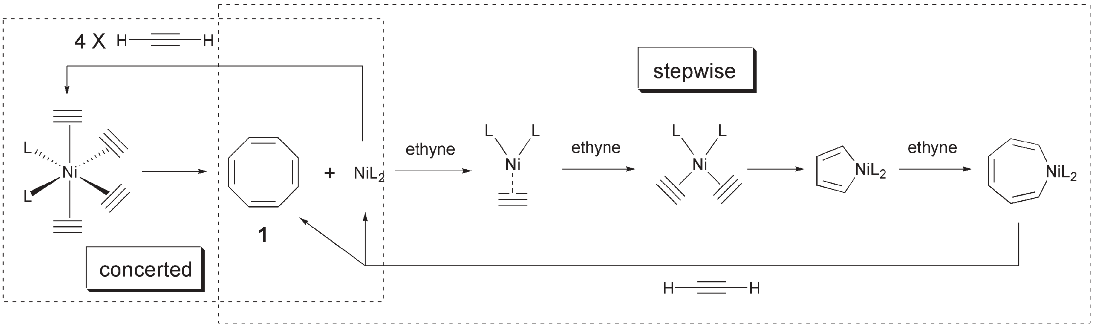
2 Ni-mediated synthesis of COT

2.1 Mechanistic aspects of the Reppe reaction

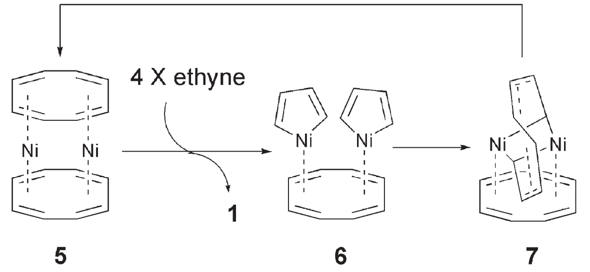
Although more than half a century has passed since Reppe *et al.* reported their results, the mechanism of this synthetically useful reaction has remained an unsolved puzzle for organic and organometallic chemists. Numerous studies of the mechanism of this reaction have been carried out. The simplest mechanism to envision, postulated by Schrauzer *et al.*,[6] is a concerted one in which all four ethyne molecules simultaneously bind to the nickel atom forming a pseudo-octahedral nickel complex before the coupling occurs. Another plausible pathway is characterized as stepwise coupling.[5,7] According to this speculation, alkynes enter the catalytic cycle and interact with the metal center at different steps. Scheme 5 shows these two processes. From the view nowadays, these two supposed mechanisms are quite simplified modes, somewhat analogous to the real reaction route. Thereby more complicated versions of mechanisms are successively drawn and investigated.

Besides the above two mechanisms, there are still other types suggesting that the mechanism may be involved with a carbon–carbon bond cleavage. For example, COT might be formed through the insertion of alkynes into cyclobutadiene or benzene intermediates.[5,8] However, the last conclusion was excluded by Colborn and Vollhardt when they utilized ^{13}C-labeling ethyne as a substrate for the catalytic systems of either nickel acetylacetonate–calcium carbide or nickel acetylacetonate–diethylaluminum ethoxide.[5] Both results show that the dicarbon fragment of ethyne remains intact in the product. This pattern is consistent with either a stepwise coupling or concerted mechanism and the possibility of any carbon–carbon bond cleavage processes may thus be ruled out.

Wilke proposed an attractive mechanism for the catalytic generation of COT,[9] reporting the high activity and selectivity of dinuclear sandwich-like compound **5** as active species in the catalytic cycle. Two pairs of acetylene molecules undergo oxidative cyclization on two nickel centers, releasing a COT ligand and forming the nickelacyclopentadiene **6**, in which two



Scheme 5



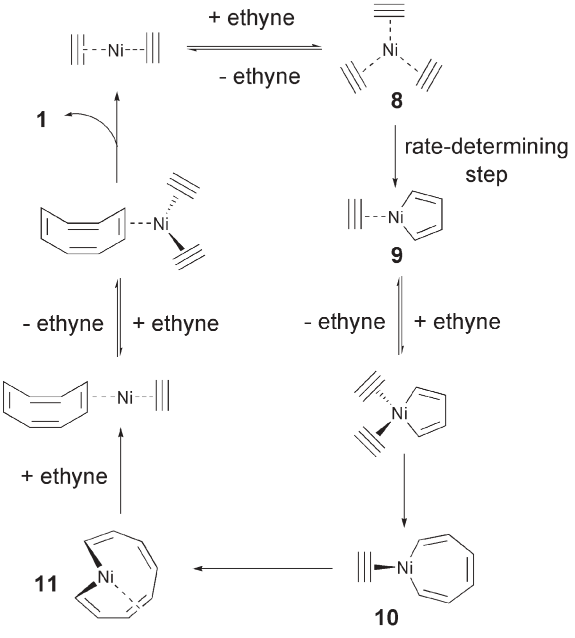
Scheme 6

metallacycles are very close to each other bridged by a COT ligand. These two metallacycles are subsequently coupled together *via* a twisted intermediate **7** to give a new COT ring (Scheme 6).

Straub and Gollub proposed a complete stepwise–insertion catalytic cycle for the nickel-catalyzed ethyne tetramerization to COT *via* a quantum-chemical gas-phase model study.[10] In this predication, the catalyst resting state of nickel-catalyzed ethyne tetramerization is a homoleptic ethyne Ni(0) complex **8**, in which ethyne ligand coupled to form the monoethyne nickelacyclopentadiene **9** as the rate-determining step. Rapid coordination and insertion of ethyne are followed thereafter, giving monoethyne *trans*-nickelacycloheptatriene **10**. This *trans*-intermediate is unable to undergo reductive elimination before tautomerizing into a highly strained nickelacyclononatetraene **11** which can then eliminate COT induced by coordinating an additional two molecules of ethyne. Finally, the catalyst is regenerated by liberating COT (Scheme 7).

2.2 Development of Ni-mediated synthesis of COT

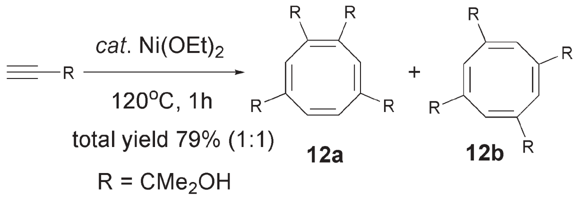
The Reppe reaction is very successful for ethyne oligomerization into unsubstituted parent COT. Mono-substituted alkyne are also readily tetramerized catalyzed by either Ni(0) or Ni(II) systems, making some functionalized COT, however, the regio- and chemo-selectivity are very low and different tetrasubstituted isomers are always obtained as a mixture, together with the trimerized and polymerized products (benzene and polyene).[11] For example, when propargylic alcohol is used with $Ni(OEt)_2$, two isomers including 1,2,4,7-COT **12a** (1,2,4,7-tetrasubstituted-COT, similarly hereinafter) and 1,3,5,7-COT **12b** are both formed in 1 : 1 ratio (Scheme 8),[12] while ethyl propiolate provides two isomers of COT, **12c** and **12d**, and two trisubstituted benzenes, **13a** and **13b**, when treated with $Ni(PCl_3)_4$ (Scheme 9).[13]



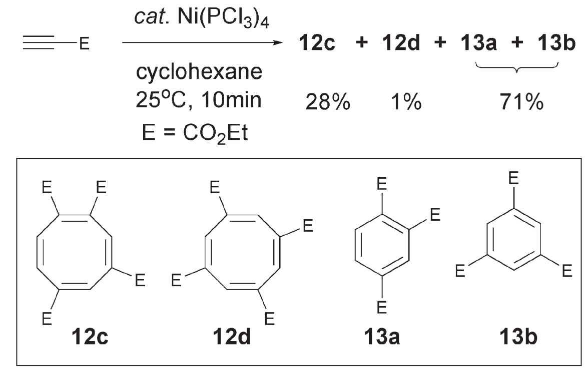
Scheme 7

In some cases the reaction can proceed selectively and one isomer then becomes the only or predominant product, depending on substituents of alkynes and the catalyst used, which remain hard to explain and predict. For example, unlike the ethyl analog, the methyl propiolate can tetramerize into 1,2,4,6-COT **12e** as the main product in 83% yield together with a small amount of **13c** (Scheme 10).[13]

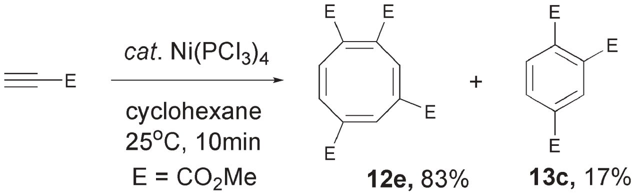
Tom Dieck and co-workers have reported the adoption of a series of diazadiene (dad)–Ni(0) compounds **14a–c** (Fig. 1) in alkyne tetramerization.[14] These Ni–dad catalytic systems show



Scheme 8

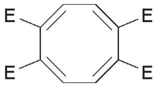
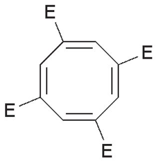
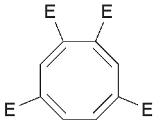


Scheme 9

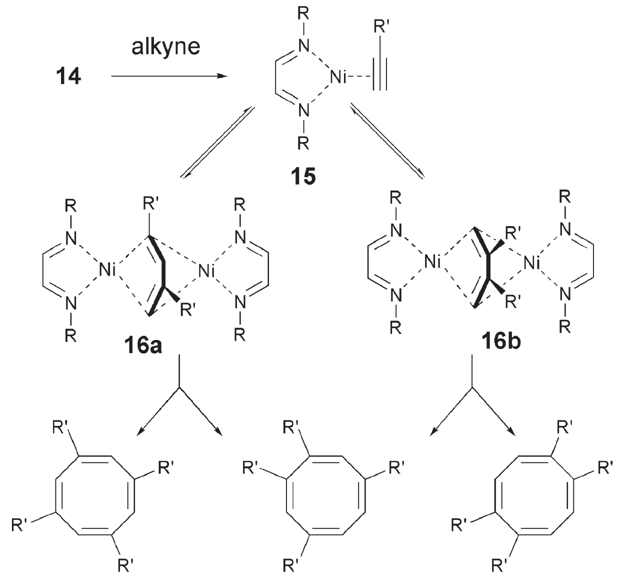


Scheme 10

Table 1

≡—E	COT	method
E = *p*-TolylOCH$_2$	**12f** 	*A*
E = CH$_2$OH	**12g** 	*B*
E = CO$_2$Me	**12h** 	*C*

A: **14a** [R = CH(*i*-Pr)$_2$], cyclohexane, 50 °C, 24 h, 45%. *B*: **14a** [R = CH(*i*-Pr)$_2$], THF, 0 °C, 24 h, 100% conversion, constitutes 70% of the tetramer fractions. *C*: **14b** [R = 2, 6-(*i*-Pr)$_2$C$_6$H$_3$, R′ = CO$_2$Me], cyclohexane, 10 °C, 24 h, 95%.



Scheme 11

different regio-selectivity according to alkynes used. When propargyl *p*-tolyl ether is treated with **14a** [R = CH(*i*-Pr)$_2$], a sole product 1,4,5,8-COT **12f** can be obtained in 45% yield,[14a] whilst propargylic alcohol reacted with the same catalyst to afford 1,3,5,7-COT **12g** as a major product.[14b] In the third case, almost only 1,3,6,8-COT **12h** was formed as a result of oligomerization of propiolate catalyzed by **14b** [R = 2,6-(*i*-Pr)$_2$C$_6$H$_3$, R′ = CO$_2$Me].[14b] These results are listed in Table 1.

A reasonable explanation has been brought forward for these notable dissimilarities. Tom Dieck assumed for this terminal-alkyne-involved Reppe reaction a stepwise mechanism which is similar to that of ethyne.[14b] Initially one molecule of alkyne coordinates to the metal center and forms the mononuclear complex **15** as the first intermediate which is then in equilibrium with dinuclear butadienylmetal **16** complexes as a result of dimerizations of alkynes *via* diverse combinations. The major intermediate **16** varies under different reaction conditions and thus account for the corresponding substituted isomers of COT (Scheme 11).

Interestingly when propargyl methyl ether reacts with compounds **14b** [R = 2,6-(i-Pr)$_2$C$_6$H$_3$], the above mentioned intermediate, **16b** (R = 2,6-(i-Pr)$_2$C$_6$H$_3$, R′ = CO$_2$Me), is obtained and also characterized by X-ray diffraction analysis.[14d] This alluring observation convincingly supports tom Dieck's assumption, not only suggesting that formation of **16** is indeed an elementary step for this reaction, but also indicating that the diene moiety of **16** may be the starting point for the uncertain and mutative selectivity in these reactions.

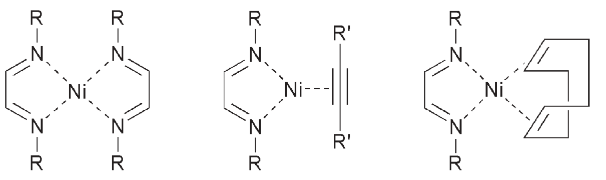
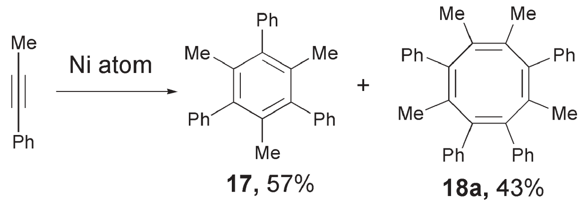
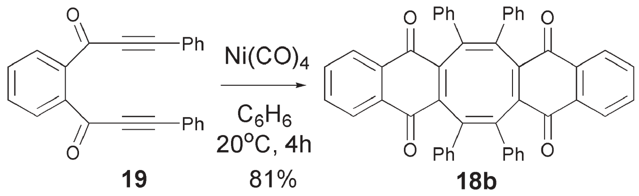


Fig. 1

Internal alkynes generally can not be cyclotetramerized with typical Ni catalysts for ethyne and terminal alkynes.[15] For example, **14b** is just formed by treating Ni(dad)$_2$(CO)$_2$ with disubstituted alkyne which cannot be further oligomerized.[14b] However, a method developed by Cope *et al.* allows these disubstituted acetylenes to react together with acetylene itself to produce incompletely-substituted COTs.[16] An alternative pathway for oligomerization of 1-phenyl-1-propyne into hexa-substituted benzene **17** and octa-substituted COT **18a** is using Ni atoms from vapor deposition as active catalyst



Scheme 12

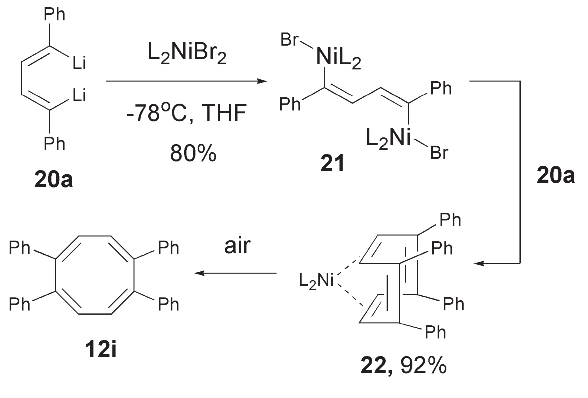


Scheme 13

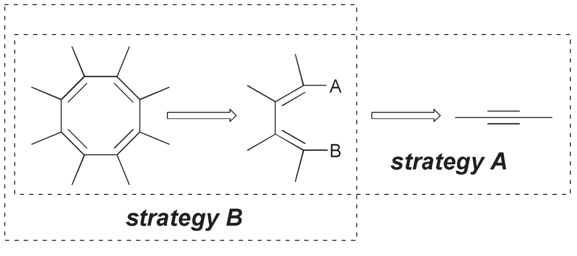
(Scheme 12).[17] Besides, intramolecular synthesis of COT **18b** has also been reported employing diyne **19** to undergo dimerization by catalysis of Ni(CO)$_4$ (Scheme 13).[18]

2.3 Other types of Ni-mediated synthesis of COT

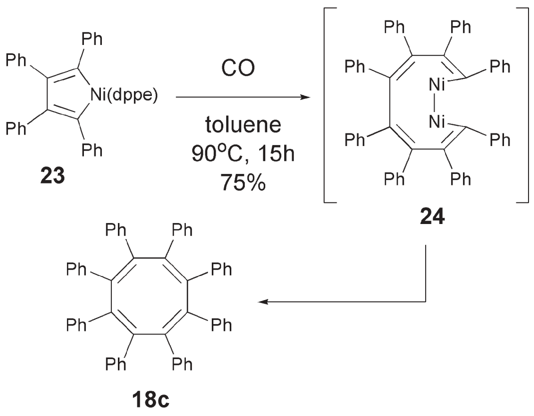
A selective method affording only one isomer was reported by Carpenter and co-workers using *in situ* generated Ni–diene complexes.[19] Treating Ni(PEt$_3$)$_2$Br$_2$ with 1,4-dilithio-1,4-diphenyl-1,3-butadiene **20a** afforded the dinuclear complex **21**, which can again react with **20a** to yield COT–Ni complex **22** nearly quantitatively. The compound **22** slowly decomposed and rearranged to 1,4,5,8-COT **12i** (Scheme 14). Compared with the strategy involving direct tetramerization of alkynes (Scheme 15, *strategy A*), this strategy applying diene units (Scheme 15, *strategy B*) could generate COT derivatives with high selectivity.



Scheme 14



Scheme 15



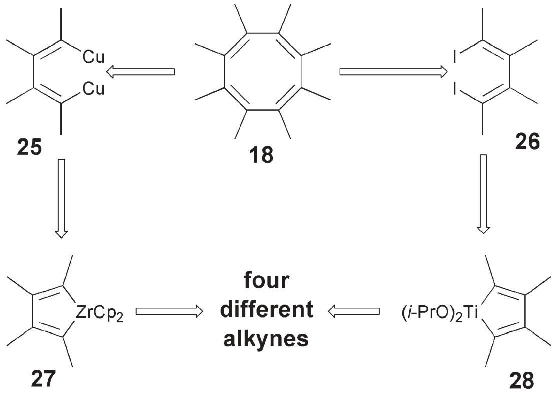
Scheme 16

Nickelacyclopentadienes, which can be easily prepared from dilithiodienes or aluminacycles,[20] also contain the diene moiety and can be transformed into COTs when raising the temperature. For example when **23** was heated in toluene under the CO atmosphere, octaphenyl-COT **18c** was obtained in good yield. The Ni–cyclobutadiene **24** was proposed as the crucial intermediate in this process (Scheme 16).[20a]

3 Cu-mediated synthesis of COT

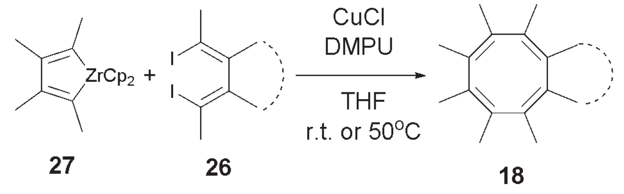
3.1 Cross-coupling between organocuprates and halides

The above illustrated strategy employing diene synthons can also be applied in systems including metals beyond nickel. Yamamoto *et al.* reported Cu-mediated selective synthesis of COT by [4 + 4] coupling between two different diene units, 1,4-dicupra-1,3-butadienes **25** and 1,4-diiodo-1,3-butadienes **26** (Scheme 17).[21] It is well known that coupling of organocuprates with alkenyl halides is a fundamental protocol for synthesis of olefins. Of the two diene units mentioned above, the 1,4-dicupra-1,3-butadienes **25** can be prepared *in situ* by transmetallation of their corresponding zirconacyclopentadienes **27** with CuCl as reported by Takahashi *et al.*,[22] and the diiodides **26** can readily be obtained from iodization of their corresponding zirconacyclopentadienes **27**[23] or titanacyclopentadienes **28**.[24]



Scheme 17

Table 2



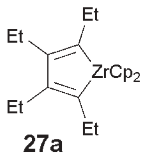
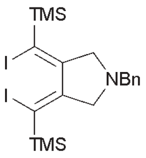
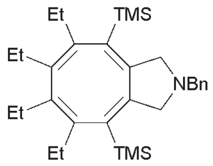
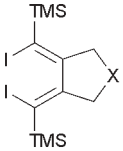
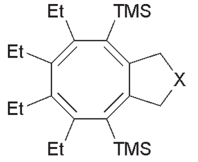
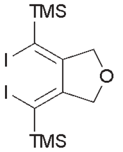
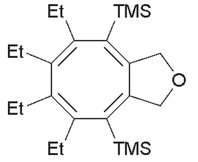
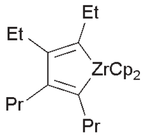
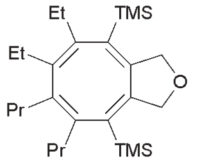
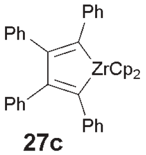
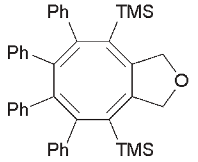
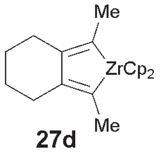
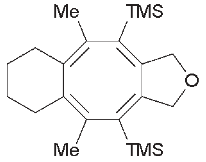
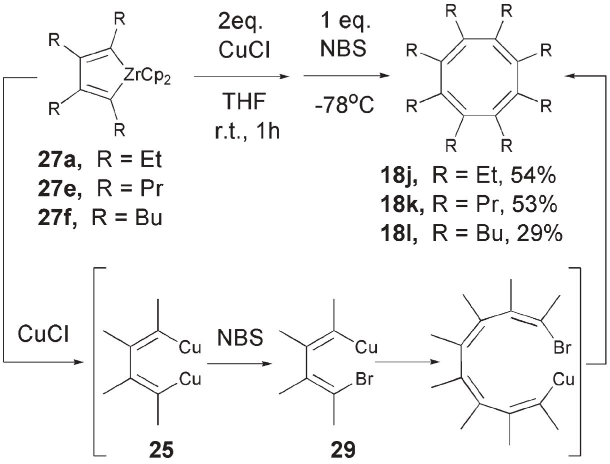
 **27a**	 **26a**		**18d** 84%
27a	 **26b**		**18e** 65%
27a	 **26c**		**18f** 88%
 **27b**	**26c**		**18g** 79%
 **27c**	**26c**		**18h** 56%
 **27d**	**26c**		**18i** 52%

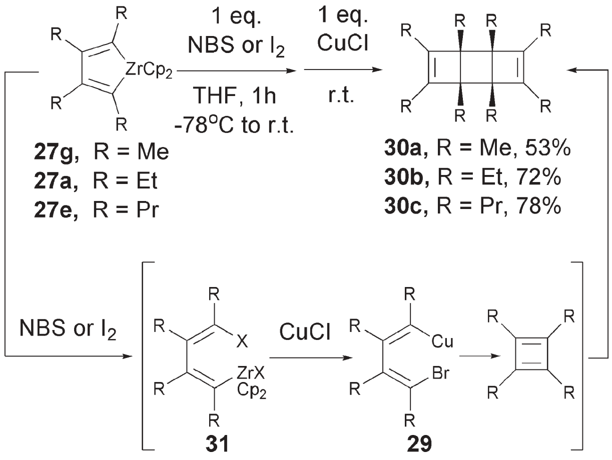
Table 2 shows some results obtained from reactions of diiodobutadiene **26** and zirconacyclopentadienes **27** in the presence of CuCl and DMPU. A wide variety of zirconacyclopentadienes **27** could be used. However, on the contrary, only those diiodobutadienes **26** with cyclic structures could undergo this reaction affording their corresponding COT derivatives. No reaction was observed when linear 1,4-diiodo-1,3-butadienes **26** were used. These results suggested that the *s-cis* conformation of **26** might be more favored for the above reaction, probably due to the bulky iodine atoms.

This disadvantage was conquered by Takahashi *et al.*[25] They reported an efficient method using cupriohalodiene **29** *via* mono halogenation of dicupriodiene **25** instead of the two different dimetallic and dihalo diene units and thus acyclic substituents can be also applied (Scheme 18). When CuCl was added to zirconacyclopentadiene **26**, dicupreousdiene **25** was then formed. With NBS at −78 °C, monobromination of **25** gave bromocupreousdiene **29** which underwent dimerization forming the desired octa-substituted COT **18**.



Scheme 18

What is more interesting is that temperature plays a role of switch for the reactivity. As depicted above, when the reaction was carried out at a low temperature such as −78 °C, COT was the main product. However if it was treated at relatively higher temperature like room temperature stereo-defined tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene derivative **30** (TCOD), which is an isomer of COT was generated in high yields (Scheme 19).[26] On this basis a brief mechanism is illustrated as the releasing and dimerization of cyclobutadiene afforded by intramolecular coupling of bromocupriodiene **29** which is transformed from dienyl zirconium intermediate **31**. The rate of this intramolecular coupling may decrease at low temperature, probably because the steric repulsion of copper and bromine atoms in the *s-cis* conformation. When the temperature rises, the steric resistance above may be overcome and thus the coupling rate would increase greatly. The cyclobutadiene is unstable and is quickly dimerized into the final



Scheme 19

product. Molecules such as TCOD **30** are highly strained and readily rearrange into COT when heated. So this reaction is also a good preparative method for COT as well as TCOD.

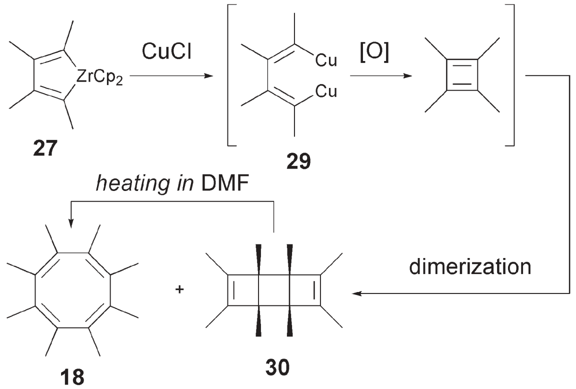
3.2 Homo-coupling of organocuprates

After the discovery that oxidants can greatly facilitate the coupling of ligands on the oganocuprates,[27] creation of carbon–carbon bonds by this type of homo-coupling of organocuprates has been very useful including the formation of medium rings, diene synthesis and the coupling of tertiary carbon centres.[28]

Beside the treatment of dicupriodiene with halogenation reagents such as NBS, Xi and co-workers reported the formation of COT by homo-coupling of dicupriodiene mediated by oxidants such as quinone.[29] When zirconacyclopentadienes **27** were treated with CuCl and benzoquinone, tricyclic compounds **30** were determined in a constant ratio with COT products **18** (Scheme 20). When heated in DMF, products **30** could change to **18** quantitatively (Table 3). Obviously TCOD **30** is a product of dimerization of cyclobutadiene by way of the mechanism similar to Scheme 19. The function of benzoquinone is to facilitate the intramolecular homo-coupling of the **29** forming a cyclobutadiene intermediate with the release of copper. Dicupriodienes here can be prepared also by transmetallation of 1,4-dilithio-1,3-butadiene reagents.

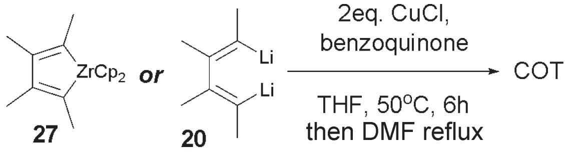
Interestingly, when zirconaindenes such as **27k** and **27m** were used instead, the result was rather different from those obtained by using structurally similar dilithiobutadiene **20b**. 5,6,6a,10b-Tetraethyl-6a,10b-dihydrobenzo[*a*]biphenylene **31** is observed as the only product in reasonable yield (Scheme 21).[30] This polycyclic compound **31** can also undergo thermo-rearrangement converting totally into dibenzosemibullvalenes **32** which are another type of isomers of COT mentioned above. A mechanism is supposed for the formation of **31** as the result of tautomerization of the proposed intermediate benzo-TCOD **30**. Quinone here is considered as an oxidant because some reductive products such as naphthalene-1,4-diol were detected.

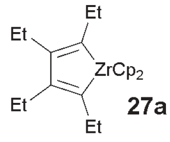
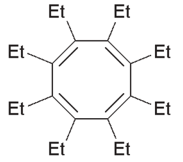
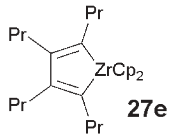
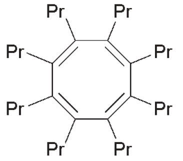
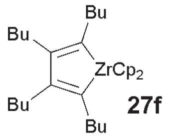
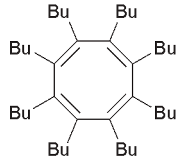
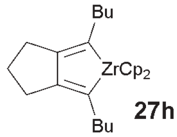
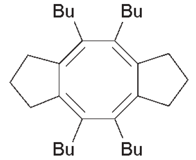
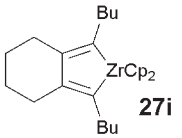
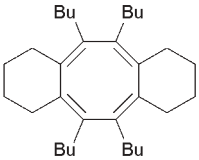
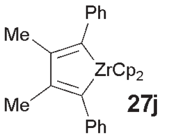
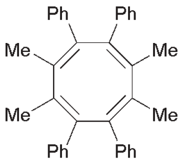
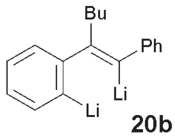
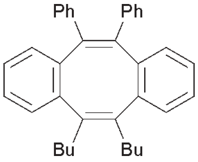
Dicupriodiene **29** can also be made from dilithiodiene **20**, which is one of the organo-bimetallic reagents extensively investigated in our group.[31,32] Organo-bimetallic reagents containing dienyl skeletons such as dilithiodiene, bis(bromomagnesio)diene, *etc* have shown different reaction patterns with various organic substrates compared to those of normal organometallic reagents. As part of the project of this group, research on reactivity of dicupriodiene is in process. Generally, there are three types of dicupriodienes **29** compared with their corresponding dilithiodienes **20**. According to the reactivity of dicupriodiene introduced above, multi-substituted COT **18** could be the expected product if it was utilized in homo-coupling (Scheme 22).



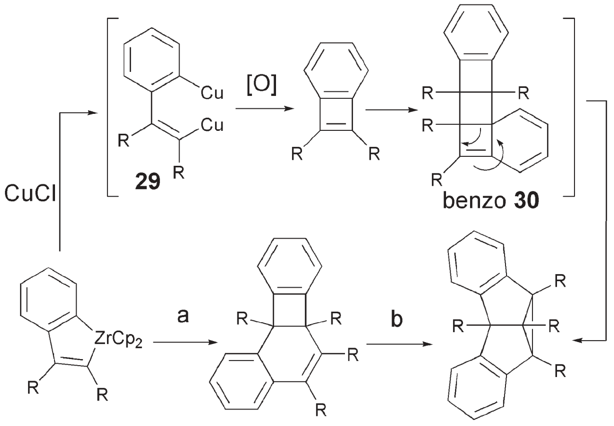
Scheme 20

Table 3



Dicupriodiene precursor	COT		yield (%) *
 27a		18j	73 (51)
 27e		18k	68 (56)
 27f		18l	40 (23)
 27h		18m	(43)
 27i		18n	(40)
 27j		18o	(33)
 20b		18p	(38)

[a] GC yields. Isolated yields are given in parentheses.



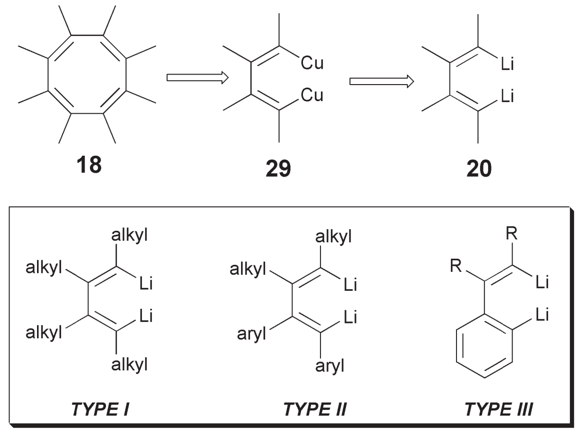
27k, R = Et
27l, R = Pr
27m, R = Bu

31a, R = Et, 62%
31b, R = Pr, 65%
31c, R = Bu, 58%

32a, R = Et
32b, R = Pr
32c, R = Bu

a: 1 eq. 1,4-naphthoquinone, 2 eq. CuCl, THF, r.t., 12h
b: DMF, reflux, 6h, 100%

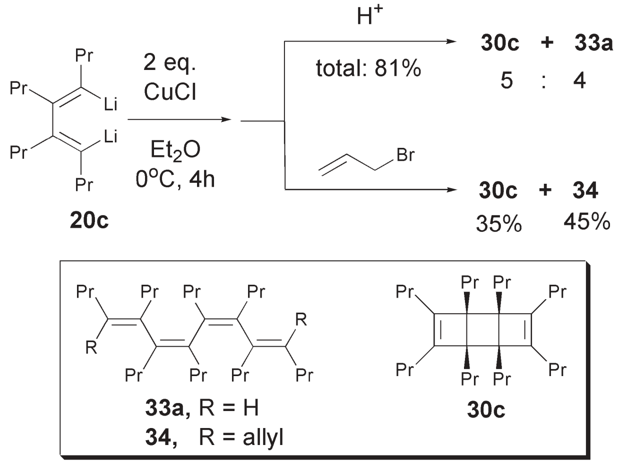
Scheme 21



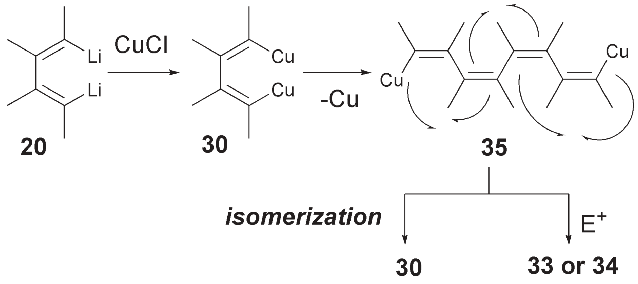
Scheme 22

It was surprising that when adding CuCl to tetrapropyldilithiodienes (Type I in Scheme 22) **20c** in diethyl ether without any other additives, mixtures of TCOD **30** and 1,3,5,7-octatetraene derivatives **33** were obtained with a fixed ratio (Scheme 23).[33] Adding allyl bromide into this reaction system, bisallylated product **34** was obtained, implying two carbon–copper bonds exist before quenching. Use of dicupriodienes prepared from zirconacyclopentadienes gave only unknown mixtures under the same or similar conditions. These experimental data suggested that the two types of dicupriodienes **30** might have different reactivity probably due to their different compositions. Capture of **33** indicates that formation of TCOD in this case may have a different mechanism compared with the above-mentioned case (Scheme 19 and 20), probably *via* radical cyclization of intermediate **35** (Scheme 24).[33b]

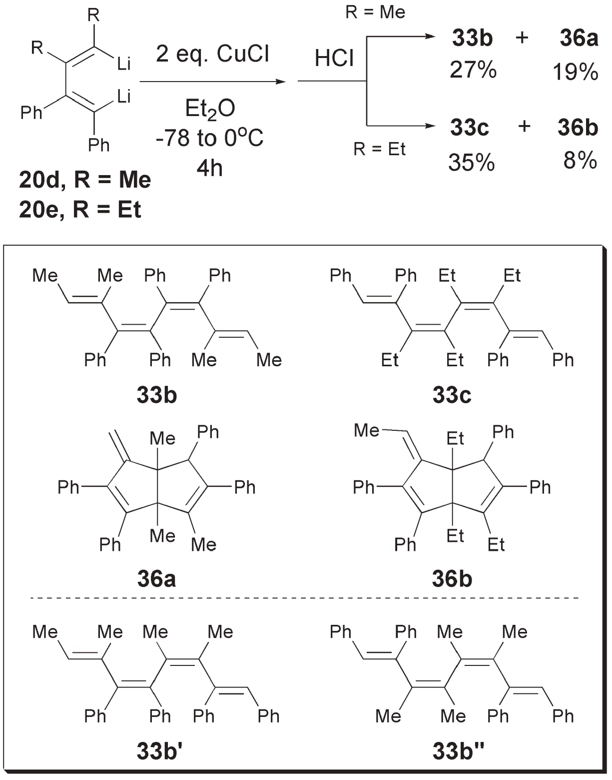
More interestingly, when dilithiodienes with phenyl groups (Type II in Scheme 22) such as **20d** and **20e** were used in diethyl ether solvent, in addition to octatetraene **33**, two different stereodefined cyclic isomers of COT, pentalene **36** (Scheme 25)



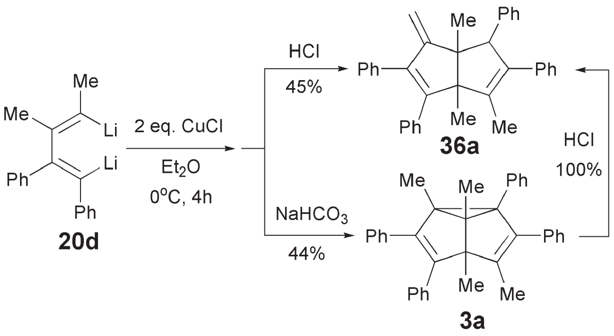
Scheme 23



Scheme 24



Scheme 25

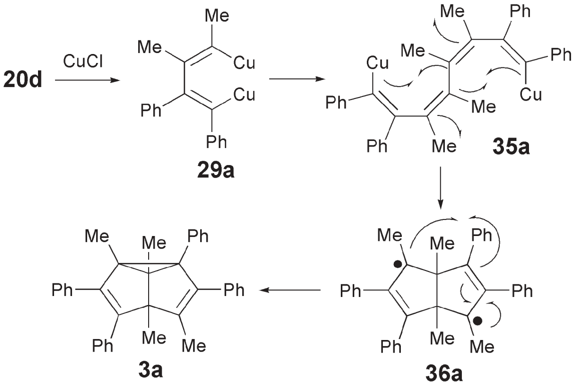


Scheme 26

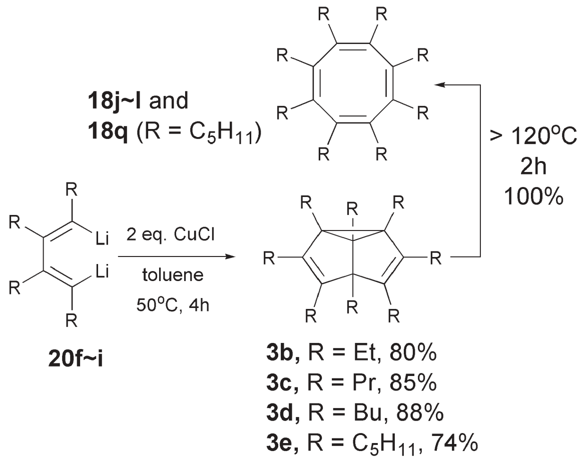
and SBV **3** (Scheme 26, and the mechanism is shown in Scheme 27), were also observed according to quenching conditions.[33,34] Under specific conditions the cyclic products **3** or **36** could be the only one in reasonable yields (Scheme 26).[34] SBV **3** could be easily transformed to **36** in an acidic system. Noticeably, **33** was formed selectively. For example, in case of **20d**, neither **33b′** nor **33b″** was obtained among the three proposed isomers.

In these dimerizations of dilithiodiene **20** with CuCl, the formation of intermediate **35** is a very important step. Probably because of the coordination of ether to copper, the activity of **35** may be lowered and thus remained as octatetraene **33** after being quenched. Based upon this speculation, solvents with less coordinative ability were expected to change the situation.

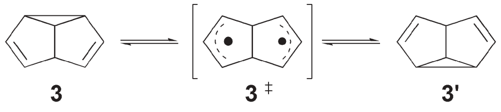
When tetraalkyldilithiodienes **20** were used in toluene with CuCl, exciting results were obtained: only octaalkyl-SBVs **3** were obtained as the only products in excellent yields (Scheme 28).[34] Like most cases of SBV (Scheme 2), octaalkyl derivatives such as **3b** and **3e** could undergo thermo-isomerization to give their corresponding octaalkyl COT **18** in quantitative yields. Therefore, this reaction is also a good preparative method for COT in addition to SBV.



Scheme 27



Scheme 28

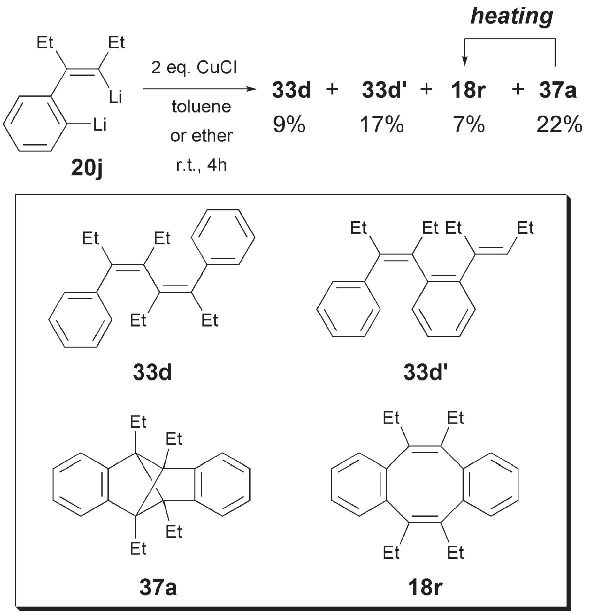


Scheme 29

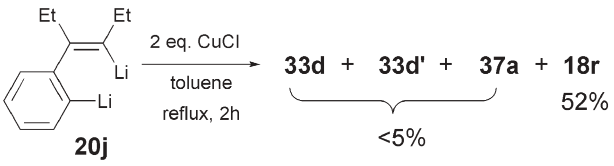
The product in the above reactions, semibullvalene, is one of the most important isomers of COT. Since Zimmerman and others reported the synthesis of semibullvalene in 1966,[35] great interest has been continuously paid to the synthetic methods and skeletal rearrangement studies of this type of strained ring systems. SBV demonstrates the extremely rapid degenerate Cope rearrangement (Scheme 29), which has long been of great interest on both theoretical and experimental investigations.[36] The relatively complicated multicyclic structure with strained ring has increased the synthetic difficulty and thus practical synthetic methods are always needed. Early syntheses of SBV employing photolysis of COT and its isomers, except for a few cases,[37] were essentially useless for the synthetic scale due to a large amount of by-products. Current multi-step synthesis contains a long route often lowering the total efficiency. Contrastively this synthesis protocol *via* CuCl mediated dimerization of dilithio reagent, namely a two-step synthesis with a very common starting material (the diiodide can be prepared from alkyne in one step) is highly efficient. To the best of our knowledge, it is the first synthesis of semibullvalenes using the metal-mediated C–C bond forming approach in a short process.

When styrene-skeleton-containing dilithiodienes (Type III in Scheme 22) **20j** was treated with CuCl either in ether or toluene, no semibullvalenes were detected but another type of isomers of COT, dibenzotricycle[3.3.0.0^{2,6}]-1,2,5,6-tetra-alkyloctanes **37a**, appeared with dibenzo-COT **18r** and some linear-structural products **33d** and **33d′** (Scheme 30).[38] Like semibullvalenes, **37a** could also convert clearly into more stable **18r** if heated in toluene. Colligating these two reactions by treating dicupriodiene in refluxing toluene afforded **18r** as the dominating major product with only trace amounts of other products (Scheme 31). According to the proposed mechanism (Scheme 32), high temperature not only helped the tautomerization but also promoted the transformation from linear intermediate **35** to cyclic final products.[33a]

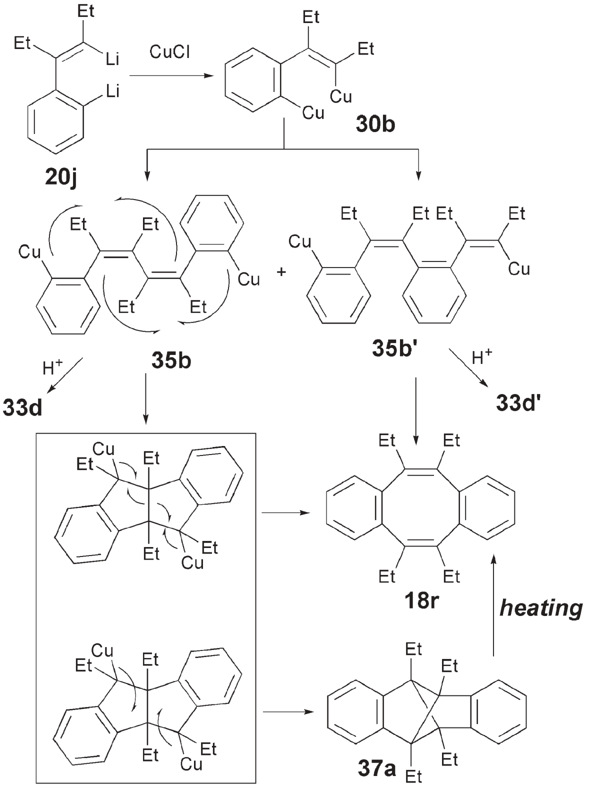
Tricyclo[3.3.0.0^{2,6}]octadienes such as **37a** is also a significant member of COT valence isomers and has attracted much attention due to its special structure with highly strained ring system. Compounds of this type have been looked upon as intermediates of the skeletal rearrangement of disubstituted dibenzo-COT since Stiles and Burckhardt reported the novel



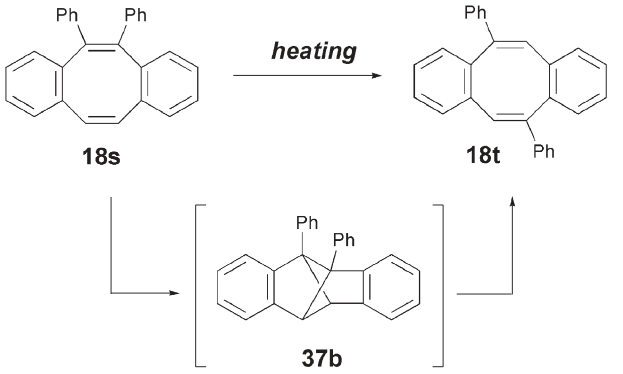
Scheme 30



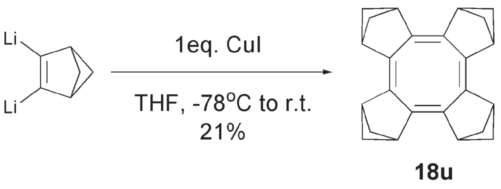
Scheme 31



Scheme 32



Scheme 33



Scheme 34

reaction in 1964.[39] For example, **37b** was assumed as a key intermediate of the isomerization of dibenzo-COT **18s** to **18t** (Scheme 33). During years thereafter, compounds such as this pivotal intermediate have never been successfully prepared until our example of **37a**.

Matsuura and Komatsu reported an intriguing instance of synthesis of COT **18u** by tetramerizing homo-coupling of 1,2-dilithioethene with CuI (Scheme 34).[40] The product **18u** is quite different because it shows a rare planar structure which has been confirmed by X-ray diffraction analysis, while other COTs, as mentioned in the first part of this review, are always non-planar and tub-shaped.

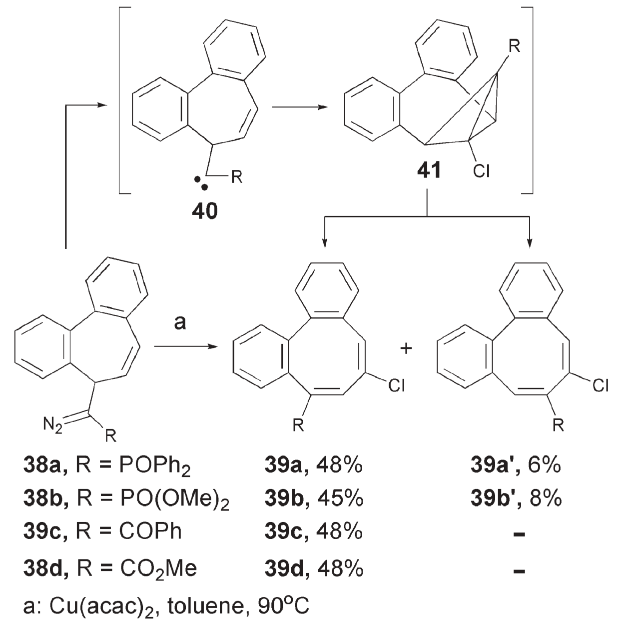
3.3 Rearrangement of diazo compounds

Metal mediated decomposition of diazo compounds has become a powerful tool in organic synthesis. Use of this implement for preparation of COT was reported by Regitz. When diazo reagents **38** were heated in toluene with a catalytic amount of $Cu(acac)_2$, a pair of COT isomers **39** and **39′** could be generated, with isomer **39** as the major in most cases. The possible mechanism is reckoned as a ring enlargement of intermediate **41** formed *via* intramolecular cyclopropanation (Scheme 35).[41]

4 Synthesis of COT *via* Cr-mediated cycloaddition

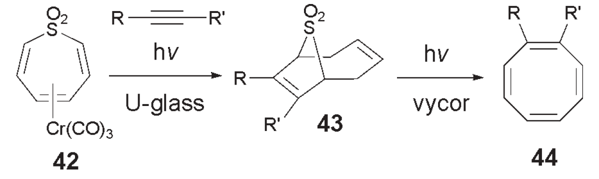
Metal-promoted [6 + 2] cycloaddition is a valuable method for synthesis of eight-membered ring. Rigby and Warshakoon have reported a convenient synthesis of 1,2-disubstituted COT derivatives in two steps employing a Cr(0)-promoted [6*n* + 2*n*] thiepin dioxide–alkyne cycloaddition followed by photo-activated sulfur dioxide extrusion.

As listed in Table 4, different alkynes react very smoothly providing the COT products. COT with cyclic substituent or bridged COT is also available *via* this way.[42]



Scheme 35

Table 4



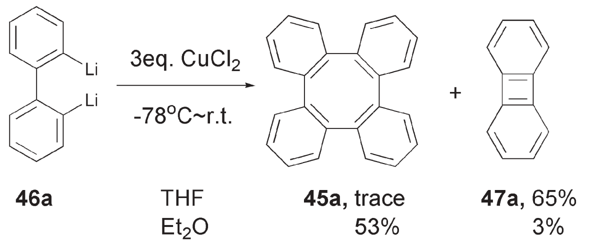
R	R′	**43** (yield, %)	**44** (yield, %)
Me	TMS	**43a**, 65	**44a**, 95
Pr	TMS	**43b**, 41	**44b**, 90
Bu	TMS	**43c**, 65	**44c**, 95
Ph	TMS	**43d**, 78	**44d**, 90
Ph	Et	**43e**, 42	**44e**, 85
–$(CH_2)_6$–		**43f**, 35	**44f**, 85

5 Synthesis of tetraphenylene mediated by transition metals (Cu, Zn, Ni, Pd, Pt)

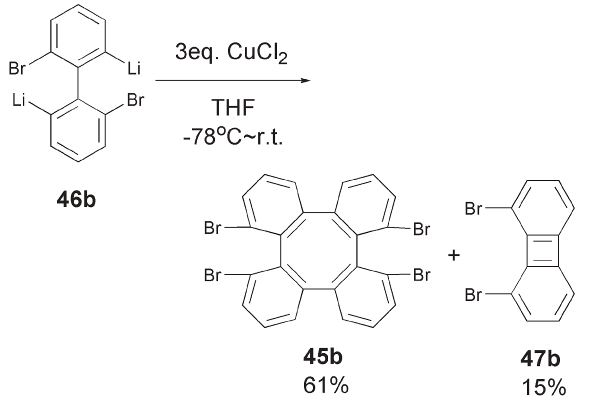
Tetraphenylene (TPL) **45** is one type of interesting and attractive derivatives of COT, not only due to forming clathrate inclusion compounds with a wide variety of guest species, but also by virtue of exhibiting particular electronic properties.[43] Based on the importance and specific of this COT individual, this article will take the following special section reviewing its well-investigated synthetic methods.

5.1 Homo-coupling of biaryl metal compounds mediated by Cu, Pd and Ni

Since Rapson *et al.* reported the first synthesis of TPL **45a** by $CuCl_2$ mediated dimerization of 2,2-dilithiobiphenyl **46a**,[44] this homo-coupling reaction mode has been widely studied and all along been the principal preparative method for this compound. Besides TPL as the major products, always there is a minor amount of biphenylene **47** observed simultaneously. The selectivity between TPL and biphenylene is not constant and changes dramatically depending on different factors during the whole reaction process. One remarkable effect comes from the solvent displaying a distinct role (Scheme 36). These results suggest that THF is favored for biphenylene synthesis,[45] whereas Et_2O is favoured for TPL synthesis.[46a] Substituents on the reactants also influence the reaction. For example, the dilithio derivative of 2,2′,6,6′-tetrabromobiphenyl **46b** gave TPL **45b** as main product instead of **47b**, even in THF, contrasting sharply to the unsubstituted **45a** (Scheme 37).[46b]



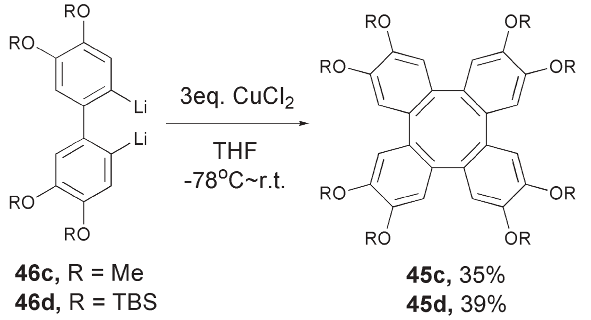
Scheme 36



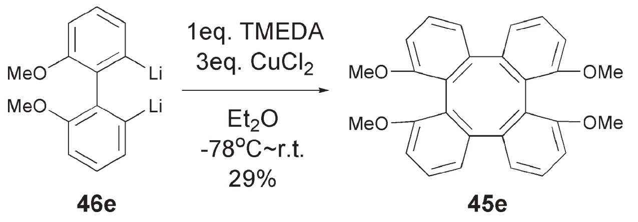
Scheme 37

The effect of substituents and solvents on the selectivity is also exhibited in some recent examples about synthesis of functionalized TPL *via* this protocol. Reactions of those dilithiobiaryls **46c–f** containing alkoxy groups seem disposed to form TPL in either THF (Scheme 38)[46b] or Et_2O solvent (Scheme 39 and 40).[47] The alkoxy groups on these molecules can easily go through further transformations under different conditions.

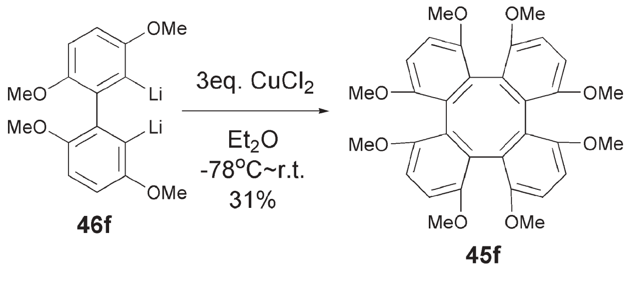
Rajca *et al.* reported an asymmetric synthesis of substituted TPL by using (−)-sparteine and $CuBr_2$ mediated coupling.[48]



Scheme 38



Scheme 39

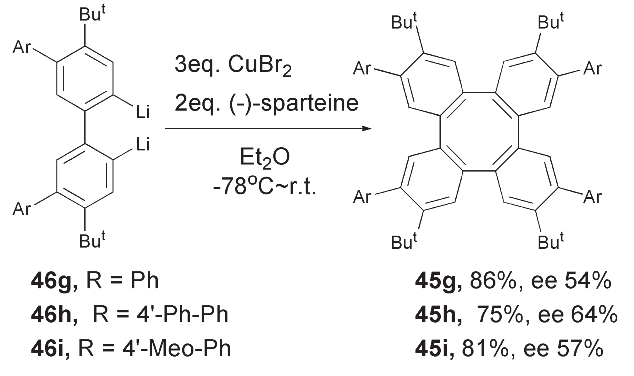


Scheme 40

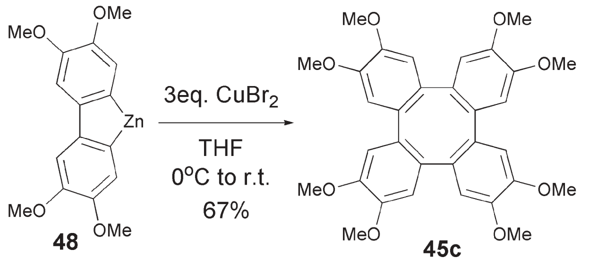
Two aryl–aryl bonds are formed and the configuration of four chiral axes is set in excellent yield with around 50% ee value (Scheme 41). The solvent here is still a crucial factor for selectivity because the ee value decreased to a rather low 8–9% when THF was employed instead of Et$_2$O. When the reaction is done without (−)-sparteine in Et$_2$O the racemic product will be obtained, however, the same condition in THF will then bring out biphenylene as a dominant product with minor amount of TPL.

Dibenzozincacyclopentadienes or dizincobiaryls, synthesized from their corresponding dilithiodiaryls **46** with two equivalents of ZnBr$_2$, can also undergo homo-coupling with Cu(II) but with a different selectivity. Different from dilithiodiaryls the zinc analogs generally form biphenylene as the primary products. Hence this reaction is often looked upon as a method for synthesis of biphenylene rather than TPL.[49] However, in some cases the situation varies. For example, the dibenzozincacyclopentadiene **48**, generated from **46c** with ZnBr$_2$ can afford TPL **45c** in good isolated yields (Scheme 42).[46]

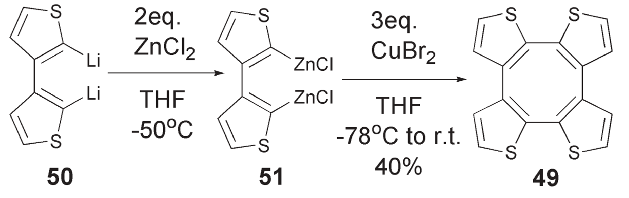
The Cu(II) mediated homo-coupling of dilithio- or dizincobiaryl can also be applied in synthesis of some TPL analogs.



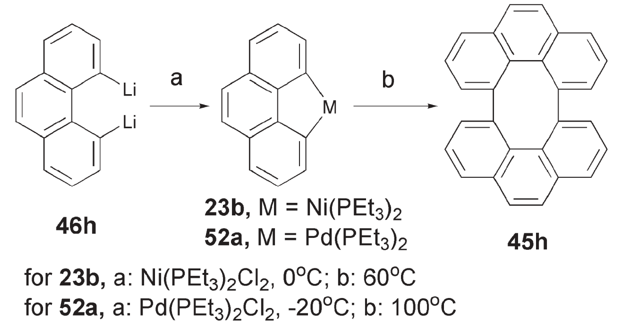
Scheme 41



Scheme 42



Scheme 43



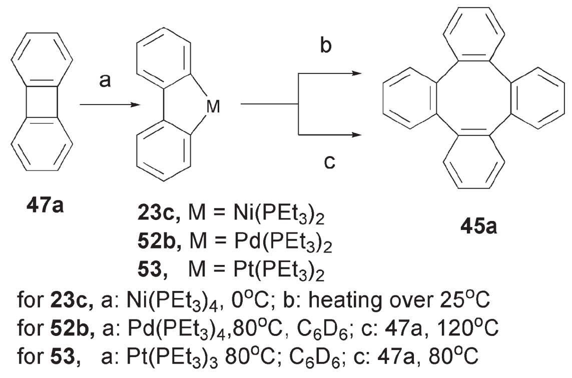
Scheme 44

Iyoda *et al.* also utilized a similar method for the synthesis of cyclotetrathiophene **49**.[50] Treatment of dilithio compounds **50** with one equivalent of ZnBr$_2$ afforded the dizinco-replacer **51**. The reaction of **51** by adding CuBr$_2$ gave the product in 40% yield (Scheme 43).

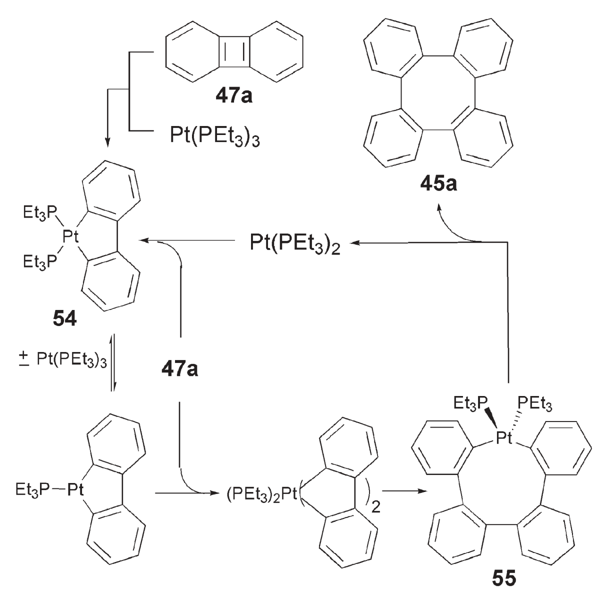
Likewise, dilithiobiaryl compounds can conduct the homocoupling *via* transmetallation to Ni and Pd. The metallacyclopentadienes of Ni **23b** and Pd **52a** can be synthesized by the dilithiophenanthrene and Ni(II) or Pd(II) compounds, respectively.[51] After heating TPL, **45h** is formed (monitored by NMR) and characterized by X-ray diffraction analysis (Scheme 44).

5.2 Homo-coupling of biphenylenes mediated by Ni, Pd and Pt

Metallacyclopentadienes of the above type can be synthesized also from biphenylene **47** and their corresponding transition metals. The four-membered ring in the biphenylene is highly strained and can readily be broken by insertion of transition metals.[52] For example, metallacyclopentadienes of Ni **23c**, Pd **52b** as well as Pt **53** were formed when combining **47a** with different metal complexes.[52–54] The sequentially formed metallacyclopentadienes were able to undergo not only thermolysis but also further reactions with another molecule of **47a** to provide TPL **45a** (Scheme 45). This



Scheme 45



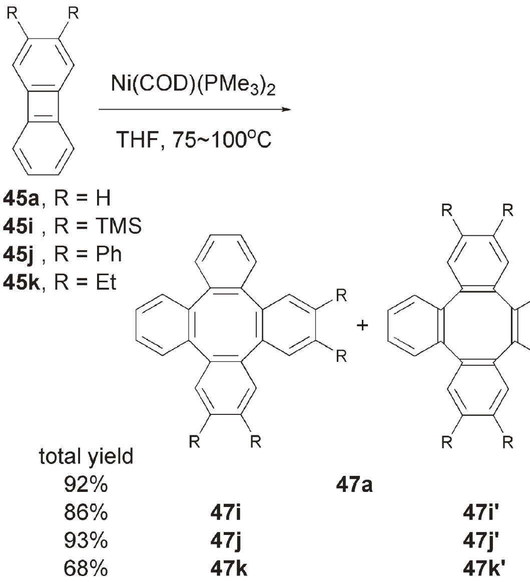
Scheme 46

reaction pattern has been developed into a catalytic preparative method for TPL. For example, either $Pt(PEt_3)_3$ or **54** and **55**, which can be synthesized respectively, are well capable of serving as catalysts for the dimerization of biphenylene to make tetraphenylene (Scheme 46).[54]

A practical Ni-catalyzed case of this type was reported by Vollhardt and co-workers to synthesize some substituted TPLs. When biphenylene **47a** was treated with $Ni(COD)(PMe_3)_2$ as a catalyst, TPL **45a** could be obtained almost quantitatively. When di-substituted biphenylenes **45i–k** were employed, two isomers of tetra-substituted TPL **47i–k** and **47i′–k** are produced equimolarly in high combined yields (Scheme 47).[55] TPL products containing active substituents such as in **45i** could undergo further transformation to prepare more complicated derivatives.

6 Conclusion and perspective

We have reviewed the synthesis of COT and derivatives mediated by various transition metals. The high efficiency for the formation of ring systems in this type of method is the key point and also the most advantageous for its application.



Scheme 47

However, these methods have still been limited to only some metals. Therefore development of new metal catalysts or additives are promising fields for this subject. For example, till now there is no report of synthesis of COT *via* Rh and Ru catalyzed reactions. However, many examples about the eight-membered analogs of COT have been well documented, such as the synthesis of cyclooctenone *via* Rh catalyzed [6 + 2] or [5 + 2 + 1] cycloaddition containing strained ring cleavage by Wender *et al.*,[56] synthesis of cyclooctadiene *via* Rh-catalyzed [4 + 2 + 2] cycloaddition of enyne and diene moieties by Evans *et al.*,[57] and synthesis of cyclooctatriene *via* Rh-catalyzed [4 + 2 + 2] cycloaddition of enyne and alkyne moieties by Gilbertson and DeBoef,[58] or *via* Ru-catalyzed [4 + 2 + 2] cycloaddition of diyne and diene moieties by Saá and co-workers.[59] Considering the high efficiency during the constructions of the ring framework and the possibility or potential for these analogs changing to COT, it can be predicted that Rh and Ru mediated cycloaddition may be also applied for synthesis of COT in the future.

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