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Highlight Review

Triptycene Derivatives: Synthesis and Applications

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Abstract

The family of triptycene derivatives have special structures, unique electrochemical and photochemical properties and have been found versatile for materials chemistry, in host–guest interactions and as molecular rotors. This present review summarizes the synthesis of triptycene and derivatives and their use in synthesis and as ligands.

◆ Introduction

Triptycene (**1**) (9,10-dihydro-9,10[1′,2′]-benzenoanthracene) is a C_{20} hydrocarbon with D_{3h} symmetry and has a rigid, 120° orienting, three-pronged framework. Bartlett and co-workers first reported its synthesis in 1942, they named it as "the triptych of antiquity, which was a book with three leaves hinged on a common axis."[1] Triptycene (**1**) is the smallest compound within the iptycene family, which is a class of structurally unique compounds consisting of arenes that are fused together through a bicyclo[2.2.2]octane framework, another iptycene recently studied is pentiptycene (**2**) (Figure 1).

The triptycenes, due to their special structure and their unique electrochemical and photochemical properties, have been found versatile usages in constructing molecules of both fundamental and practical importance. Triptycenes and their expanded pentiptycenes have been well studied in material chemistry, such as liquid crystals and polymers, which have been recently reviewed well and will not be discussed herein.[2]

Porous triptycene-containing polymers can adsorb gases such as hydrogen,[3] and theoretical studies showed that the spatial orientation of the phenyl rings in triptycene make it particularly suited for the adsorption.[4] It has also been reported that triptycene derivatives have potential pharmaceutical properties, such as anticancer and antimalarial activities.[5]

It has been long recognized the three phenyl rings forming a three-bladed structure that can rotate around an axis running through the bridgehead, and the rotational barrier is high, this behavior has been used for the investigation of artificial molecular machinery recently by many groups.[6] The 1,9-disubstituted triptycene system is a valuable tool in the examination of arene–arene interactions.[7] Triptycenes with unique three-dimensional rigid structure and electron-rich cavity, have been developed for supramolecular systems for study host–guest chemistry.[8] This type molecular also can be served as molecular tweezer.[9] The unique three-dimensional framework is also suitable for nanosized molecular cage,[10] and encapsulating small neutral molecules.[11]

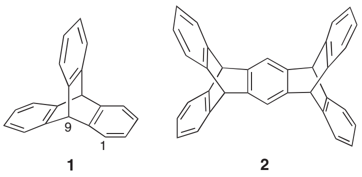


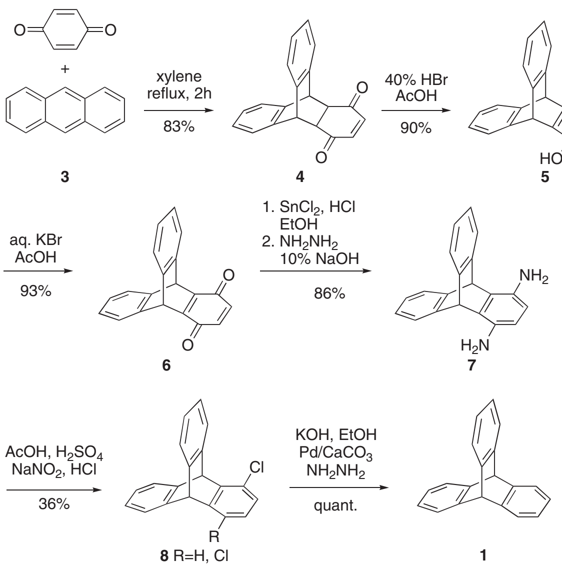
Figure 1.

In this review we focus on the synthesis of various triptycene derivatives, selenium substitution and the use as ligands in recent 10 years.

◆ Synthesis of Triptycene

Bartlett and co-workers reported the synthesis of triptycene (**1**) in 1942 which is shown in Scheme 1.[1]

In 1959 Craig and Wilcox reported a simple and direct route to **1**. Compound **4** was reduced with $LiAlH_4$ or $NaBH_4$ and the crude product was then refluxed with ethanolic hydrochloric acid followed by chromatography on acidic alumina yielding triptycene (**1**) in 15% yield.[12]



Scheme 1.

Dr. Liwei Zhao,[1,2] Prof. Zhong Li,[2] and Prof. Thomas Wirth*[1]
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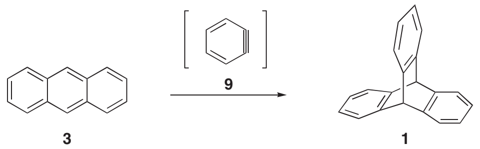
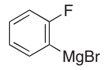
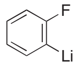
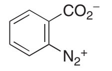
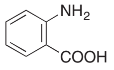
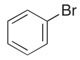
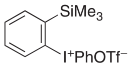
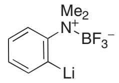
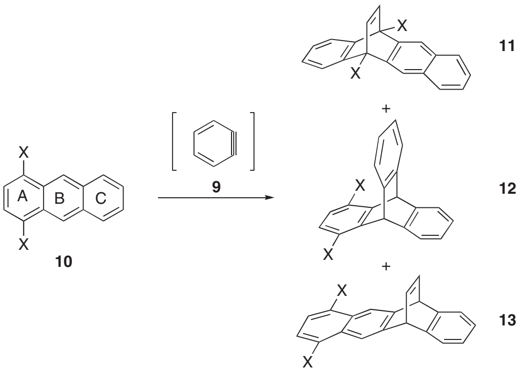
Table 1.



Precursor	Activation	Yield/%
	Heat	28[13]
	Room temperature	10[14]
	Heat	30[15]
	Isopentyl nitrite Heat	59[16]
	*t*-BuOK	21[17]
	Bu$_4$NF	86[18]
	Heat	11[19]



Scheme 2.

At the same time, another practical way by reacting benzyne with anthracenes was discovered, first reported by Wittig in 1956. Benzyne (**9**) can be released in situ by various precursors, their generation method and the corresponding yields are shown in Table 1.

Early in 1969, Klanderman et al. studied the reactivity of benzyne toward substituted anthracenes **10**. Benzyne reacts with anthracene to form Diels–Alder adducts with either the central ring **A** leading to **11** or one of the terminal ring systems **B/C** to **12/13** as shown in Scheme 2. The nature and position of the substituents influence the relative amounts of center and end-ring adducts; the electrophilic nature of benzyne and its steric requirements have been elucidated. The relative reactivities generally parallel those of anthracenes toward maleic anhydride. In their study, substituents in one ring do not affect the reactivity of the other ring toward benzyne, except 9,10-diphenylanthracene.[20]

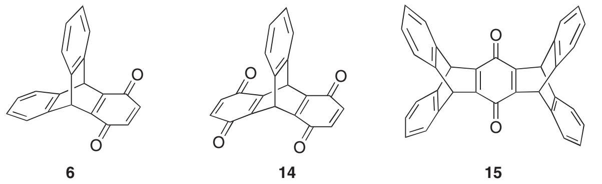
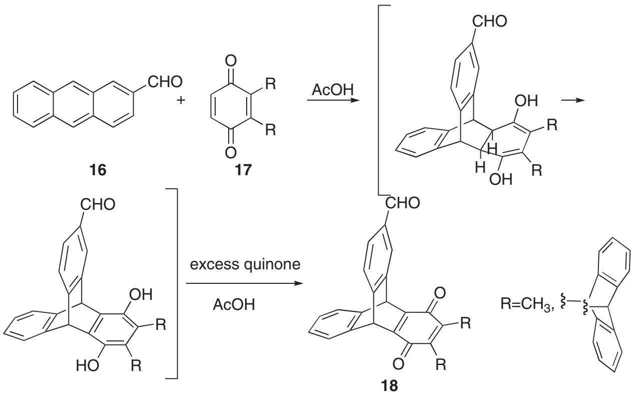


Figure 2.



Scheme 3.

♦ *Synthesis of Triptycene Derivatives*

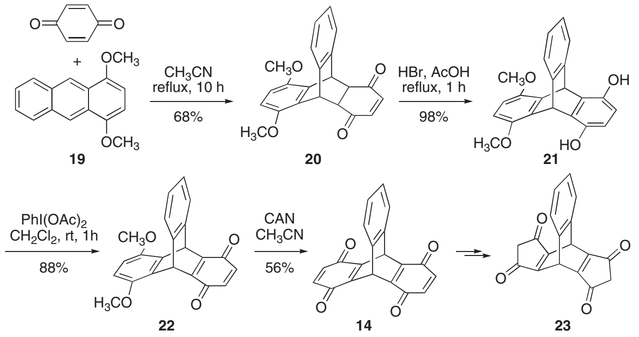
Diels–Alder Reactions with Quinone as Dienophile.

Although this reaction has been known for some time, it is still important for the synthesis of functionalized triptycenes, as it can easily introduce two phenol moieties or forms quinone derivatives such as compounds triptycene quinone **6**, triptycene bisquinone **14**, and pentiptycene quinone **15**. It is also an important method to prepare other iptycene derivatives (Figure 2).

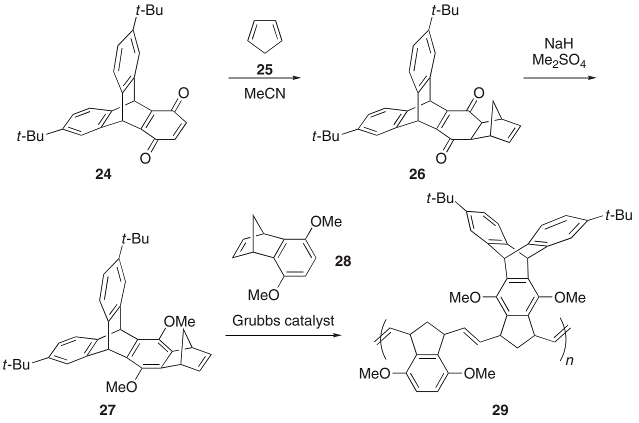
Wiehe et al. developed a general method for triptycene quinones, which are readily accessible by the reaction between an anthracene derivative **16** and excess of quinone **17** in acetic acid as shown in Scheme 3. Under these conditions, the initial [4 + 2] cycloadduct tautomerizes in situ to a triptycene hydroquinone which is then oxidized by the excess of quinone to the corresponding triptycene quinone **18**. This method tolerates a variety of functional groups and is perfectly suited for the construction of building blocks incorporating two quinones in a triptycene system. Applications of this synthetic strategy for the synthesis of various porphyrin quinones such as diads, triads, and tetrads have been reported.[21]

Spyroudis et al. prepared triptycene bisquinones starting from a Diels–Alder reaction of 1,4-dimethoxyanthracene (**19**) and *p*-benzoquinone, which was then transformed to triptycene bis(cyclopentenedione) **23** as shown in Scheme 4.[22] Later it was found that triptycene haloquinones react with sodium alkoxides in refluxing alcohol to afford pentiptycene quinone, besides the expected substitution products.[23] The central ring of pentiptycene quinone **15** can be further substituted as useful building block, one side substituents can be bromo, iodo, amino, nitro, cyano, or formyl group and the other side is hydroxy or alkoxy group.[24]

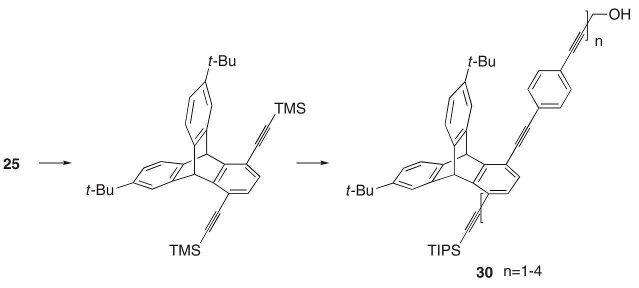
Polytriptycene derivatives are important for material science, Long et al. prepared polymers incorporating the triptycene subunit, these polymers exhibited low dielectric constant, low



Scheme 4.



Scheme 5.



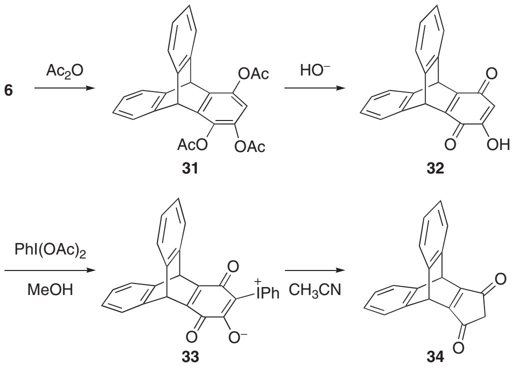
Scheme 6.

water absorption and high thermal stability. The monomer **26** was efficiently synthesized directly from triptycene-1,4-quinone derivative **24** by a Diels–Alder reaction with an excess of cyclopentadiene (**25**), and subsequently polymerized with **28** by a metathesis reaction (Scheme 5).[25]

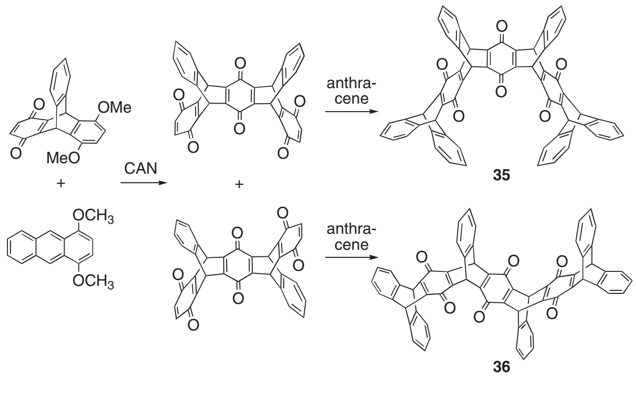
The triptycene-1,4-quinone derivative **24** was also used to make a key iptycene building block for the preparation of monodisperse oligo(*p*-phenyleneethynylene)s which contains one triptycene unit such as compounds **30** (Scheme 6).[26]

Spyroudis et al. prepared a triptycene quinone which was converted to triptycene cyclopentenedione **34** through the formation of a hydroxyquinone–phenyliodonium ylide **33** and thermal ring contraction of the latter as shown in Scheme 7.[27]

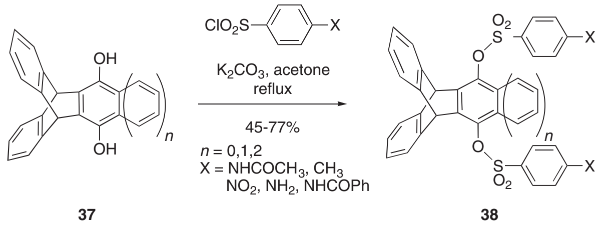
Zhu and Chen developed a practical and efficient method to synthesize iptycene quinones, and pentiptycene quinones **35** and **36** were conveniently synthesized by one-pot reaction of triptycene quinone with anthracene and its derivatives in refluxing acetic acid in the presence of *p*-chloranil followed by cerium ammonium nitrate (CAN) oxidative demethylation. They also made U-shaped heptitycenes in a similar way (Scheme 8).[28]



Scheme 7.



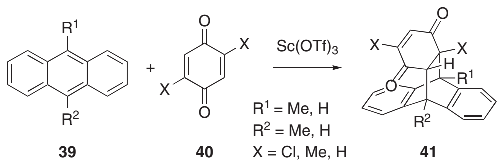
Scheme 8.



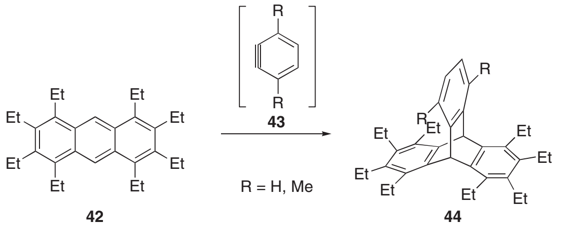
Scheme 9.

Yang et al. synthesized triptycene-derived disulfonates **38** to study molecular folding. In order to achieve a more regular shape for compact crystal packing, the bulky triptycene groups tend to pack in pairs (Scheme 9).[29]

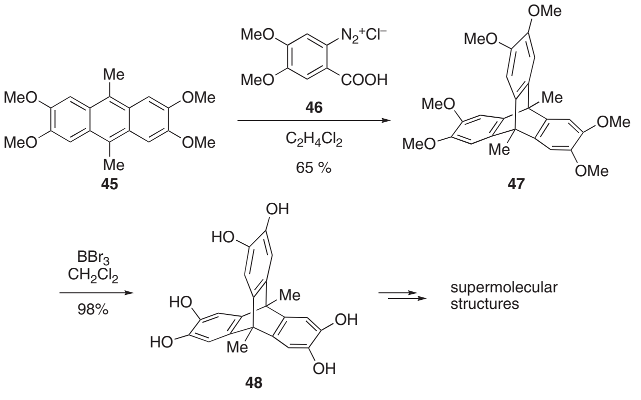
The Diels–Alder reaction between anthracene and benzoquinone is the key step of triptycene synthesis, but this reaction has not been studied in all details. Fukuzumi and co-workers reported that a variety of metal ions act as effective catalysts to accelerate Diels–Alder reactions of anthracenes **39** with *p*-benzoquinone derivatives **40**, which have been regarded as inert or weak dienophiles. Scandium triflate [Sc(OTf)$_3$] was found to be the most effective in reactions to **41** as compared to other metal ions, magnesium perchlorate was also efficient. (Scheme 10).[30]



Scheme 10.



Scheme 11.



Scheme 12.

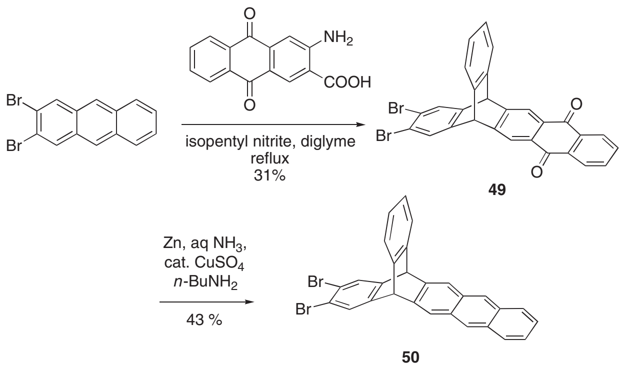
Diels–Alder Reactions with Arynes as Dienophile.

Compared with benzoquinones as dienophile, arynes are much more often used in triptycene synthesis. As described earlier, benzyne can be formed from various precursors (Table 1) and substituted benzynes can introduce functional group to triptycene derivatives easily.

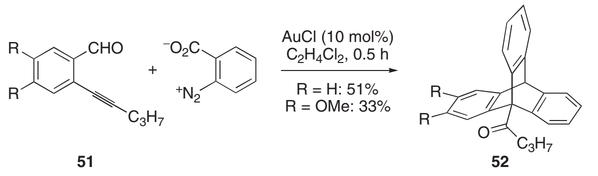
Recently Marks et al. prepared polyethylated triptycene derivatives **44** by reaction of octaethylanthracene **42** with benzynes **43** to study the orientation of the ethyl substituents, as any ethyl group can have up or down arrangement (Scheme 11).[31] Pascal et al. made crowded triptycene derivative from tetraphenylbenzyne with octaphenylanthracene, due to the steric interactions imposed by the phenyl groups, the yield was only 11%.[32]

Chen and co-workers developed a series of triptycenes as supramolecular systems, 4,5-dimethoxybenzyne precursor **46** is used to introduce phenol moieties into triptycene **48** as shown in Scheme 12.[33]

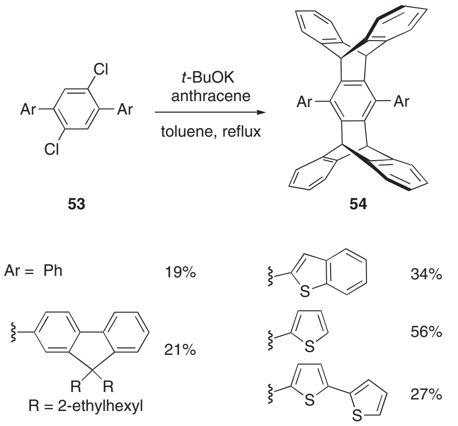
Holý and co-workers prepared extended triptycenes such as **49** and **50**, which can be served as convenient building blocks for a stepwise ramification of the parent triptycene by Diels–Alder oligomerizations (Scheme 13).[34]



Scheme 13.



Scheme 14.

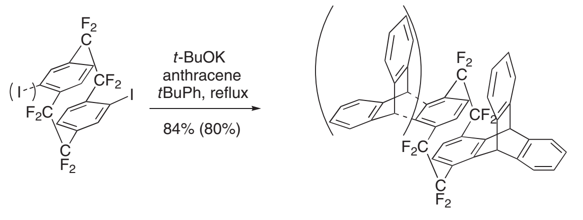


Scheme 15.

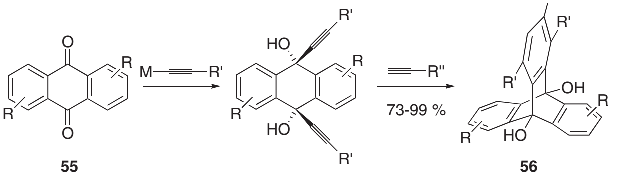
Recently Sato et al. found that the reaction of *ortho*-alkynylbenzaldehydes **51** with benzenediazonium 2-carboxylate afforded triptycyl ketones **52** using AuCl catalysis. The reactions most probably proceeded through the formation of a zwitterionic intermediate by the gold-induced electrophilic cyclization of *ortho*-alkynyl(oxo)benzenes, followed by the cycloaddition of benzyne as shown in Scheme 14.[35]

1,4-Diarylpentiptycenes were synthesized by Zyryanov et al. from 1,4-dichloro-2,5-diarylbenzene **53** by double base-promoted dehydrohalogenation to give the corresponding arynes, which in the presence of anthracene undergo cycloaddition providing 1,4-diarylpentiptycenes **54** in moderate overall yields (Scheme 15). The resulting 1,4-diarylpentiptycenes show fluorescence which is modulated by the 1,4-aryl residues. The fluorescence is quenched in the presence of vapors of nitroaromatic compounds suggesting potential application in sensing of explosives.[36]

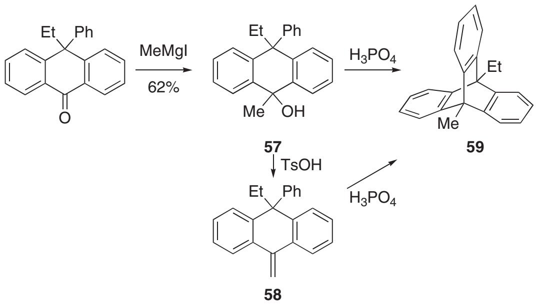
Dehydroiodination of 4-iodo- and 4,15-diiodooctafluoro[2.2]paracyclophane by treatment with *t*-BuOK in the presence of anthracene afforded the corresponding mono- and bis-cycloadducts in high yield (Scheme 16).[37]



Scheme 16.



Scheme 17.



Scheme 18.

Rhodium-catalyzed [2 + 2 + 2] Cycloaddition.

Taylor et al. reported a new application of metal-catalyzed alkyne cyclotrimerization reactions ([2 + 2 + 2] cycloadditions) that provide access to substituted 9,10-triptycenediols (**56**) in only two or three steps from readily available anthraquinones **55** and alkynes in high yield as shown in Scheme 17.[38]

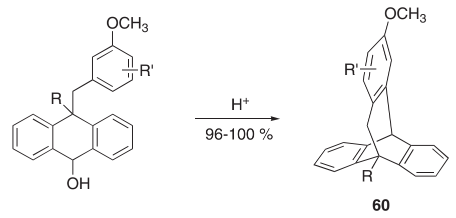
Acid-catalyzed Cyclizations.

Walborsky et al. discovered in 1968 that 9-ethyl-10-methyltriptycene (**59**) is formed in excellent yield when 9-phenyl-9-ethyl-10-methylene-9,10-dihydroanthracene (**58**) or the precursor **57** is placed in polyphosphoric acid (Scheme 18).[39]

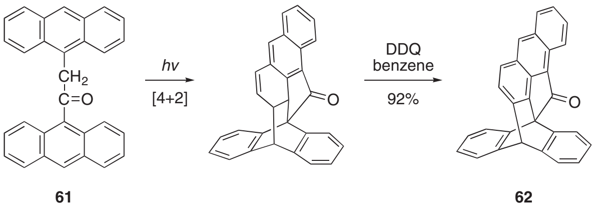
Recently homotriptycene derivatives such as **60** were synthesized using the same strategy of an acid-catalyzed cyclization of anthracenol derivatives (Scheme 19).[40] It was also found that 10-benzyl-9,10-dihydroanthracen-9-ols, with high electron densities in the benzene ring, undergo a transannular ring closure to the corresponding homotriptycenes in the presence of acid in almost quantitative yields.

Photochemical Cyclizations.

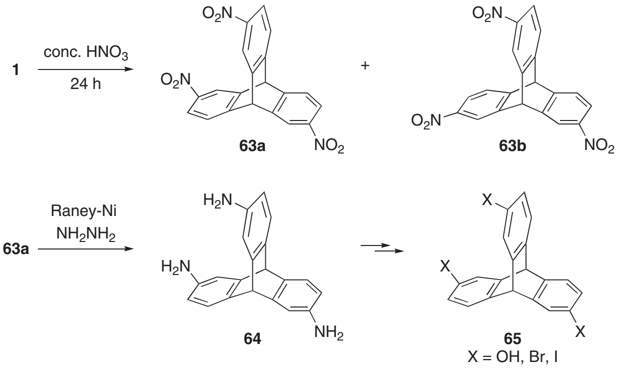
Kurata et al. prepared a new triptycene derivative **62** with an anthracene moiety, after photocyclization of **61** and dehydration of the resulting ketone (Scheme 20).[41]



Scheme 19.



Scheme 20.



Scheme 21.

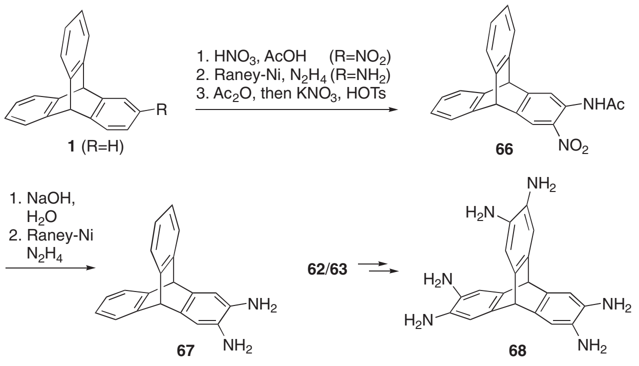
Substitution of Triptycenes.

Triptycene can easily be nitrated by HNO_3, and a series of 2,6,14- and 2,7,14-trisubstituted triptycene derivatives **63–65** have been prepared by Zhang et al.[42] These trisubstituted triptycenes (Scheme 21) are potential building blocks for constructing novel receptors, synthetic molecular machines and porphyrin arrays.[43] Similarly, 2,6-dibromo- and 2,6-diiodotripticenes were prepared which were employed in nickel(0)-mediated Yamamoto-type polycondensations forming novel aromatic poly(2,6-triptycenes).[44]

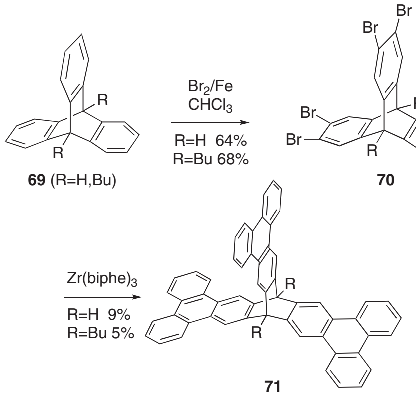
Chong and MacLachlan successfully synthesized a series of triptycene-based ligands containing pyrazine groups for use in forming coordination frameworks and as model compounds toward shape-persistent dendrimers and macrocycles. 2,3-Diaminotriptycene (**67**) and 2,3,6,7,14,15-hexaaminotriptycene (**68**) were formed from nitrated triptycene intermediates as shown in Scheme 22.[45]

Biphenylation using a zirconium complex of hexabromotriptycenes bearing either a hydrogen or *n*-butyl moiety at the bridgehead carbon atoms gave triptycenes **71** with triphenylene blades as reported by King et al. (Scheme 23). The blades extend in both, perpendicular and parallel orientation to the 3-fold axis and generate a large intramolecular free volume.[46]

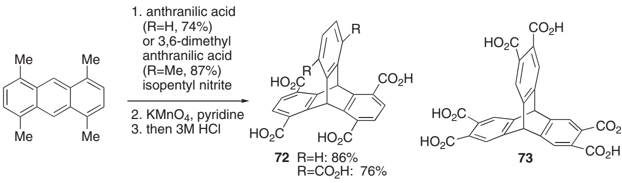
Závada and co-workers synthesized highly symmetric triptycene tetra- and hexacarboxylates **72** and **73** by oxidation



Scheme 22.



Scheme 23.

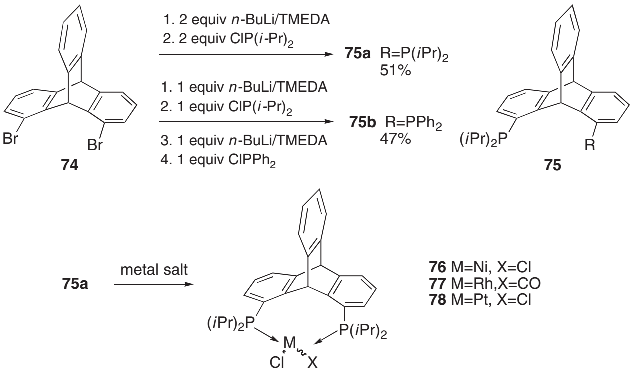


Scheme 24.

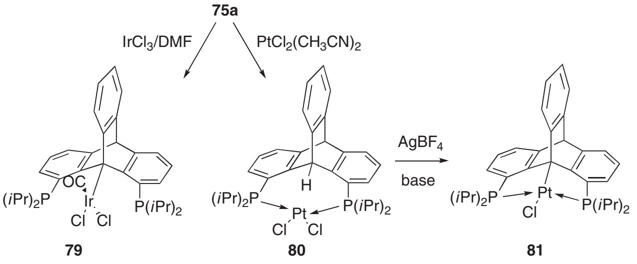
of the corresponding methyl derivatives as exemplified for compound **72** in Scheme 24.[47]

◆ *Triptycene Derivatives as Ligands*

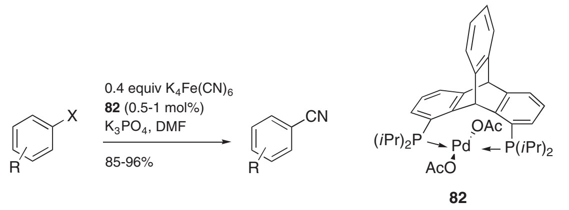
Recently Gelman et al. developed a series of chelating diphosphine ligands based on triptycenes from readily available stating materials as shown in Scheme 25. The catalytic activity of the new ligands **75** was tested in palladium-catalyzed cross-coupling reactions of aryl chlorides with phenylboronic acids and excellent yields were obtained.[48] To evaluate the coordination diversity of triptycene-based bidentate ligands, some transition metal complex compounds **76**–**78** were prepared and fully characterized. The comparative structural analysis revealed that 1,8-bis(diisopropylphosphino)triptycene **75a** is able to access a variety of bite angles and to stabilize metal centers in different geometries.[49] It has also been demonstrated that mononuclear complexes with transition-metals bearing 1,8-bis(diisopropylphosphino)triptycene **75a** and 1-diisopropylphosphino-8-diphenylphosphinotriptycene (**75b**) react with an appropriate transition-metal precursor via a ring-expansion pathway to form unusual bimetallic quasi-closed structures (Scheme 25).[50]



Scheme 25.



Scheme 26.



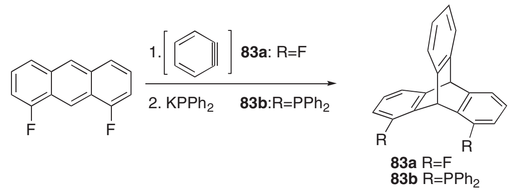
Scheme 27.

These compounds can be used for the synthesis of a new class of bridgehead-metalated pincer complexes such as **79** and **81** via C–H activation as described in Scheme 26.[51]

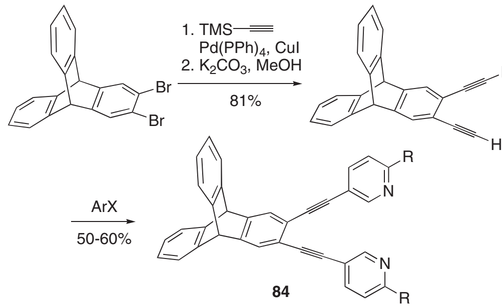
Similar palladium complexes such as **82** can serve as an efficient and selective catalyst in the cyanation of aryl halides (Scheme 27). The reaction conditions are mild, allow the functionalization of a large range of substrates, and circumvent the need for an inert atmosphere and do not need amine co-ligands.[52]

Similar ligands can also be used in a new protocol for palladium-catalyzed Buchwald–Hartwig aminations of aryl chlorides and bromides with benzophenone imines as ammonia surrogates.[53]

Vogt et al. developed an improved route for a triptycene-based diphosphine **83b** (Scheme 28), investigated the coordination behavior of this ligand, and also determined the X-ray crystal structure of its Pt-complex. The complex of **83b** with



Scheme 28.



R = CO$_2$Me,C(Me$_2$)CO$_2$Me, OMe,CH$_2$OTBS, 2-pyridyl, CH$_2$NR^{1}R^2

Scheme 29.

Ni(cod) was applied in the hydrocyanation of butadiene, with acetonecyanohydrine as cyanide source, showing excellent selectivities of up to 98% toward the synthesis of 3-pentenenitrile.[54]

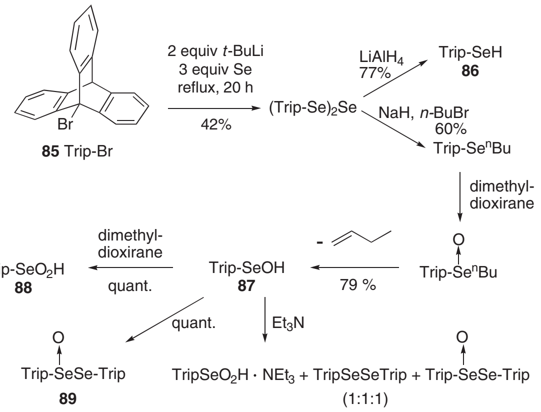
A new family of dinucleating ligands has been synthesized by Kodanko et al. using a convergent strategy involving the dual Sonogashira cross-coupling of 2,3-diethyltriptycene with a vartiety of functionally diverse 5-bromopyridines to yield triptycene compounds of type **84** (Scheme 29).[55]

Compound **84** has been used to prepare carboxylate-bridged heterodinuclear sodium–iron complexes which are used to study the substitution of iron for sodium.[56]

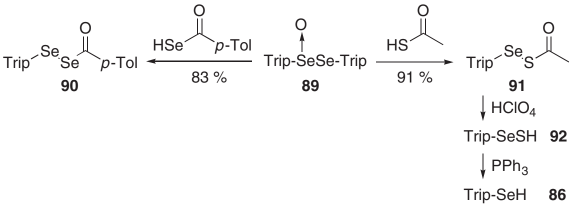
Selenium Substitution.

Ishii and co-workers prepared a series of selenium-containing compounds based on triptycene.[57] Simple selenols such as **86** were accessible, but also seleninic acid **87** or selenenic acid **88** as well as a series of different selenoseleninates as shown in Scheme 30.

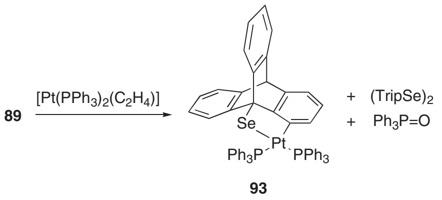
Selenoseleninate **89** can react either with *p*-toluenecarboselenoic acid to form the acyl 9-triptycyl diselenide **90**,[58] later the same research group prepared triptycene-9-thioselenenic acid **91** as the precursor for the first isolable thioselenenic acid **92** by reaction with thioacetic acid (Scheme 31).[59]



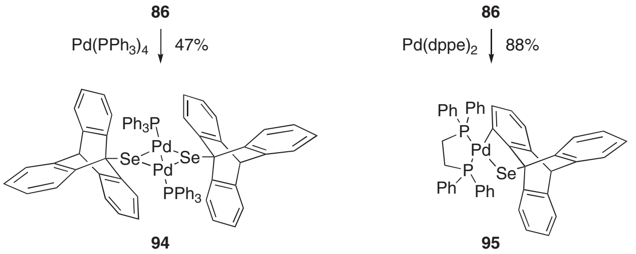
Scheme 30.



Scheme 31.



Scheme 32.



Scheme 33.

Recently, the same authors found that the reactions of selenoseleninate **89** with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] gave selenaplatinacycle **93** by intramolecular C–H bond activation. They also succeeded for the first time in the full characterization of a corresponding hydrido selenolato platinum(II) complex. These results give additional insight into the reaction of selenium compounds with low-valent transition-metal complexes. In the formation of **93**, the bulkiness of the substituents both on the selenium and on the platinum play an important role (Scheme 32).[60] The comlex **93** was tested in hydroselenylation and carboselenylation with electron-deficient alkynes recently.[61]

The oxidative addition reaction of the selenol **86** with [Pd(Ph$_3$P)$_4$] produced a new dinuclear palladium(I) complex **94** with bridging selenolato ligands. In contrast, the reaction of **86** with [Pd(dppe)$_2$] resulted in the formation of the five-membered selenapalladacycle **95** (Scheme 33).[62]

Nakanishi and co-workers studied the ^{77}Se NMR of 9-(arylselanyl)triptycenes, to determine the structures of these compounds in solutions.[63]

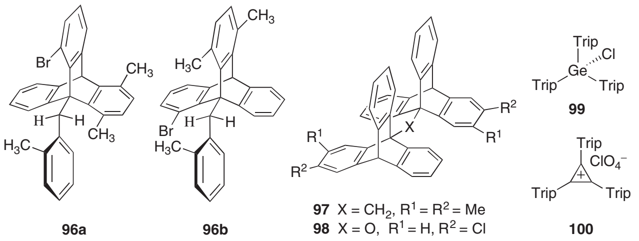


Figure 3.

Chiral Triptycene Derivatives

Chiral Triptycenes due to Hindered Rotation.

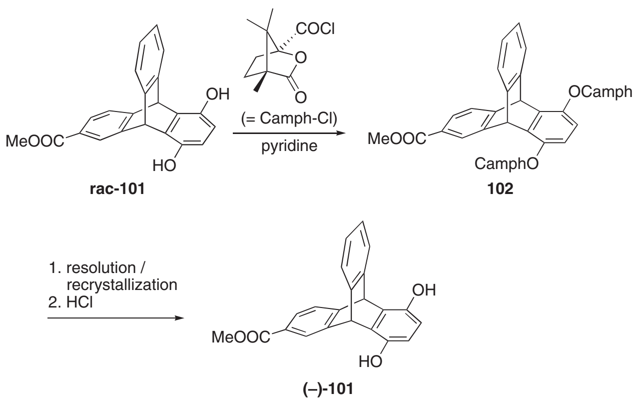
Previous studies by Oki and co-workers on the rotation in bridgehead-substituted triptycenes had shown that the 9-triptycyl group functions as a molecular rotor with an exceptionally high torsional barrier.[64] Some 9-alkyl-substituted triptycene derivatives were made to study this behavior,[65] Yamamoto reported that atropisomers 8-bromo-1,4-dimethyl-9-(2-methyl)triptycene **96a** and **96b** (Figure 3) can be separated and isolated as stable entities at room temperature,[66] and other compounds have also been investigated.[67]

Iwamura and Mislow reported a molecular gear system in ditriptycyl ethers ($Trip_2O$)[68] and ditriptycylmethanes ($Trip_2CH_2$),[69] these systems are nearly barrierless in rotation ($<1\,kcal\,mol^{-1}$). Mislow investigated bis(2,3-dimethyl-9-triptycyl)methane (**97**)[70] and Iwamura studied bis(4-chloro-1-triptycyl) ether analog **98**,[71] the diastereomers were observable and separable and the barrier to isomerization was quite high with about $34\,kcal\,mol^{-1}$ for **97** and $24.5\,kcal\,mol^{-1}$ for **98**. Larger compounds were also synthesized and dynamic gearing could be observed. Information can be transferred in large molecules from one side to the other via cooperatively torsional chains.[72]

Mislow studied three-cogged compounds such as tris(9-triptycy1)germanium chloride (**99**) and tris(9-triptycy1)cyclopropenium perchlorate (**100**), the racemization barrier for these compound is about $20\,kcal\,mol^{-1}$. The torsion of the three tiptycene rotors are frozen because both uncorrelated and correlated rotation is mechanically disallowed in a closed cyclic array consisting of an odd number of securely meshed gears.[73] Dynamic stereochemistry with similar stannane derivatives has been studied recently by Yamamoto et al.[74] and has been reviewed as well.[6b]

Inherent Chiral Triptycenes.

Nakagawa and co-workers synthesized a series of optically active triptycenes in the seventies.[75] Compound (−)-**101** was obtained by optical resolution of the diastereomers **102** which were obtained by reaction of *rac*-**101** with champhanoyl chloride, the synthesis is shown in Scheme 34.[75f] Similar compounds have also been reported by Harada et al., the absolute configuration has been determined by applying the circular dichroism (CD) method.[76]



Scheme 34.

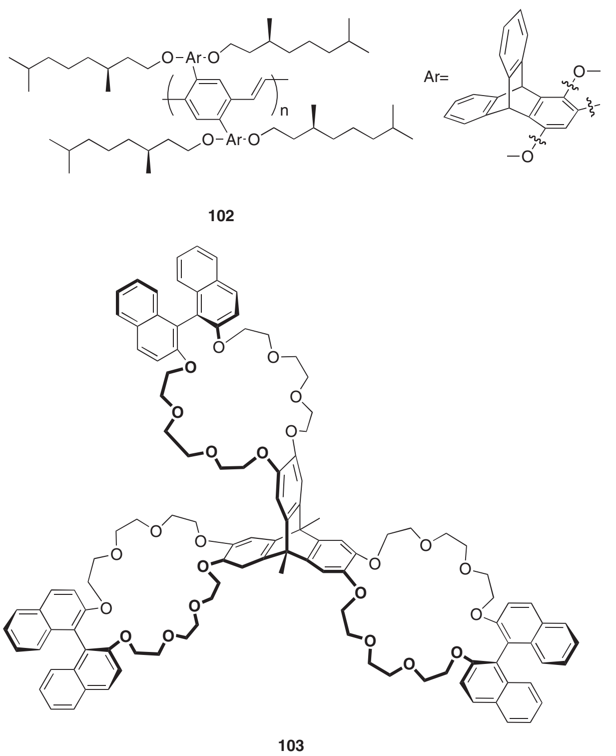


Figure 4.

Triptycenes with Chiral Substituents.

Satrijo et al. prepared chiral π-conjugated polymers to study the nature of polymer aggregation in spin-cast films. To induce optical activity in the conjugated backbone, enantiomerically pure chiral side chains were incorporated into the polymers, and triptycene-containing polymers such as **102** were synthesized in order to study the effects of bulky, interlocking side groups on the chiral organization.[77] Recently Zhu et al. synthesized novel interlocked molecules such as chiral [4]pseudocatenane derivatives, using chiral triptycene-based tri(crown ether) **103** as a key intermediate (Figure 4).[78]

Conclusion

Recently research of triptycene chemistry flourished in many areas, and the synthesis method can guide the preparation of novel compounds in an efficient way. Compared to other applications, the unique framework for designing ligands is still rare, and the synthesis of chiral triptycenes is still a considerable challenge.

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