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Review

# Dibenzometallacyclopentadienes, boroles and selected transition metal and main group heterocyclopentadienes: Synthesis, catalytic and optical properties

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## Contents

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## ABSTRACT

The review discusses the synthesis, structures and properties of transition metal and main-group containing heterocyclopentadienes, with particular focus on dibenzometallacyclopentadienes (2,2′-biphenyl complexes), diethynylmetallacyclopentadienes, boroles and related main-group systems, and their catalytic and optoelectronic properties.

## 1. Introduction

There has been considerable interest in the incorporation of metal atoms into conjugated, five-membered rings as the properties of the metallacycles can be tuned through the use of a variety of ligands and metal oxidation states. Metal complexes of diimines (a) [1], bipyridines (b) [2] and 2-phenylpyridines (c) [2b,c,3] have been comprehensively studied due to their importance as catalysts, as redox active systems and for applications in electrolu-

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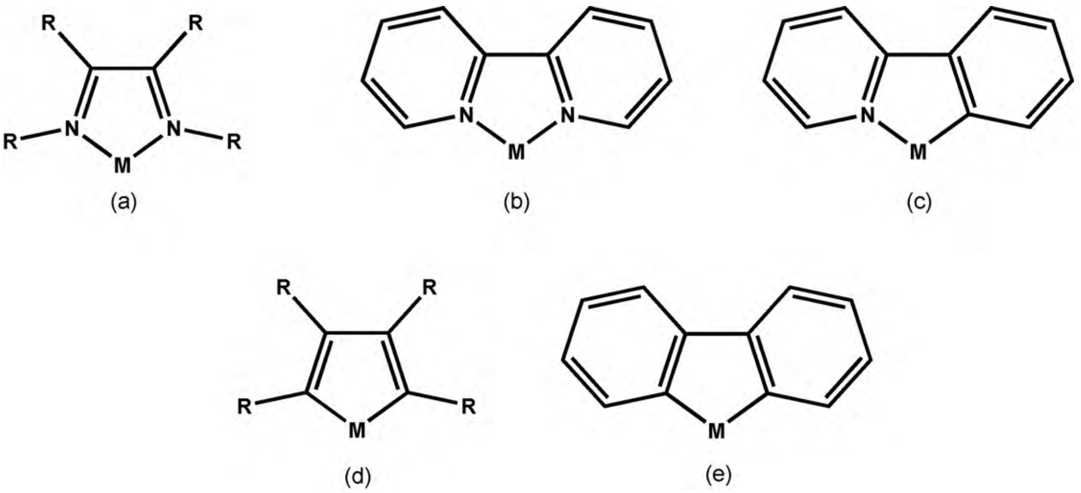


**Fig. 1.** (a) Metal diimine complex; (b) metal bipyridine complex; (c) metal 2-phenylpyridine complex; (d) metallacyclopentadiene; (e) metal 2,2′-biphenyl complex.

minescent devices. Whereas related metallacyclopentadienes (d) are well known as intermediates in catalytic cyclotrimerization reactions of alkynes and alkyne/nitrile combinations [4], there are fewer examples of analogous $MC_4$ metal 2,2′-biphenyl (2,2′-bph) complexes (e) (Fig. 1).

Structurally related to the above mentioned M(2,2′-bph) complexes and metallacyclopentadienes are main-group $EC_4$ systems such as boroles, siloles, phospholes and thiophenes. Interestingly, in contrast to their transition metal analogues, these classes of compounds have attracted attention mainly due to their optical and electron transporting properties, although exploration of M(2,2′-bph) transition metal complexes in these fields of research has increased recently as well.

This review highlights recent advances in $MC_4$ heterocycle chemistry with emphasis on 2,2′-biphenyl complexes (dibenzometallacyclopentadienes), and briefly introduces related $EC_4$ main-group systems, especially boroles, which have attracted recent attention and have not been reviewed elsewhere. The catalytic and optical properties of the compounds will be discussed as appropriate to their behavior.

## 2. Transition metal 2,2′-biphenyl (2,2′-bph) complexes

Metal 2,2′-bph complexes are known for a number of transition metals including Co [5], Ni [6], Pt [7], Pd [8], Ir [9,10] and Rh [11]. There are few synthetic routes to these complexes and the methods employed are such that substituted 2,2′-bph complexes are relatively difficult to prepare.

### 2.1. Synthesis by C–C activation of biphenylene

The main method used for complex formation is direct insertion of a nucleophilic metal center into the strained, four-membered ring of biphenylene (Fig. 2). This approach has been utilized for a range of transition metals [5,6,8,12].

The thermodynamic driving force for such a reaction is the cleavage of the strained biphenylene C–C bond through oxidative addition to the metal giving two new metal-aryl σ-bonds. The C–C bond strength in biphenylene of 65.4 kcal/mol was obtained by calculating the difference of heats of formation of biphenylene and the 2,2′-biphenyl diradical (Fig. 3), and this strained C–C bond is 53 kcal/mol easier to cleave than the Ph–Ph C–C bond in biphenyl itself.

The reactivity of weakly nucleophilic metal centers with the strained C–C bond of biphenylene is much lower than that of strongly nucleophilic metals, but it has been observed that when the manganese complex $[Mn(\eta^6\text{-biphenylene})(CO)_3]^+$ is used in place of biphenylene, the reaction with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ giving $[Pt(2,2'\text{-bph})(PPh_3)_2]$ occurs in seconds [7]. On standing, the product scavenges CO from Mn with loss of phosphine to form $[Pt(2,2'\text{-bph})(PPh_3)(CO)]$, a transformation which has been speculatively linked to the relief of steric crowding around Pt.

Jones et al. carried out mechanistic studies concerning the C–H bond activation of biphenylene mediated by an *in situ* generated carbene-like $\{Rh(Cp^*)(PMe_3)\}$ fragment. The proposed reaction pathway proceeds through a series of $\eta^2$ coordination and C–H activation steps prior to attack on the C–C bond of the biphenylene, as depicted in Fig. 4 [12].

Reaction of $[RhH(Ph)(Cp^*)(PMe_3)]$ (**1**) with 1.5 equivalents of biphenylene in cyclohexane-$d_{12}$ at 65 °C resulted in the quantitative formation of $[RhH(1\text{-bph})(Cp^*)(PMe_3)]$ (**2**) along with a small amount of $[Rh(2,2'\text{-bph})(Cp^*)(PMe_3)]$ (**3**). $[RhH(1\text{-bph})(Cp^*)(PMe_3)]$ (**2**) reacts slowly upon further heating at 65 °C and is completely converted to $[Rh(2,2'\text{-bph})(Cp^*)(PMe_3)]$ (**3**) in 19 days. This reaction can be accelerated considerably by increasing the temperature to 85 °C, allowing complete conversion in only 5 days. Apparently, the cleavage of the α-C–H bond is favored over that of the less sterically demanding β C–H bond. Electrophilic substitution of biphenylene occurs at the β (2) position exclusively and metalation takes place at the α (1) carbon. Thus, the C–H activation is more consistent with the build-up of negative charge on

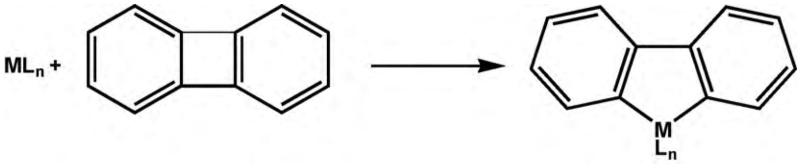
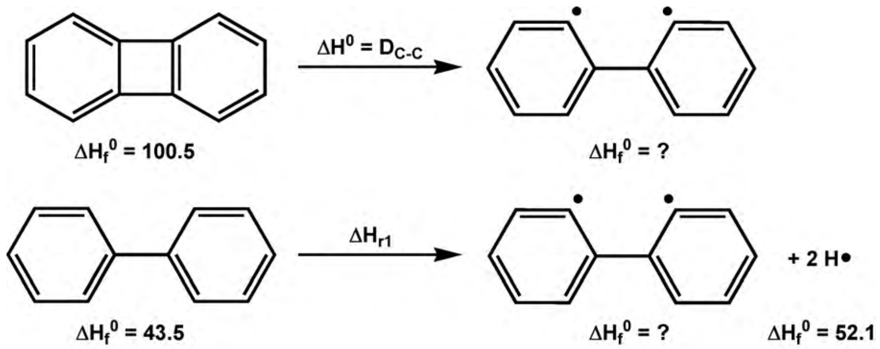


**Fig. 2.** Formation of a metal 2,2′-bph complex from biphenylene.



$$\Delta H_{r1} = 2(D_{Ar\text{-}H}) = 2(113.3) = 226.6$$
$$\Delta H_{r1} = \Delta H_f^0 + 2(52.1) - 43.5$$
$$\Delta H_f^0 = \Delta H_{r1} - 2(52.1) + 43.5 = 165.9$$

$$D_{C\text{-}C} = 165.9 - 100.5 = \underline{65.4\ \text{kcal/mol}}$$

**Fig. 3.** C–C cleavage in biphenylene.

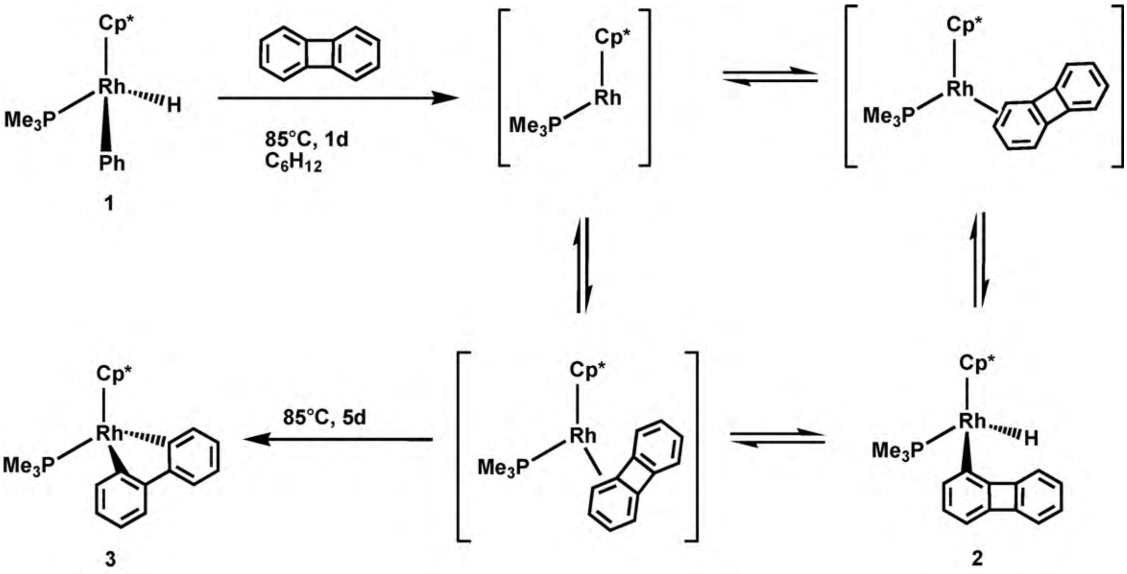


**Fig. 4.** Proposed mechanism for biphenylene activation based on mechanistic studies [12].

the biphenylene than with electrophilic attack by the metal. The negatively charged biphenylene shows a reduction in its antiaromatic character and this may contribute to the stability of the C–H activation product.

Jones and co-workers also found that reaction of [M(Cp*)($\eta^2$-$C_2H_4$)$_2$] (M = Co, Rh) with biphenylene, when heated for over 2 days, produced a bimetallic [$M_2$(Cp*)$_2$(bph)] complex [11]. The first {M(Cp*)} unit inserted into the strained C–C biphenylene bond, but the second coordinated to the metallacycle in an $\eta^5$ fashion. When the Rh analogue **4** was heated at 120 °C under a CO atmosphere, a 1:1 mixture of two mono-rhodium species, [Rh(Cp*)(CO)$_2$] and [Rh(Cp*)(2,2′-bph)(CO)] (**5**) was formed (Fig. 5).

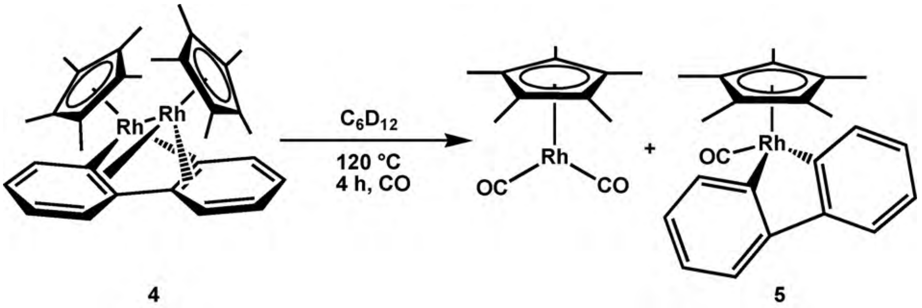


**Fig. 5.** Formation of a Rh 2,2′-bph complex from a bimetallic starting material [11].

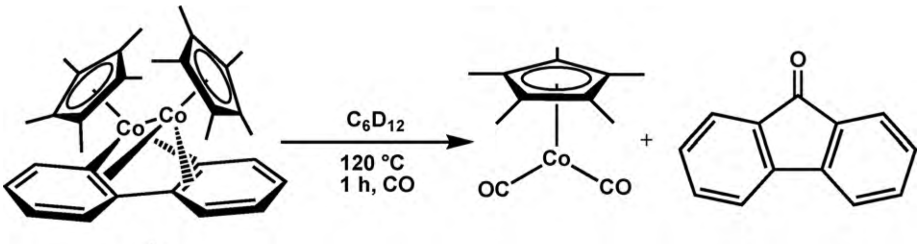


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**Fig. 6.** Formation of fluorenone from a bimetallic bph Co complex [11].

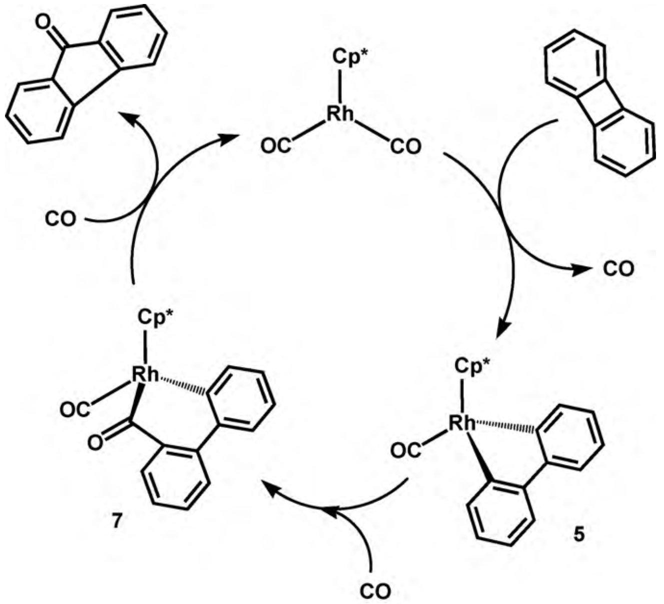

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**Fig. 7.** Proposed mechanism for the catalytic carbonylation of biphenylene [11].

Attempts to form the 2,2′-bph complex directly from [Rh(Cp*)(CO)$_2$] and biphenylene under thermal conditions were unsuccessful, but photolysis of the starting material and biphenylene resulted in slow conversion to product, with the reaction reaching completion after 3 days. The Co analogue reacts similarly under these conditions; however, the insertion product is apparently unstable. Heating of the bimetallic species under a CO atmosphere gave a 2:1 mixture of [Co(Cp*)(CO)$_2$] and fluorenone, with no evidence of any bph complex (Fig. 6), although the authors proposed it to be an intermediate.

The proposed mechanism for the catalytic carbonylation of biphenylene to fluorenone mediated by rhodium is depicted in Fig. 7. Dissociation of CO from [Rh(Cp*)(CO)$_2$] is believed to occur prior to coordination of biphenylene and subsequent insertion of the {Rh(Cp*)(CO)} fragment into the strained C–C bond. The M–C(bph) σ-bond is susceptible to intramolecular carbonyl insertion, the 16-electron intermediate being trapped by a new CO ligand. Reductive elimination of fluorenone, and binding of another CO regenerates [Rh(Cp*)(CO)$_2$]. It is expected that the analogous Co complex undergoes the same process [11].

Both the Rh and Co bimetallic species **4** and **6** are fluxional, and low temperature $^1$H NMR spectroscopy of the complexes showed two distinct $C_5Me_5$ peaks ($\delta$ 1.73 and 1.16 ppm) which coalesce to a singlet at −25 °C ($\Delta G^\ddagger$ = 11.4 kcal/mol) for the Co analogue and at 77 °C ($\Delta G^\ddagger$ = 16.8 kcal/mol) for the Rh analogue. The structures of both the Rh and Co bimetallic species [M$_2$(Cp*)$_2$(bph)] have been determined by X-ray crystallography and show Rh–Rh and Co–Co bond distances of 2.683(2) Å and 2.4792(6) Å, respectively. Although the complexes are described as having a single M–M bond, electron counting suggests that a dative bond from an 18-electron “M(Cp*)($\eta^2$-$C_6H_4$)$_2$”, M(I) species to a 16-electron “M(Cp*)(2,2′-bph)”, M(III) species would provide a localized, formal description of the bonding. When PMe$_3$ was used in place of CO, the Co species [Co(2,2′-bph)(Cp*)(PMe$_3$)] (**8**) analogous to the rhodium example **3** was formed, and a 1:1 mixture of the compound along with [Co(Cp*)(PMe$_3$)$_2$] was obtained from the bimetallic compound **6**. Neither the Rh nor Co binuclear complexes react with hydrogen, even at high temperature or $H_2$ pressure.

Vollhardt and co-workers demonstrated the stereo- and regioselective double insertion of {CoCp} fragments in the strained C–C bonds in angular [3]phenylene, resulting in a tetrametallic complex **9** in which the $\eta^4$-coordinated Co atoms are located *anti* with respect to the terphenyl ligand plane (Fig. 8) [13]. The connectivity has been confirmed by NMR spectroscopic investigations and by X-ray diffraction studies (Fig. 9). No coalescence of the signals for the Cp groups was found in the $^1$H NMR spectrum even upon heating to 100 °C, suggesting that the complex exhibits no fluxionality around the dinuclear moiety.

Crabtree et al. reported that reaction of [Ir(COD)Cl]$_2$ with biphenylene gave a dimeric chloride-bridged 2,2′-bph complex which reacted with PPh$_3$ resulting in the formation of a 16-electron Ir(III) biphenylene adduct, [IrCl(2,2′-bph)(PPh$_3$)$_2$], whereas reaction with the smaller and more electron donating phosphine, PMe$_3$ resulted in the 18-electron compound [IrCl(2,2′-bph)(PMe$_3$)$_3$] (**10**) [10]. The iridacycle **10** reacted with CO, PhC≡CPh, PR$_3$ or NaBH$_4$, but disruption of the Ir(2,2′-bph) metallacycle was only observed upon addition of NOBF$_4$ and, after treatment with NaBPh$_4$, the unusual

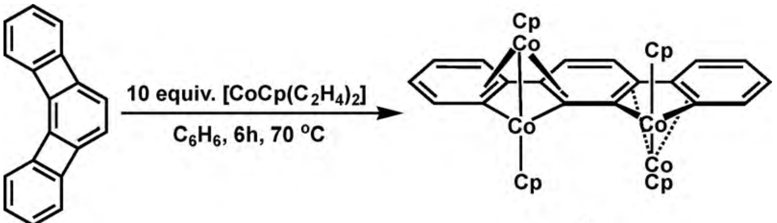

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**Fig. 8.** Double regio- and stereoselective Co insertion in angular [3]phenylene to give **9** [13].

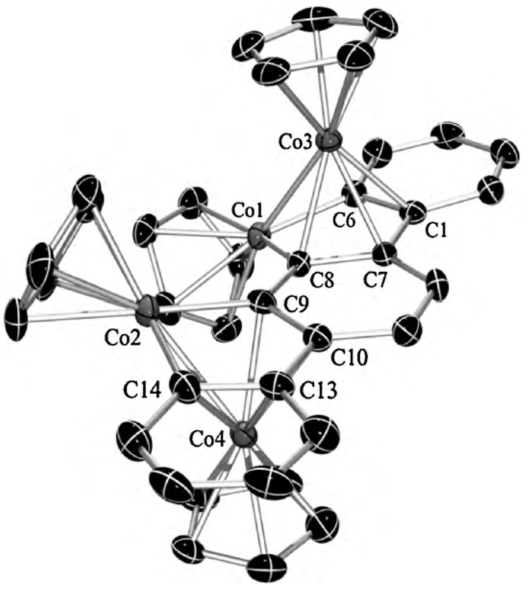

**Fig. 9.** Molecular structure of **9** in the solid state [13].

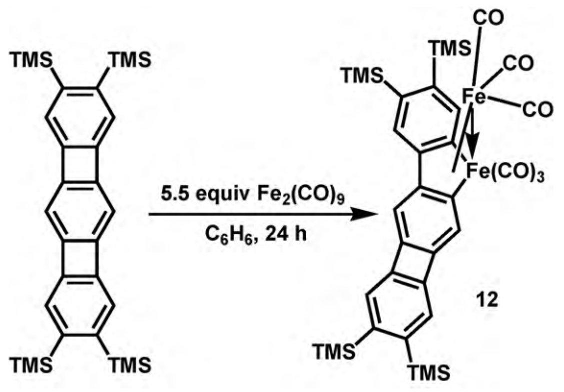

**Fig. 11.** Formation of a dibenzoferrole derivative [14].

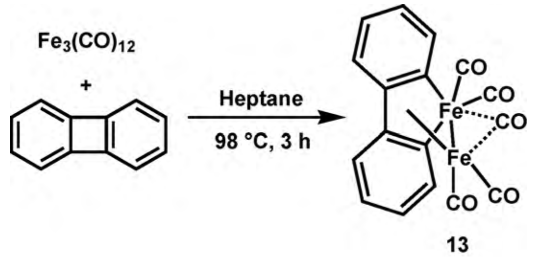

**Fig. 12.** Formation of $[Fe_2(CO)_5(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}\eta^4\text{-}bph)]$ (**13**) [15].

cationic Ir(IV) BF insertion product **11** was isolated (Fig. 10) and characterized by single-crystal X-ray diffraction.

Group 8 transition metals have been successfully inserted into the strained C–C bond of biphenylene and the related compound, benzocyclobutadienoid-[3]-phenylene [14,15]. Vollhardt et al. reported the first example of Fe insertion into benzocyclobutadienoid-[3]-phenylene to give a dibenzoferrole derivative **12** (Fig. 11) and a second, minor dibenzoferrole-$Fe(CO)_3$-π-complex. This conversion is related to the Rh and Co examples; however, in this instance, the authors depict the M–M bond as a dative interaction.

Reaction of $[M_3(CO)_{12}]$, (M = Fe, Ru, Os) directly with biphenylene gives major products of the type $[Fe_2(CO)_5(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}\eta^4\text{-}C_6H_4)_2]$ (**13**) (Fig. 12), $[Ru_2(CO)_5(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}\eta^4\text{-}C_6H_4)_2]$ (**14**) and $[Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\eta^4\text{-}C_6H_4)_2]$ (**15**), the Ru and Os analogues **14** and **15** of which have been characterized by X-ray crystallography [15]. The reactions for Fe and Ru can be completed within just a few hours at elevated temperatures (3 h/98 °C and 4 h/126 °C, respectively); however, the Os cluster is much less reactive, with 33% of $[Os_3(CO)_{12}]$ remaining even after heating to 200 °C under nitrogen in a sealed flask for 15 h. This observation is consistent with stronger M–M and M–CO bonds found in third row transition metal complexes compared to those of first and second row metals.

Garcia et al. have reacted dibenzothiophene with $[Ru_3(CO)_{12}]$ in refluxing heptane resulting in C–S bond activation and desulfurization under mild conditions to give $[Ru_2(CO)_5(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}\eta^4\text{-}C_6H_4)_2]$ (**16**) in 10% yield after column chromatography (Fig. 13) [16]. The Ru atoms are linked by a Ru–Ru bond (2.6965(9) Å) and a bridging carbonyl, and the structure has been confirmed by X-ray diffraction. The compound is readily cleaved by $H_2$ to give biphenyl. A similar reaction involving the $[NiH(^iPr_2PCH_2)_2]_2$ dimer has also been used to achieve C–S bond activation, resulting in Ni(2,2′-bph) complexes in moderate yields, although bph complexes were not the sole reaction products [17].

### 2.2. Synthesis by transmetallation

A second method for the synthesis of 2,2′-bph complexes involves transmetallation, e.g. with the help of dilithio-biphenyl or with biphenyl Grignard reagents, although this approach further limits the use of biphenyls substituted with reactive functional groups. Reaction occurs between a metal dihalide and 2,2′-dilithiobiphenyl, which can be easily prepared from 2,2′-dibromobiphenyl. Elimination of lithium halide leads to the metallacycle product. This approach is less common in the literature, but was used by Rausch and co-workers in 1973 to synthesize 2,2′-bph complexes of Co (**17**), Rh (**18**), Ir (**19**), Pt (**20**) and the first examples of Zr (**21**) and Hf (**22**) biphenyl species (Fig. 14) [18]. King and Hilton were successful in preparing the mono-, di- and tetraanionic Zr complexes $[ZrCp(2,2'\text{-}bph)_2]^-$ (**23**), $[Zr(2,2'\text{-}bph)_3]^{2-}$ (**24**) and $[Zr(2,2'\text{-}bph)_4]^{4-}$ (**25**) (Fig. 15), by reaction of 2,2′-dilithiobiphenyl with $[ZrCl_2Cp_2]$ [19]. This method has also been used for the synthesis of Pd [20,21] and other Pt [22,23] 2,2′-biphenyl complexes. Romeo et al. and Rillema et al. have both employed this route to prepare Pt(2,2′-bph) complexes

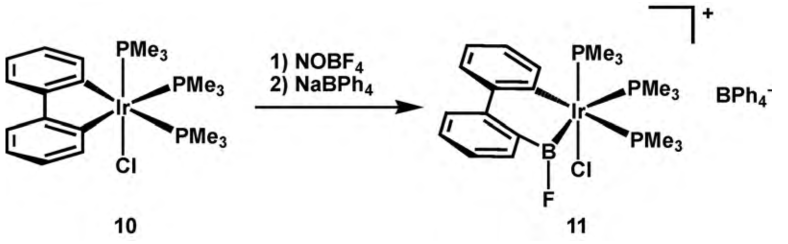

**Fig. 10.** Cleavage of the Ir–C bond in $[IrCl(2,2'\text{-}bph)(PMe_3)_3]$ (**10**) by $NOBF_4$ and BF insertion [10].

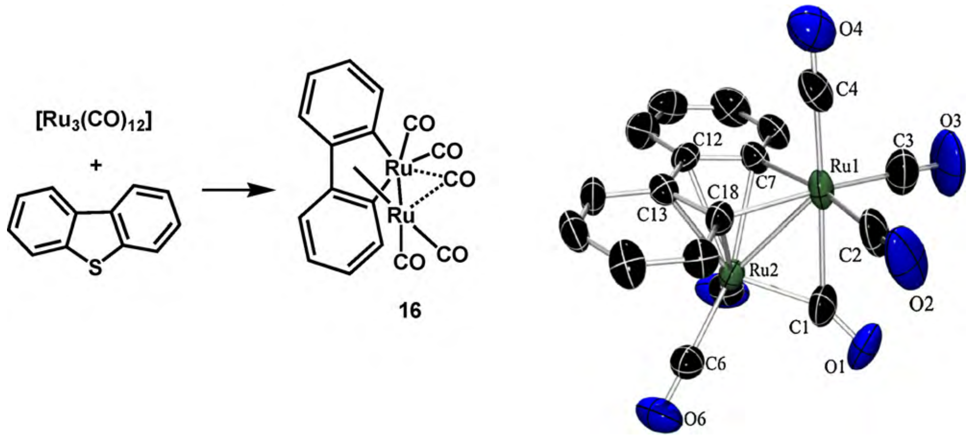

**Fig. 13.** Desulfurization of dibenzothiophene by reaction with $[Ru_3(CO)_{12}]$ (left); molecular structure in the solid state of **16** (right) [16].

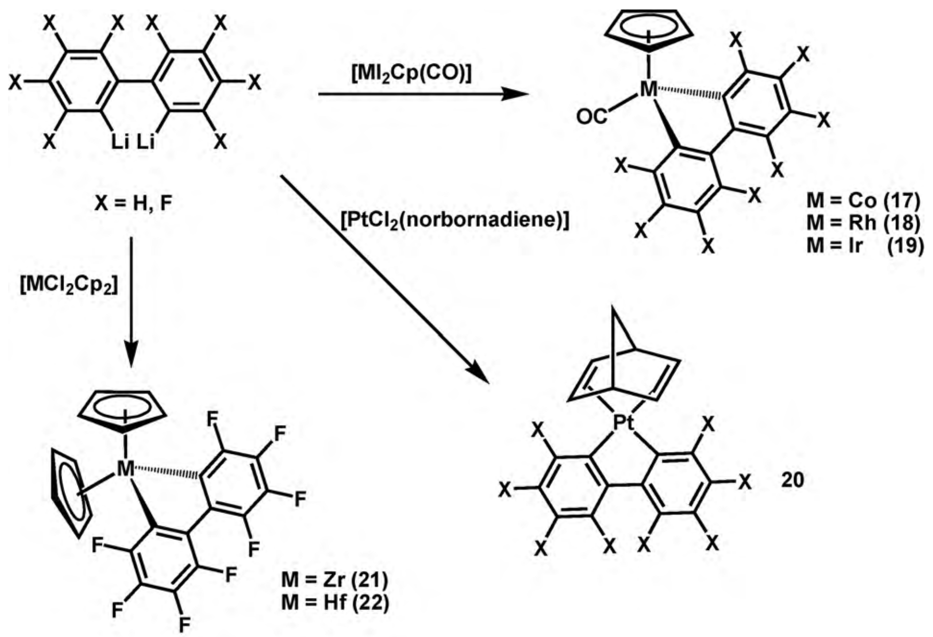

**Fig. 14.** Synthesis of transition metal 2,2′-bph complexes with 2,2′-dilithiobiphenyl [18].

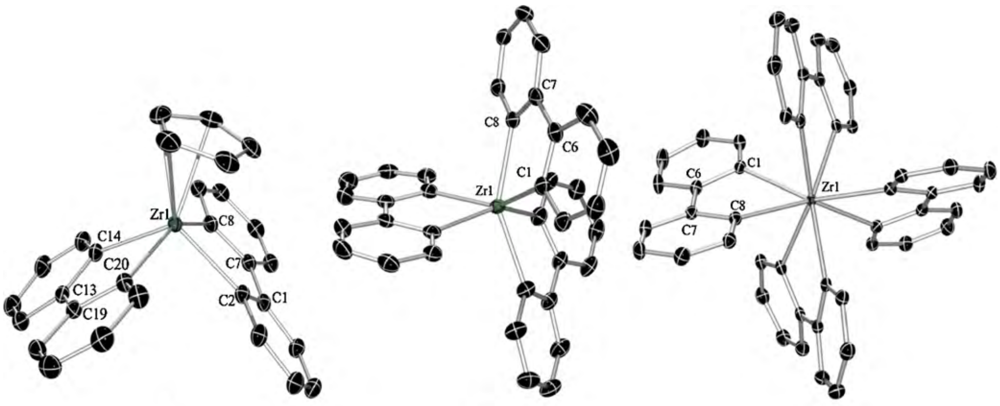

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**Fig. 15.** Molecular structures in the solid state of $[ZrCp(2,2'\text{-bph})_2]^-$ (**23**), $[Zr(2,2'\text{-bph})_3]^{2-}$ (**24**) and $[Zr(2,2'\text{-bph})_4]^{4-}$ (**25**) [19].

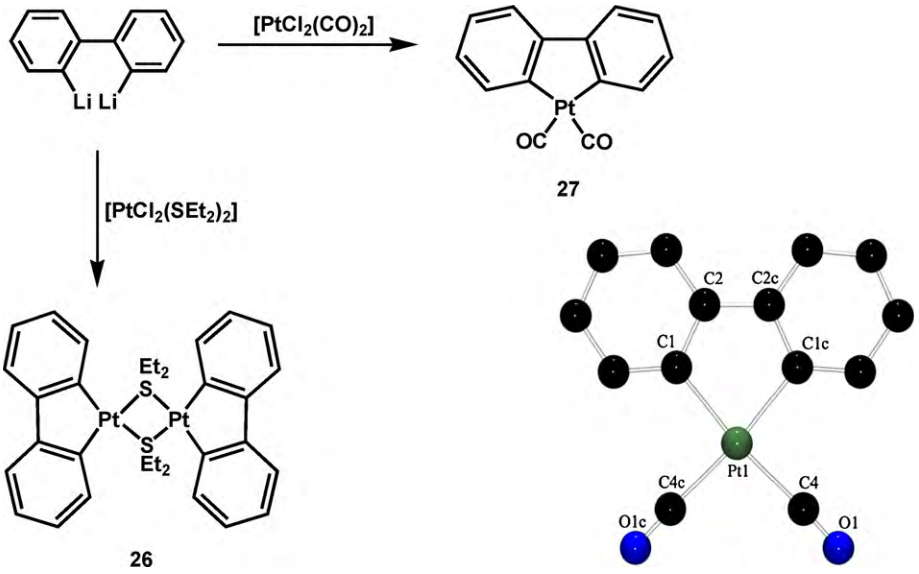


**Fig. 16.** Examples of Pt(2,2′-bph) complexes formed from Pt chloride salts and 2,2′-dilithiobiphenyl; molecular structure of **27** in the solid state [22,23].

from [PtCl$_2$(SEt$_2$)$_2$] and [PtCl$_2$(CO)$_2$], the former group having synthesized a planar Pt$_2$(SEt$_2$)$_2$ bridged species **26** and the latter group observing mononuclear [Pt(2,2′-bph)(CO)$_2$] (**27**) (Fig. 16). Romeo and co-workers also noted that the dinuclear Pt(II) complex [Pt$_2$(μ-SEt$_2$)$_2$(Hbph)$_4$] underwent intramolecular C–H activation to afford the cyclometallated species [Pt$_2$(μ-SEt$_2$)$_2$(2,2′-bph)$_2$] (**26**) and biphenyl [22]. The strongly donating PEt$_3$ ligand is useful when synthesizing Pd and Pt 2,2′-bph complexes directly *via* insertion into the C–C bond of biphenylene. The use of less basic PPh$_3$, however, resulted in Pt/Pd complexes which were unreactive to C–C bond cleavage. Analogues can, however, be prepared by reacting [PtCl$_2$(PPh$_3$)$_2$] with 2,2′-dilithiobiphenyl [24].

Examples of titanium species synthesized *via* this route are known from as early as the 1960s, with Massey and Cohen reporting the synthesis of [TiCp$_2$(perfluorobiphenyl)] (**28**) from the 2,2′-octafluorobiphenyl dilithium salt [25]. Shortly after, Rausch and Klemann reported the related non-fluorinated analogue **29**, isolated as bright red crystals in 12% yield [26]. Buchalski and co-workers observed the formation of a Ni(2,2′-bph) complex **30**, upon addition of [NiCp$_2$] to 2,2′-dilithiobiphenyl, with a Li cation coordinated to the Ni and the C2 atom of the biphenyl ligand. The coordination of DME to the Li cation generates the free anionic [NiCp(2,2′-bph)]$^-$ complex (**31**) (Fig. 17) [27].

Dibenzostannoles have also been employed as transmetallation agents for the preparation of transition metal 2,2′-bph complexes by Vicente and co-workers, who not only prepared the dibenzoplatinole [Pt(2,2′-bph)(COD)] (**32**), but also reported a series of Au(III) 2,2′-bph complexes [28] (Fig. 18). Brune et al. explored this approach further to access Pt(2,2′-bph) complexes with different substitution patterns at the bph ligand [28b].

Bercaw and Labinger were investigating the trimerization reaction of ethylene at chromium, and during the course of their work they prepared [CrBr(2,2′-bph)(PNP$^{OMe}$)] (**37**) (PNP$^{OMe}$ = (2-MeO-C$_6$H$_4$)$_2$PN(Me)P(2-MeO-C$_6$H$_4$)$_2$) by reaction of [CrCl$_3$(PNP$^{OMe}$)] with the Grignard reagent 2,2′-(MgBr)$_2$-bph [29].

### 2.3. Other routes to metal 2,2′-biphenyl complexes

Jones et al. have demonstrated the formation of Pt 2,2′-biphenyl complexes directly from CF$_3$-substituted biphenyls [30]. Reaction of 10 equivalents of 4,4′-bis(trifluoromethyl)biphenyl with [PtH(CH$_2$CMe$_3$)(dtbpm)] (dtbpm = $^t$Bu$_2$PCH$_2$P$^t$Bu$_2$) gives a transient η$^2$-arene complex which undergoes C–H activation to form two isomeric [PtH(Hbph)(dtbpm)] complexes **38** and **39**, resulting from C–H bond cleavage at the 2 or 3 position in a 5:1 ratio, respectively. Upon heating to 85 °C, a second C–H activation occurred with loss of H$_2$ giving [Pt(2,2′-(4,4′-(CF$_3$)$_2$bph))(dtbpm)] (**40**) (Fig. 19).

A seemingly unique method for preparing metal 2,2′-bph complexes has been used in the synthesis of Ir metallacycles. Wakatsuki and co-workers found that reaction of four equivalents of sodium fluorenone ketyl with [Ir(Cp*)Cl(μ-Cl)]$_2$ in THF resulted in the formation of the decarbonylation product **41** in 70% yield along with free fluorenone (Fig. 20) [9]. Presumably, this involves reduction of the Ir(III) complex to "IrCp*" followed by insertion into one of the C–C(O) bonds of fluorenone and subsequent migratory de-insertion of CO.

A rather limited route to access Ni(2,2′-bph) complexes has been discovered by Bennett et al., who reduced [NiCl(2-ClC$_6$H$_4$)(PEt$_3$)$_2$] with 1% sodium amalgam to give a nickel η$^2$-benzyne complex and the trinuclear compound **42**, which features a 2,2′-biphenylyl ligand, as a second product in up to 30% yield (Fig. 21) [31].

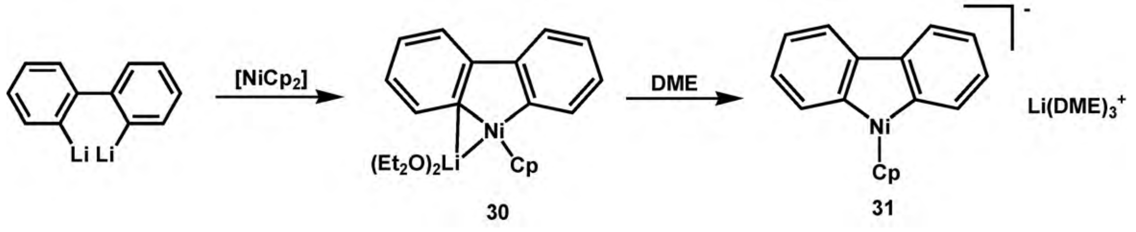


**Fig. 17.** Synthesis of the anionic [NiCp(2,2′-bph)]$^-$ complex (**31**) [27].

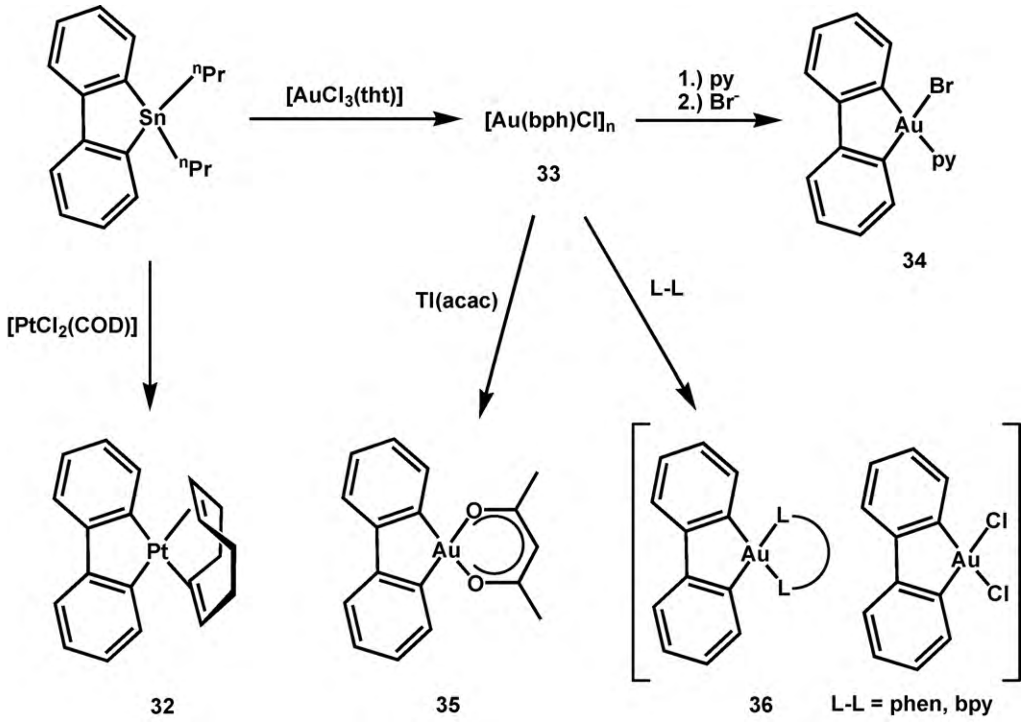


**Fig. 18.** Synthesis of Pt and Au 2,2′-bph complexes by transmetallation with dibenzostannoles (py = pyridine, phen = phenanthroline, bpy = 2,2′-bipyridine) [28].

A compound structurally similar to **42** was synthesized by Johnson et al. during their investigations on aromatic C–H bond activation mediated by nickel. They observed the formation of the trinuclear cluster $[\{Ni(PEt_3)\}_3(\mu^3\text{-}4,5\text{-}F_2C_6H_2)(\mu^3\text{-}4,5\text{-}F_2C_6H_2\text{-}4',5'\text{-}F_2C_6H_2)]$ (**43**) by C–C coupling of two 4,5-$F_2C_6H_2$ aryne units (Fig. 22) [32]. The cluster **43** exhibits one uncoupled aryne and a biarylyl unit, which forms an $MC_4$-Ni(bph) ring system (Fig. 23).

### 2.4. Catalysis by metal 2,2′-biphenyl complexes

There are a number of examples whereby metal 2,2′-bph complexes catalyze reactions that form C–C bonds or act as catalysts for the reduction of biphenylene.

Eisch [6] and Vollhardt [33] have both identified Ni(2,2′-bph) moieties as intermediates in the formation of tetraphenylene from biphenylene. Vollhardt and co-workers found that $[Ni(COD)(PMe_3)_2]$ reacted stoichiometrically with biphenylene to form tetraphenylene at 25 °C, and that the reaction proceeded catalytically (10 mol% catalyst) at 100 °C. Jones and co-workers have studied the dimerization of biphenylene to tetraphenylene at 120 °C using Pt and Pd catalysts [20]. The group has studied the mechanistic pathway and proposed that catalysis proceeds first *via* $[M(2,2'\text{-bph})(PEt_3)_2]$ (M = Pt (**44**), Pd), a compound that they have synthesized independently and characterized by X-ray crystallographic analysis, and then *via* a transient six coordinate, $[M(IV)(2,2'\text{-bph})_2(PEt_3)_2]$ intermediate (Figs. 24 and 25). The Pd analogue of $[Pt(IV)(2,2'\text{-bph})_2(PEt_3)_2]$ (**46**) was not observed, although this may be due to faster reductive elimination from Pd(IV) than from Pt(IV). The rate of the Pd catalysis was 100 times that for Pt, and decreased as the ratio of free phosphine to biphenylene increased. This observation is consistent with the formation of a $[M(2,2'\text{-bph})(PEt_3)]$ intermediate (M = Pt **45**) prior to coordination of the second equivalent of biphenylene. At this point, rearrangement can occur, and $[M(2,2'''\text{-tetraphenylene})(PEt_3)_2]$ may be formed before tetraphenylene is reductively eliminated, forming an active, coordinatively unsaturated "$M(PEt_3)_n$" species. The group has isolated and characterized $[Pt(2,2'''\text{-tetraphenylene})(PEt_3)_2]$ (**47**), with the molecular structure showing a highly distorted square-planar geometry around the metal (Fig. 25). When catalysis was attempted under an atmosphere of $H_2$, the formation of tetraphenylene was low, as biphenyl was the major product formed, the rate of which was much faster for Pd than Pt.

The room temperature addition of $H_2$ to **44** to give *trans*-$[PtH(\alpha\text{-bph})(PEt_3)_2]$ was not inhibited by added phosphine. This implies that prior phosphine dissociation from $[Pt(2,2'\text{-bph})(PEt_3)_2]$ (**44**) is not a prerequisite for $H_2$ addition. The reductive elimination of biphenyl from *trans*-$[PtH(\alpha\text{-bph})(PEt_3)_2]$ was inhibited by added phosphine. This is probably due to the fact that phosphine loss is required to achieve a *cis* geometry, from which reductive elimination can occur [20].

Jones and co-workers have studied the catalytic hydrogenolysis of biphenylene to biphenyl *via* a M(2,2′-bph) complex using Ni, Pt and Pd with a range of phosphines [34]. The metal used had the greatest overall effect on the rate of hydrogenolysis, with $[NiH(dippe)]_2$ proving to be the most active, giving 16 turnovers per day at 50 °C, considerably higher than that for Pd or Pt.

Crabtree et al. reported that iridium 2,2′-bph complexes are active catalysts in the dimerization of terminal alkynes to *E,Z*-enynes (Fig. 26) [35]. $[IrCl(2,2'\text{-bph})(PMe_3)_3]$ (**10**), in the presence of $AgBF_4$, is effective in head-to-head coupling, the main isomer being the thermodynamically less stable *E*-isomer, unless $PMe_3$ is present which can block the isomerization of the intermediate vinyl complex. $AgBF_4$ is necessary to remove $PMe_3$ and $Cl^-$ to generate the active catalyst $[Ir(2,2'\text{-bph})(C{\equiv}CR)(\eta^2\text{-}HC{\equiv}CR)(PMe_3)_2]$ (**48**) from the initial Ir complex. The authors attribute the preference for head-to-head dimerization to the exceptionally low steric bulk of the catalyst in the plane of the insertion reaction.

In the presence of stoichiometric, or in some cases, catalytic amounts of *p*-cresol, $[Pd(PPh_3)_4]$ was a catalyst for the formation of functionalized biphenyl compounds [36]. The vinylic C–H bond of alkenes can be added across the strained biphenylene C–C bond, a reaction promoted by weak acids. Under similar conditions, ketones and nitriles that possess α-hydrogen atoms can also add across the biphenylene C–C bond to form biaryl derivatives, and

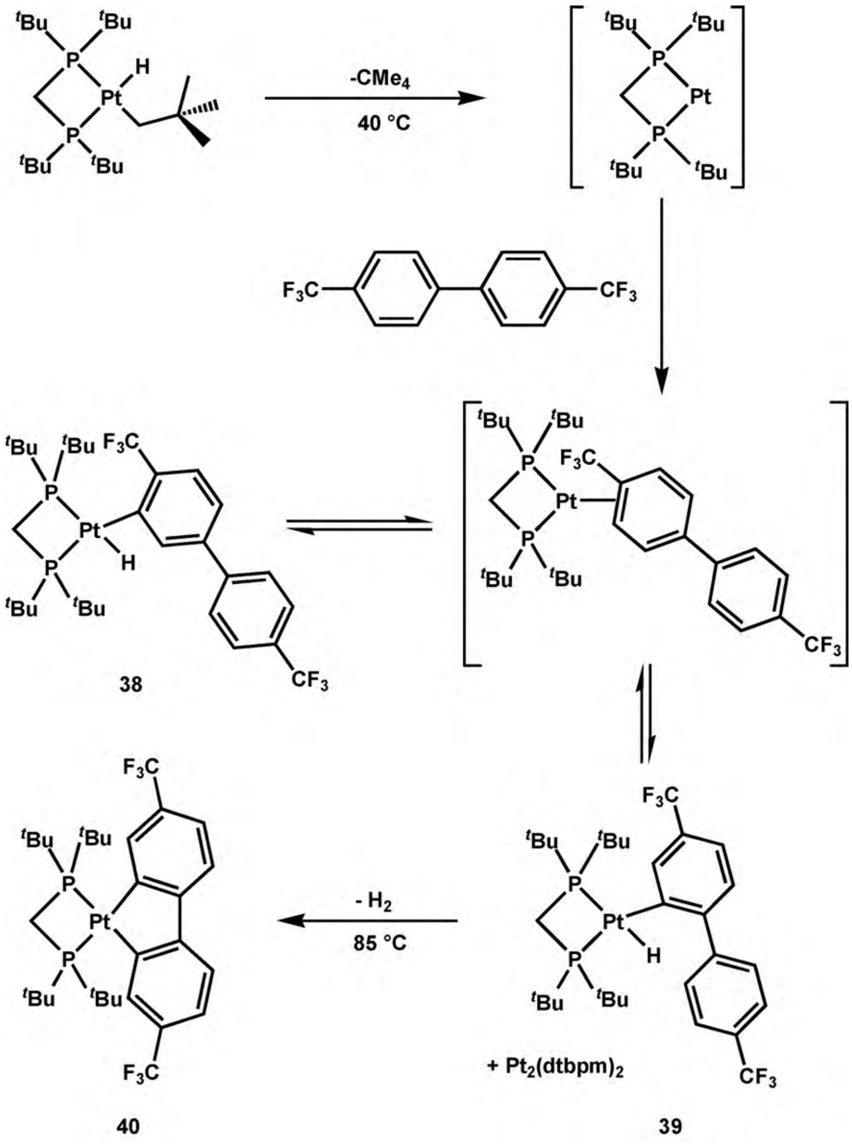


**Fig. 19.** Formation of [Pt(2,2′-bph)(dtbpm)] (**40**) by C–H activation of 4,4′-bis(trifluoromethyl)biphenyl [30].

reaction with arylboronic acids gives *ortho*-terphenyl derivatives (Fig. 27). Although [Pd(2,2′-bph)(PPh$_3$)$_2$] (**49**) was not observed in these reactions, its presence was inferred from the products formed.

A number of examples whereby Ni complexes catalyze the formation of 9,10-disubstituted phenanthrenes are known. Jones et al. used [Ni(dippe)(RC≡CR)] (R = Ph, Me) complexes with biphenylene to form disubstituted phenanthrenes catalytically in moderate yields [37,38]. Under nitrogen, the reaction proceeded slowly, even at 120 °C. Addition of 6 mol% of oxygen to the reaction vessel led to an acceleration of the rate at lower temperatures (70–80 °C) (Fig. 28). The oxygen is not involved in oxidation of the metal, but oxidizes the phosphine ligand, generating a more active, coordinatively unsaturated Ni species. N-heterocyclic carbene Ni complexes have also been used in the synthesis of phenanthrolines by reaction of alkynes with biphenylene [39]. Two mol% of [Ni$_2$($^i$Pr$_2$Im)$_4$(COD)]

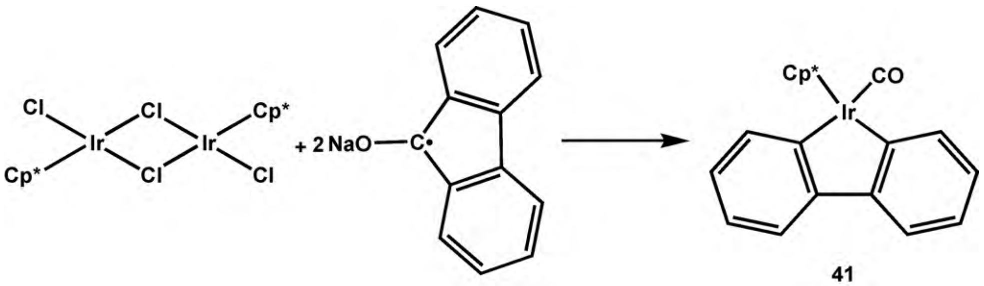


**Fig. 20.** Synthesis of [Ir(2,2′-bph)(Cp*)(CO)] (**41**) by decarbonylation of sodium fluorenone ketyl [9].

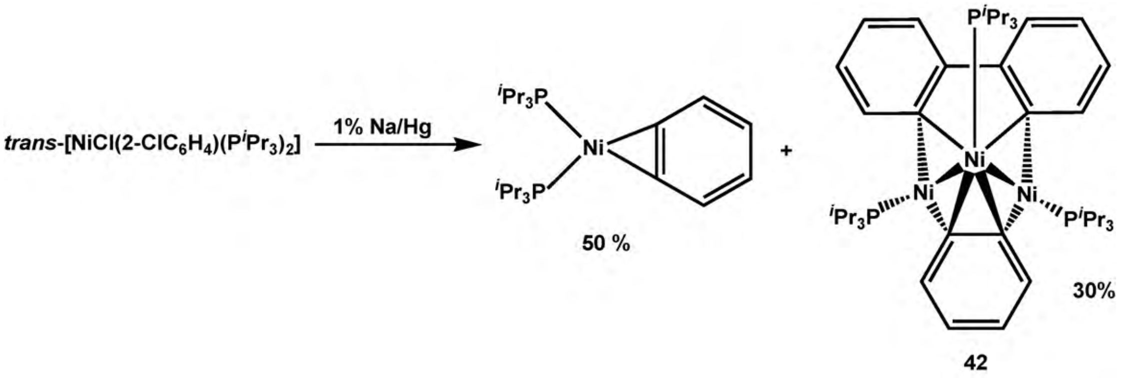


**Fig. 21.** Synthesis of the trinuclear Ni cluster **42** by reduction of *trans*-[NiCl(2-ClC$_6$H$_4$)(P$^i$Pr$_3$)$_2$] [31].

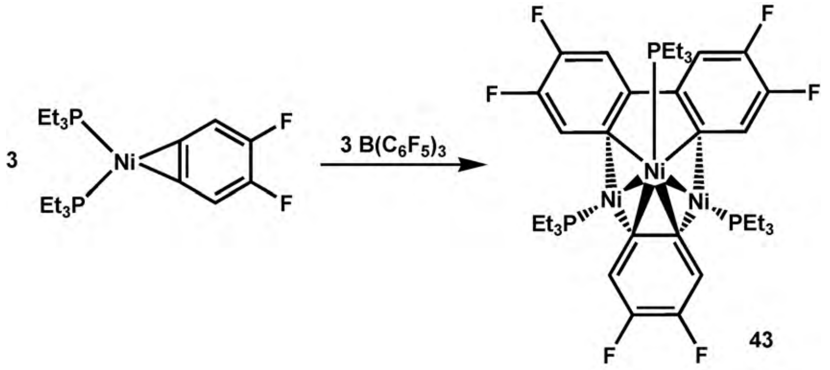


**Fig. 22.** Synthesis of **43** by C–C coupling of two 4,5-F$_2$C$_6$H$_4$ aryne units in [Ni($\eta^2$-4,5-F$_2$C$_6$H$_4$)(PEt$_3$)$_2$] [32].

($^i$Pr$_2$Im = 1,3-di(iso-propyl)imidazole-2-ylidene) as catalyst precursor at 80 °C gave quantitative conversion of biphenylene and diphenylacetylene to 9,10-diphenylphenanthrene in 30 min.

[RhCl(2,2′-bph)(dtbpm)] (dtbpm = $^t$Bu$_2$PCH$_2$CH$_2$P$^t$Bu$_2$) has been used to form substituted phenanthrenes catalytically in good yields [40]. Olefins such as norbornene and *p*-methyl styrene also undergo catalytic insertion. The complex is also reactive towards Lewis bases at room temperature, and has been used in the synthesis of 9-fluorenone and 9-(*tert*-butylimino)fluorene, although this was not catalytic.

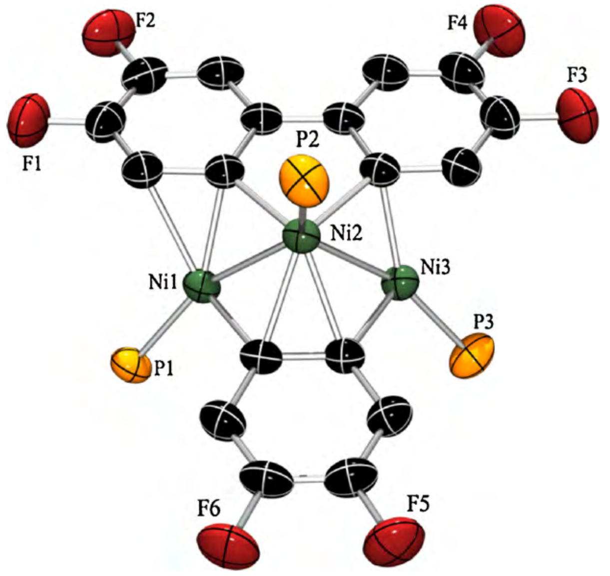


**Fig. 23.** Molecular structure of **43** in the solid state with the Et groups of the PEt$_3$ ligands omitted for clarity [32].

Jones et al. have shown that the Ni(0) complexes [Ni($\eta^2$-PhC≡CR)(PN)] (R = Ph, $^t$Bu; PN = Me$_2$NCH$_2$CH$_2$P$^i$Pr$_2$) are effective catalysts for C–C bond activation in biphenylene and functionalization with PhC≡CPh or $^t$BuC≡CPh to give 9,10-disubstituted phenanthrenes [38]. It was found that P,N-substituted Ni(0) had an enhanced reactivity over the analogous P,P-substituted Ni(0) complex. This could be due to the hemilabile character of the P,N ligand. The proposed mechanism for the formation of 9,10-diphenylphenanthrene is shown in Fig. 29.

Dissociation of the NR$_2$ group from the nickel atom, which allows for a vacant coordination site, is the first step in the proposed mechanism. The now highly reactive metal center is able to cleave the C–C bond in biphenylene to generate the Ni(II) intermediate **50**. The Ni(II) species **51** is then formed upon insertion of the alkyne into the Ni–C bond. The regeneration of the Ni(0) complex is attained by reductive elimination of 9,10-diphenylphenanthrene and complexation of a second alkyne [38].

### 2.5. Luminescent transition metal 2,2′-biphenyl complexes

Photophysical properties of several Pt [21,23,41,42] and Pd [21,43] 2,2′-biphenyl complexes have been reported. These are of interest with regard to possible use in OLEDs and other luminescent applications which require accessible triplet states, cf. the now popular 2-phenylpyridine complexes mentioned in the Introduction [3,4]. Rillema and co-workers have extensively studied the absorption and emission properties of a number of Pt(2,2′-bph) complexes with the mono- and bidentate ligands, pyridine, acetonitrile, ethylenediamine, CO (**27**) [23,42], dppm [44,45], and the bridging ligand SEt$_2$ [41]. Absorption spectra of mono-metallic [Pt(2,2′-bph)(py)$_2$] (**52**), [Pt(2,2′-bph)(NCMe)$_2$]

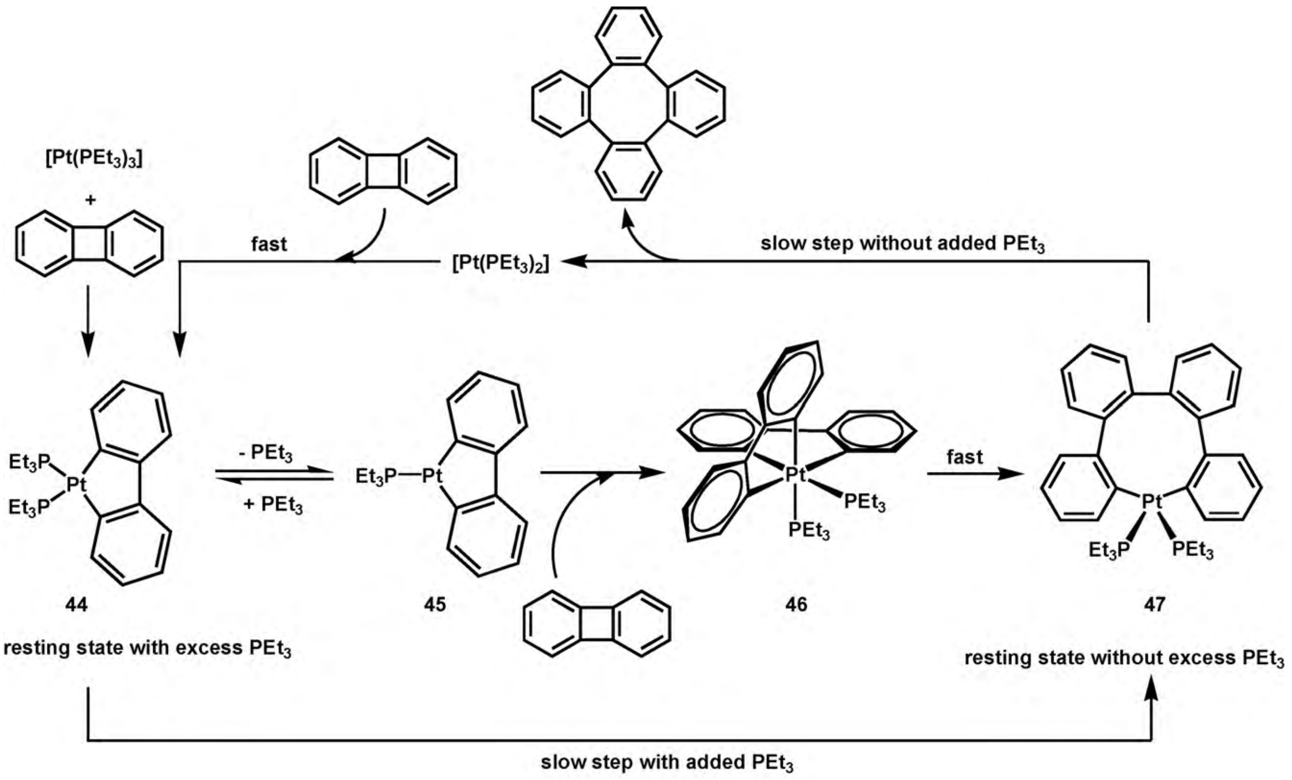
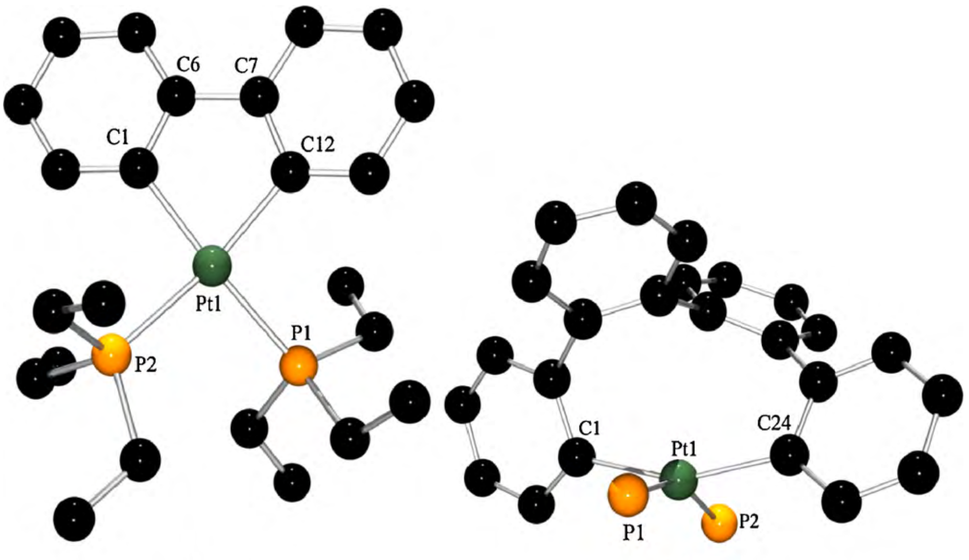


**Fig. 24.** Proposed mechanism for the catalytic dimerization of biphenylene mediated by Pt [20].

(**53**), [Pt(2,2′-bph)(en)] (**54**) and bimetallic $[Pt(2,2'\text{-bph})(SEt_3)]_2$ (**26**) complexes showed HOMO–LUMO $d\pi_{(Pt)} \rightarrow \pi^*_{(bph)}$ transitions around 300–400 nm and intra-ligand $\pi \rightarrow \pi^*$ transitions at higher energy. The compounds exhibit strong luminescence in solution, attributable to emission from excited intra-ligand triplet states ($^3$IL) dominated by the biphenyl ligand, as indicated by the vibrational progression in the photoluminescence spectra. The spectra of all of the compounds were remarkably similar, and lower energy bands between 490 and 620 nm were observed with little change in the profile at 77 K. Triplet lifetimes of 3–14 μs were recorded, and the measured quantum yields for the mono-metallic complexes were ca. 0.16, and for the bimetallic species ca. 0.08. The complex $[Pt(2,2'\text{-bph})(CO)_2]$ (**27**) was a weak emitter in solution, with emission at 562 and 594 nm, and triplet lifetimes between 2 and 3 μs in $CH_2Cl_2$ were reported. Except in very dilute solution, the complex readily self-associated leading to a number of emitting species such as dimers and higher aggregates in solution. Emission was also detected from stacked Pt(II) complexes in the solid state. Thus, the solid showed a non-structured emission band at 726 nm, with a shortened lifetime of 0.84 μs [46]. Time-dependent density functional theory (TD-DFT) studies of the spectroscopic properties related to aggregation in the Pt(II) 2,2′-bph dicar-



**44** **47**

**Fig. 25.** Molecular structures of **44** and **47** (Et groups omitted for clarity) in the solid state [20].

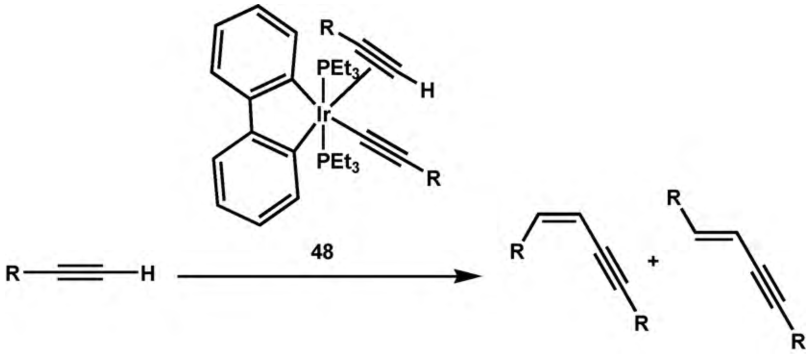


**Fig. 26.** Formation of *E,Z*-enynes by head-to-head coupling of alkynes with Ir(2,2′-bph) catalyst **48** [35].

bonyl complex **27** have been carried out to examine singlet and triplet excited states, and to compare calculated geometries with those from the X-ray crystallographic data previously obtained [42,43].

The heterobimetallic complex [Fe($\eta^5$-$C_5H_4PPh_2$)$_2$Pt(2,2′-bph)] (**55**) has been synthesized and characterized by X-ray crystallography, and the photophysical properties of the compound have been studied [47]. Upon coordination to Pt, the {Fe($\eta^5$-$C_5H_4PPh_2$)$_2$} $d\pi_{(Fe)} \rightarrow \pi^*_{(Cp)}$ MLCT transition was blue shifted from 442 to 425 nm, and a $d\pi_{(Pt)} \rightarrow \pi^*_{(bph)}$ MLCT transition was observed at 337 nm, with a lifetime of 6.7 μs (at 77 K). At room temperature, the emission lifetime was too short to be recorded using a nanosecond laser, and the work suggests quenching of the triplet emission by the ferrocenyl moiety *via* an electron transfer mechanism.

Luminescent metallopolymers based on Ir(2,2′-bph) complexes have been prepared and investigated with regard to their photophysical properties by Matsubara et al. (Fig. 30) [48]. The non-polymer analogs **56a–f** all showed similar $^1$MLCT absorptions

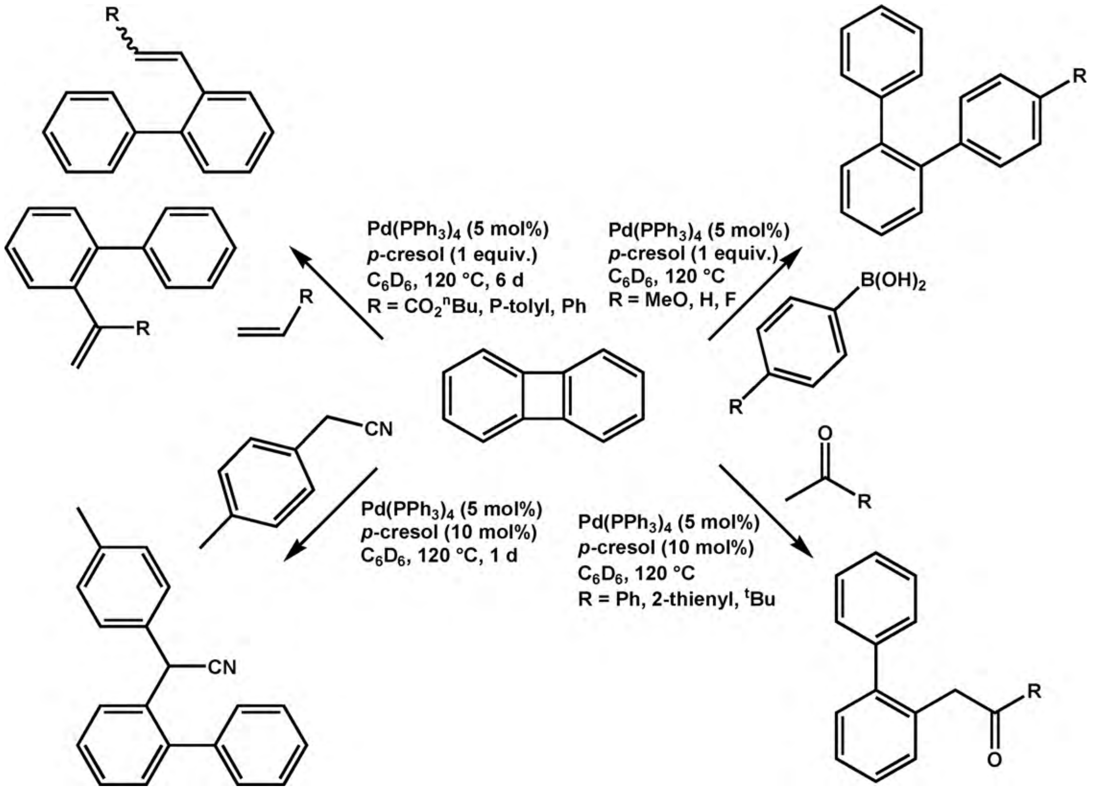


**Fig. 27.** Pd catalyzed formation of functionalized biphenylene derivatives [36].

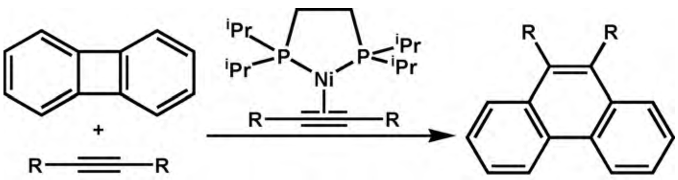


**Fig. 28.** Catalytic formation of 9,10-disubstituted phenanthrenes (R = Me, Ph, $CO_2Me$, TMS) [37,38].

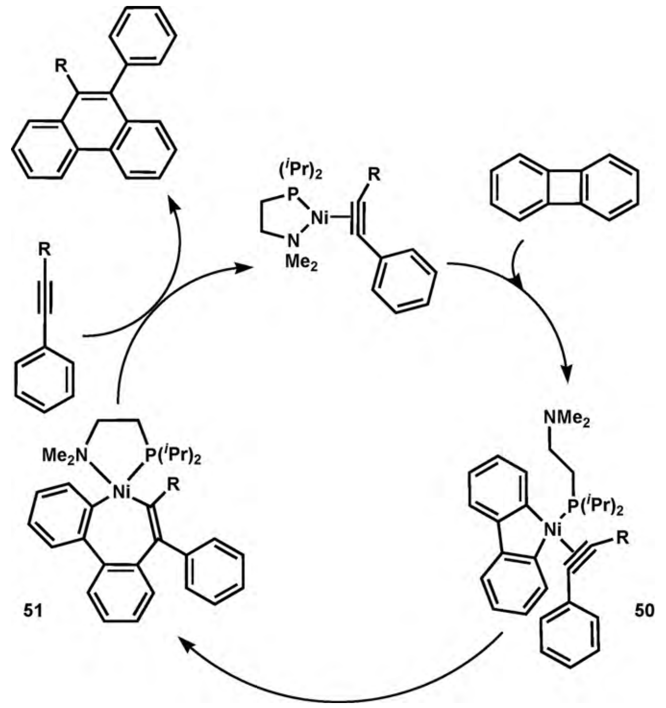


**Fig. 29.** Proposed mechanism for the formation of 9,10-diphenylphenanthrene [38].

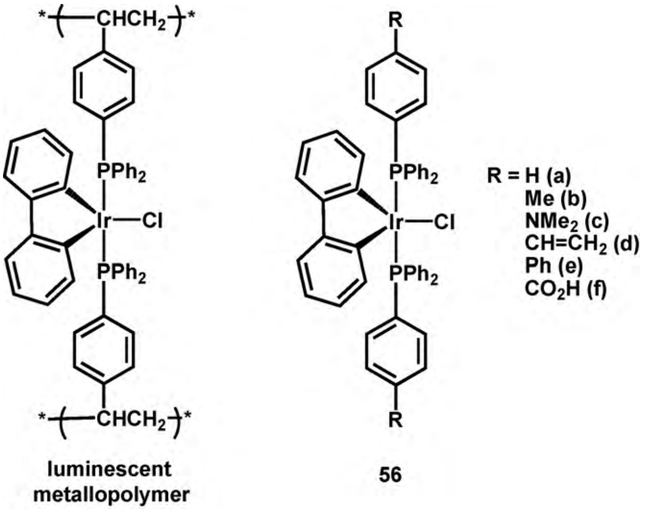


**Fig. 30.** Ir(2,2′-bph) complexes **56** employed in luminescent metallopolymers [48].

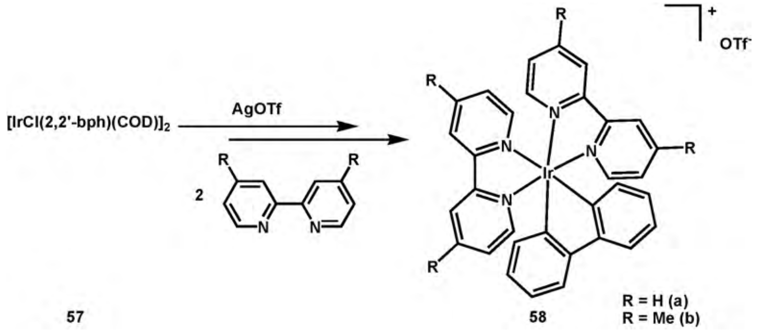


**Fig. 31.** Synthesis of phosphorescent cationic [Ir(2,2′-bph)(2,2′-bpy)$_2$]$^+$ complexes **58** [49].

between 361 and 368 nm and additional $^3$MLCT absorption around 490 nm. The emission occurred between 577 and 618 nm with a quantum yield below 0.017 in the solid state, but no lifetimes have been reported. The intensity of the photoluminescence in the polymers increased with increased Ir content; however, a self-quenching process led to lower quantum yields when the Ir content in the polymer exceeded a concentration of ca. 0.2 mmol/g.

Hur and co-workers have very recently synthesized Ir complexes **58a** and **b** with both 2,2′-bpy and 2,2′-bph ligands by successive addition of the bipyridine ligand to [IrCl(2,2′-bph)(COD)]$_2$ (**57**) (Figs. 31 and 32) [49]. $^1$MLCT absorption was observed at 375 nm, whereas the $^3$MLCT excitation occurred red-shifted at 480 nm. Both complexes, **58a** and **b**, exhibit weak phosphorescence with quantum yields of 0.007–0.013. DFT studies showed that the HOMO is an admixture of the 2,2′-bph(π) and Ir(d) orbitals, while the LUMO is located at the 2,2′-bipyridine ligand. The authors assume the $^1$MLCT and $^3$MLCT states to arise from a HOMO → LUMO transition, and thus control of the emitting excited states should be possible by proper modification of the biphenylyl and bipyridine ligands, respectively.

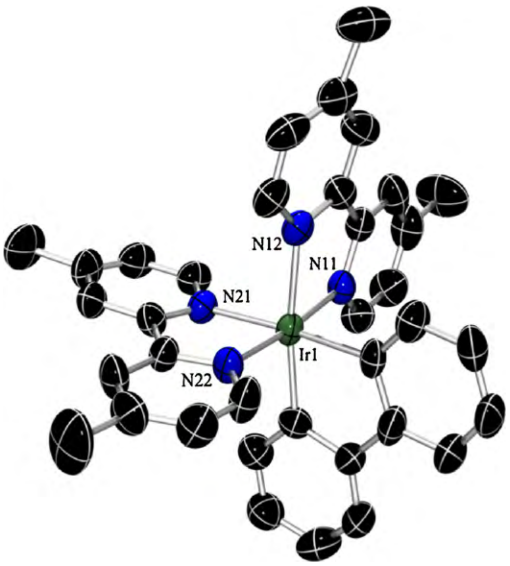


**Fig. 32.** Molecular structure of the cation [Ir(2,2′-bph)(2,2′-bpy)$_2$]$^+$ (**58b**) in the solid state [49].

## 3. Metallacyclopentadienes

### 3.1. Catalytic [2 + 2 + 2] cycloaddition reactions

Research on the mechanism of catalytic alkyne trimerizations first highlighted an MC$_4$ transient species as an intermediate in the catalytic cycle. These intermediates are formed from the reductive coupling of two equivalents of alkyne with temporary oxidation of the metal center (Fig. 33). Collman et al. used isotopically labelled substrates with Rh(I) and Ir(I) catalysts to examine the sequential cyclotrimerization of alkynes, and they proposed a mechanism from these experiments [50]. The authors highlighted the formation of metallacycle (b) and alkynyl π-complex (c) as intermediates. It was found that cyclotrimerization could be suppressed if the reaction proceeded under a 60 psi pressure of CO. By blocking the latent

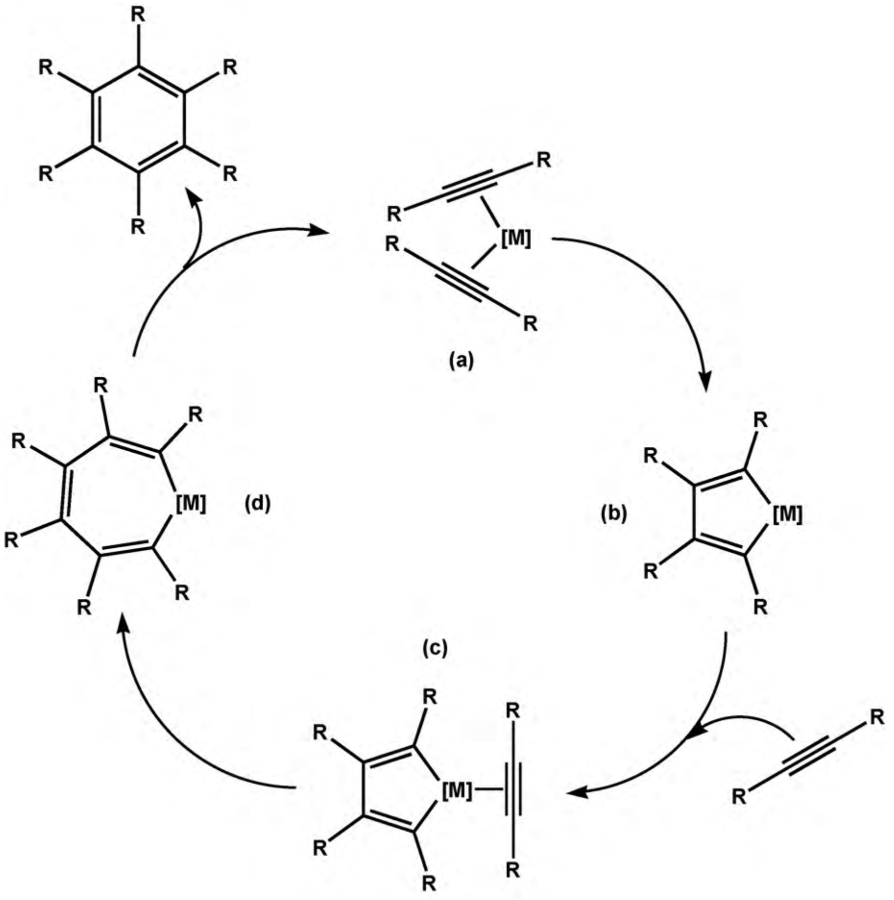


**Fig. 33.** General catalytic cycle for the cyclotrimerization of internal alkynes [50].

coordination site required for alkyne complexation using CO, the reaction could be stopped. This argues against a Diels–Alder mechanism for benzene formation, which should not be inhibited by CO coordination. They also found that even under forcing conditions, maleic anhydride did not react with (b). This also argues against the Diels–Alder mechanism for this system. Formation of a seven membered metallacycloheptatriene (d) is thus suggested, followed by reductive elimination of benzene.

Interestingly, it has been found that the use of {RuCp} fragments can lead to the formation of ruthenacyclopentatrienes, which are resonance isomers of the metallacyclopentadiene structure (b) in Fig. 33. Kirch et al. have shown that such metallacyclopentatrienes are capable of rearrangements to give allyl carbenes, butadienyl carbenes and $\eta^4$-cyclobutadienyl complexes, quenching the catalytic activity in [2 + 2 + 2] cyclotrimerization reactions [51]. However, they are key intermediates in the catalytic head-to-head coupling of terminal alkynes and additions of carboxylic acids [52].

Catalytic [2 + 2 + 2] cyclotrimerization of alkynes has been extensively investigated, and catalysts based on many early to late transition metals are known [53–56]. Recently, research has been concerned with the synthesis and characterization of metallacyclic intermediates, which can be isolated with the use of appropriate metal centers and ligands around the metal and studied as independent species [57]. Metallacyclic compounds of this type are known for a wide range of transition metals, including Ti [58,59], Zr [60], Hf [61,62], Pt [63], Pd [64], Ir [50,65], Ru [66], W [67,68], Fe [69], Au [70], Rh [71] and Co [53,72]. There are a vast number of such complexes, and their more complex derivatives, and these will not be reviewed here.

Another area which has been reviewed recently, is the [2 + 2 + 2] cycloaddition of alkynes with nitriles to form pyridines [4]. The mechanism has been investigated in great detail with Co, but has been accepted for this type of reaction in general (Fig. 34).

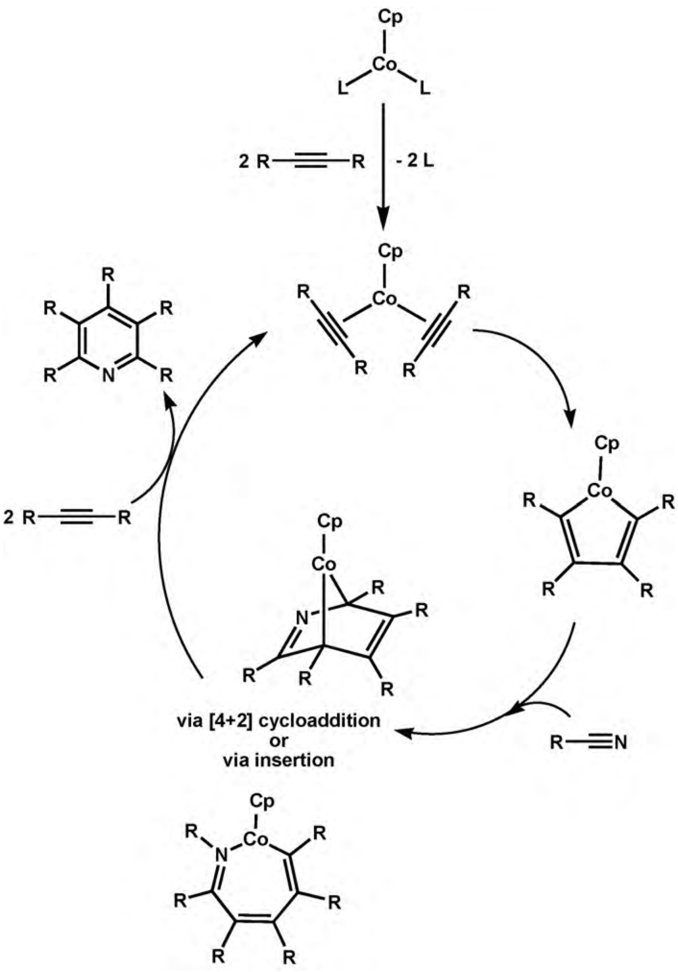


**Fig. 34.** General catalytic cycle for the [2 + 2 + 2] cycloaddition of alkynes with nitriles at Co [4].

## 3.2. Reductive coupling of buta-1,3-diynes

Reductive coupling of buta-1,3-diynes to form bis-ethynylmetallacyclopentadienes is also known, although examples are limited. Nishihara et al. reacted [CoCp(PPh$_3$)$_2$] with diphenylbuta-1,3-diynes to form a mixture of diethynylcobaltacyclopentadienes [73]. Three regioisomers **59**–**61** were found, as well as an insoluble polymeric product (Fig. 35). The major isomer formed was the asymmetric 2,4-dialkynyl isomer **60**, with the symmetrical 2,5-dialkynyl complex **59** only observed when the reaction was undertaken at elevated temperature. Interestingly, the group found that when Me$_3$Si–C≡C–C≡C–SiMe$_3$ and Me–C≡C–C≡C–Me diynes were used, only single metallacycle isomers were formed. The 2,4-dialkynyl metallacyclopentadiene was formed from the bulkier Me$_3$Si–C≡C–C≡C–SiMe$_3$, whereas the less bulky 2,4-hexadiyne afforded the 2,5-dialkynyl metallacyclopentadiene.

These results fit rules proposed by Wakatsuki et al., who previously studied cobalt metallacycle formation with a wide range of alkynes and found that regioselectivity of the cyclization reaction was determined by the steric factors of the alkynes used rather than their electronic properties [74]. Reaction of diphenylbutadiyne with [Ru$_3$(CO)$_{10}$(NCMe)$_2$] in the presence of Me$_3$NO also produced a mononuclear 2,5-dialkynyl ruthenacyclopentadiene complex, but the yield was low (1.5–4%) [75]. Marder and co-workers have

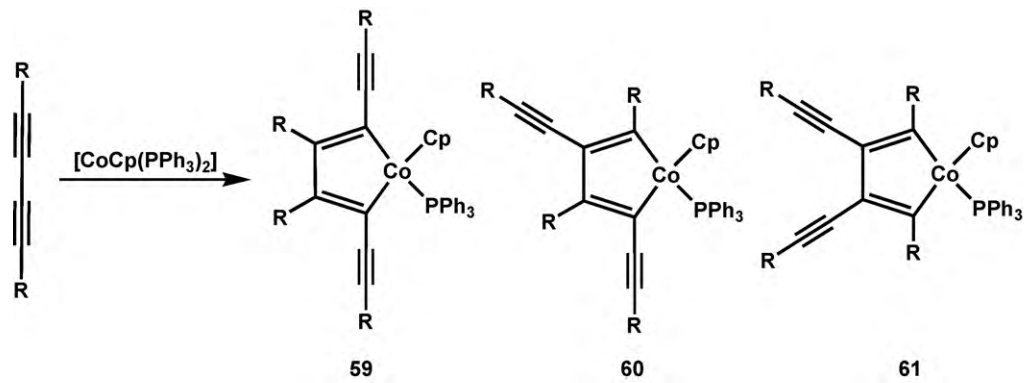


**Fig. 35.** Formation of three stereoisomers **59**–**61** by reductive coupling of butadiynes at {CoCp(PPh$_3$)} [73].

developed a high yield, one-pot, regiospecific synthesis of a luminescent rhodacyclopentadiene from 1,4-di-*p*-tolylbuta-1,3-diyne and [Rh(C≡C-TMS)$(PMe_3)_4$] [76]. The 2,5-isomer **62** is formed exclusively in quantitative yield and has been characterized by X-ray crystallography (Figs. 36 and 37).

The reductive coupling of bis-diynes at Rh precursors bearing either a TMSA or a dithiocarbamate ligand gave rhodacyclopentadienes with a rigid backbone in quantitative yields, which are structurally related to **62** (Fig. 38) [77]. Compounds **63** and **64** display highly interesting photophysical properties, namely fluorescence with lifetimes of a few ns and quantum yields of 0.3–0.7. Although singlet oxygen sensitization and ps-time resolved IR spectroscopic studies do indicate the formation of a triplet state after photo excitation, as would have been expected for transition metal compounds due to the “heavy atom effect” of the metal, the intersystem crossing from the excited singlet state $S_1$ to the triplet state $T_1$ occurs with a rate constant two orders of magnitude slower than expected for an organometallic system containing a second row transition metal. Phosphorescence in the 400–1000 nm wavelength range has not been observed in these compounds, even at 77 K in a frozen glass.

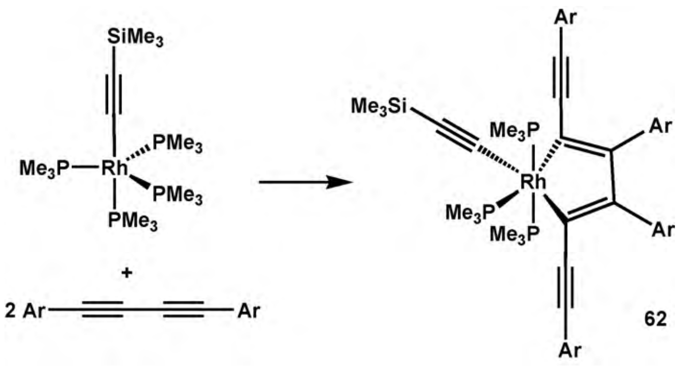


**Fig. 36.** Regiospecific formation of **62** (Ar = 4-MeC$_6$H$_4$) [76].

Hill and co-workers have explored the regioselective synthesis of the ruthenacyclopentadiene compound, [Ru{κ$^2$-(PhC≡C)=CPhCPh=(C≡CPh)}$(CO)_2(PPh_3)_2$] (**63**) and its structure has been determined by X-ray crystallography (Fig. 39) [78]. They observed the exclusive formation of the 2,5-dialkynyl isomer by

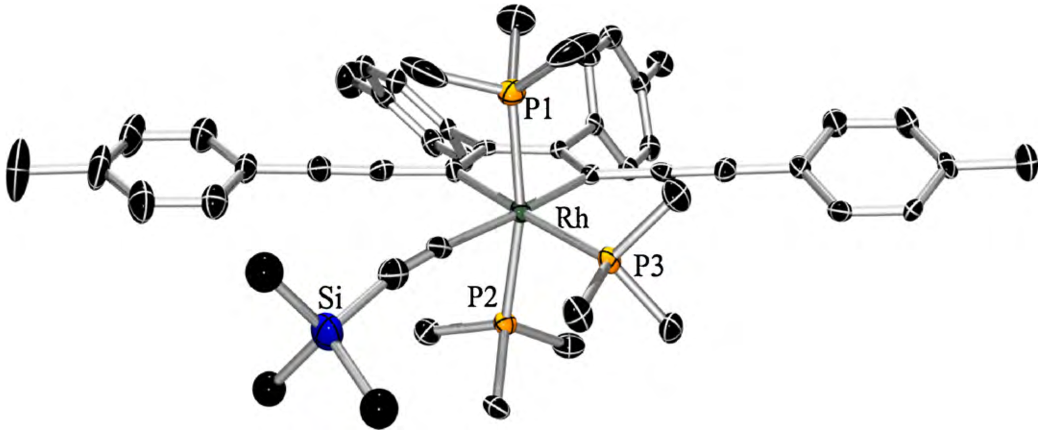


**Fig. 37.** Molecular structure of **62** in the solid state [76].

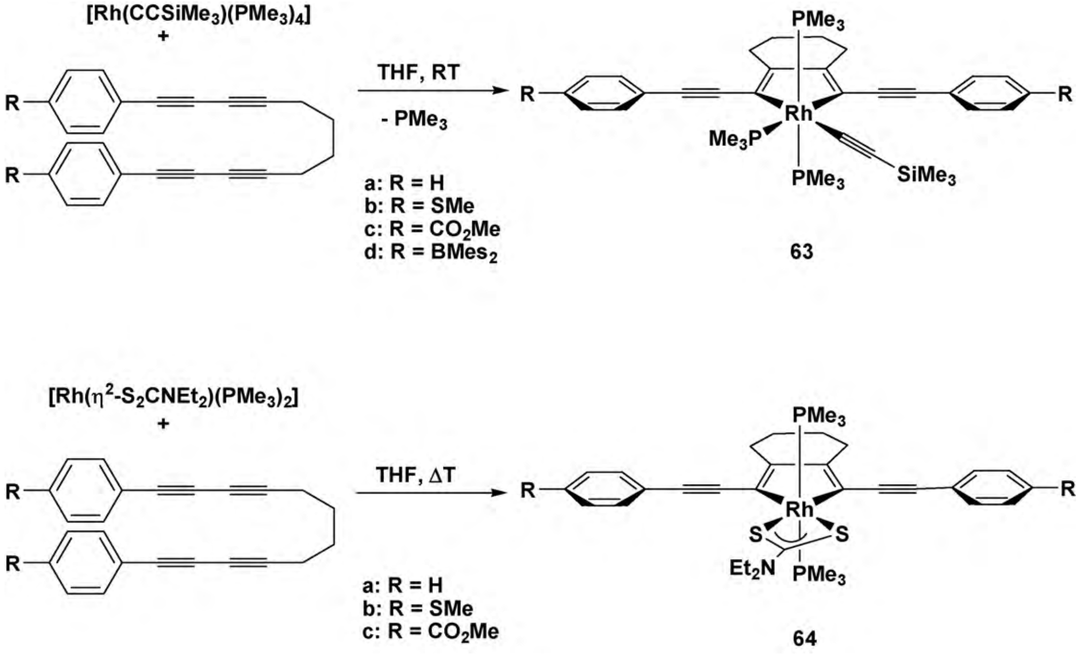
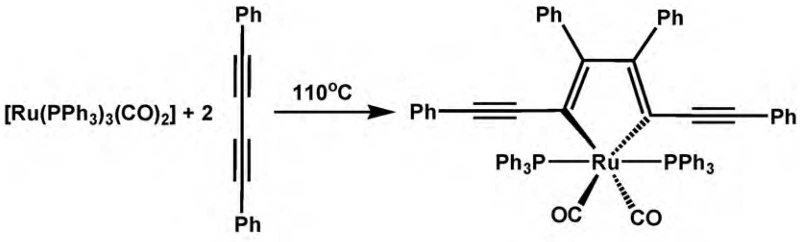
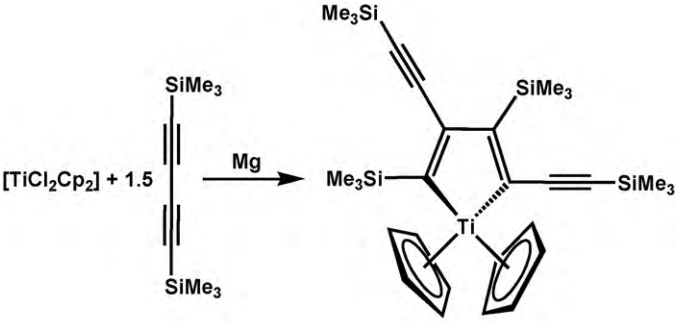


**Fig. 38.** Synthesis of **63** and **64** by reductive coupling of bis-diynes [77].



**65**

**Fig. 39.** Regiospecific formation of ruthenacyclopentadiene **65** [78].



**66**

**Fig. 40.** Synthesis of the 2,4-diethynyltitanacyclopentadiene **66** [81].

reaction of $[Ru(CO)_2(PPh_3)_3]$ with excess diphenylbuta-1,3-diyne; however, optical properties of the ruthenacycle were not reported.

Titanium analogues have also been studied [79–81]. Reaction of $[TiCl_2Cp_2]$ with two equivalents of $Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3$ afforded the 2,4-diethynylmetallacycle **66** in 65% yield, the structure of which has also been determined by X-ray crystallography (Figs. 40 and 41). Zr analogues of Ti metallacycles have been proposed as intermediates in the formation of seven-membered cyclic cumulenes, although they have not been isolated [82]. Buchwald and co-workers attribute the larger size of Zr compared to Ti as an explanation for the fact that the Ti metallacycle can be isolated without cumulene formation whilst the Zr analogue was not observed. The only other example of this type of compound is an osmium complex, formed by reaction of $[Os(en)_2(H_2O)(H_2)]$ with 2,4-hexadiyne, producing the 2,5-diethynylmetallacycle exclusively [83].

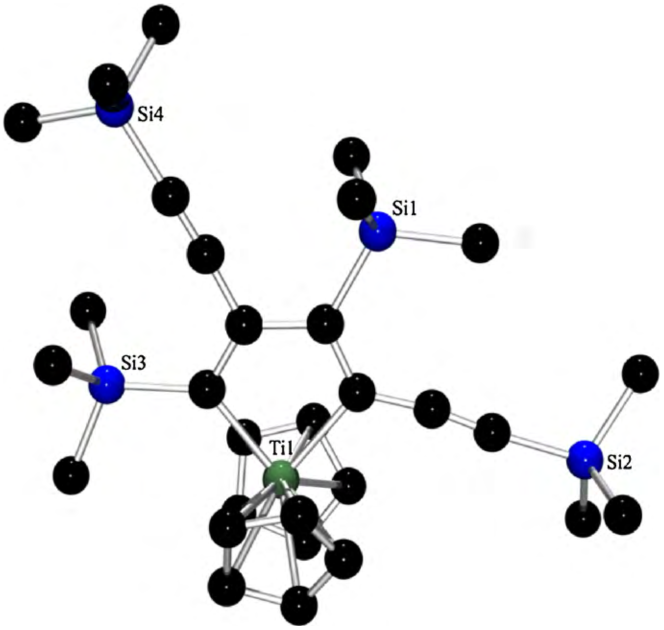


**Fig. 41.** Molecular structure of bis($\eta^5$-cyclopentadienyl)-2,4-bis(trimethylsilylethynyl)-3,5-bis(trimethylsilyl)titanacyclopenta-2,4-diene (**66**) in the solid state [81].

### 3.3. *Metallacyclopentadiene-containing polymers*

π-Conjugated polymers containing $MC_4$ units are currently under investigation. These heteroaromatic polymers are structurally analogous to organic polymers such as poly(pyrrole) and poly(thiophene). Examples are known from reactions of bisalkynes of the type $R{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}R'$ (where Ar = a range of aromatic units, R/R′ = H, Me, TMS) with transition metal compounds such as $[RuBr(^n hexCp)(COD)]$ [84], $[CoCp(PPh_3)_2]$ [85], $[Co(^n hexCp)(PPh_3)_2]$ [86,87] and "$ZrCp_2$" [88].

Nishihara and co-workers were the first group to prepare and characterize polymers of this type, successfully isolating a number of poly(arylene cobaltacyclopentadienylene)s [87]. They found that use of Cp as a ligand on Co resulted in insoluble polymers. The highest molecular weights were achieved when the ratio of bisalkyne to metal complex was close to unity. Cyclization at the metal was regiospecific, with the 2,5-isomer forming exclusively to give linear polymers. However, reaction of 1,4-diethynylbenzene with hexyl substituted $[Co(PPh_3)_2(^n hexCp)]$ gave an isomeric mixture of soluble polymers, the ratio of 2,5- to 2,4-isomers being 0.6. Reaction between $[Co(PPh_3)_2(^n hexCp)]$ and $1,4\text{-}(MeC{\equiv}C)_2C_6H_4$ at a higher temperature (40 °C) gave a greater degree of regiospecificity in favor of the 2,5-isomer, while also dramatically increasing $M_w$ and $M_n$ values.

The same group has also prepared the first examples of polymers containing unusual ruthenium metallacyclopentatrienes, capable of reversible reduction of the Ru, leading to ferromagnetic interaction between the Ru sites in the reduced state [84]. The polymer can be formed by reductive coupling of non-conjugated diynes at the Ru center, with maximum $M_w$ being obtained when the diyne:Ru ratio is 1:1. NMR spectroscopic studies on the polymers showed the presence of only one geometrical isomer from which it was concluded that only a 2,5-diaryl derivative of ruthenacyclopentatriene exists, indicating a fully π-conjugated main chain structure (Fig. 42).

Zirconocene examples can be synthesized by reaction of diynes with internal silicon substituents (e.g., $1,3\text{-}[(MeC{\equiv}C)SiMe_2]C_6H_4$) with "$ZrCp_2$" (formed *in situ* by reaction of $[ZrCp_2Cl_2]$ with two equivalents of BuLi at −78 °C) and isolated in 50–90% yields [88]. The polymers are easily hydrolyzed to give the corresponding butadienediyl polymers and also react with iodine to give iodine-containing polymers. Polymer degradation in refluxing THF solution provides a mild and high yielding route to macrocycles, the structures of which depend on the spacer groups incorporated into the polymer backbone (Fig. 43).

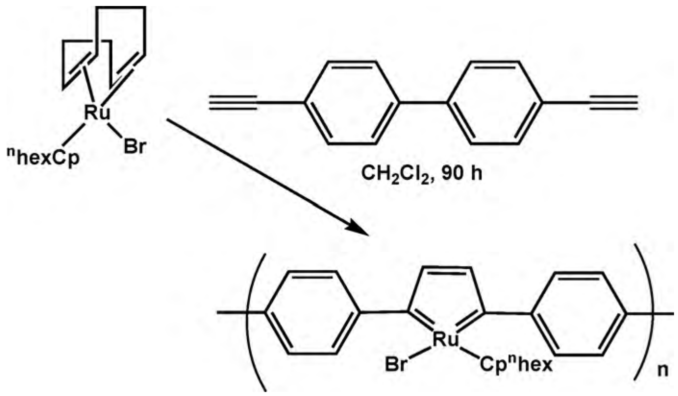


**Fig. 42.** Formation of regiospecific poly(phenyl-ruthenacyclopentatriene) [84].

Matsubara and co-workers have prepared polymer-bound photoluminescent iridium complexes bearing 2,2′-biphenyl ligands. Reaction of an $[IrCl(2,2'\text{-bph})(COD)]_2$ (**57**) (COD = 1,5-cyclooctadiene) metal precursor with a copolymer, built by the radical copolymerization of 4-styryldiphenylphosphine and methyl methacrylate, gave polymers that were cross-linked by P–Ir–P bonds (0.06–0.6 mmol/g Ir) (Fig. 31). Solid state luminescence was observed at 597 nm, the intensity of which was dependent on the molecular weight of the copolymer ligands and on the polymer Ir content [48].

## 4. Main group EC$_4$ analogues

Although these groups of compounds are outside the central metallacycle topic of this review, structurally related main group heterocycles, including siloles and many others, e.g. boroles, phospholes and thiophenes (Fig. 44), have been well studied and will be briefly introduced. As boroles have not been reviewed previously, our coverage of these is comprehensive.

### 4.1. Boroles

Reports on boroles are relatively scarce, although this class of electron-deficient compounds has gained increasing attention in the last few years. This growing interest stems, on the one hand, from fundamental questions concerning their degree of antiaromaticity and reactivity, as the parent borole, $BC_4H_5$ (I), is a 4π electron system and thus isoelectronic with the antiaromatic cyclopentadienyl cation $C_5H_5^+$ (II). However, neither I nor II have been successfully isolated and characterized because of their exceptional high reactivity. On the other hand, the empty $p_z$ orbital located at the boron atom gives boroles strong acceptor character and makes them potentially interesting for the design of luminescent molecules, non-linear optical systems, or for use as charge transport layers in OLEDs (cf. siloles, *vide infra*).

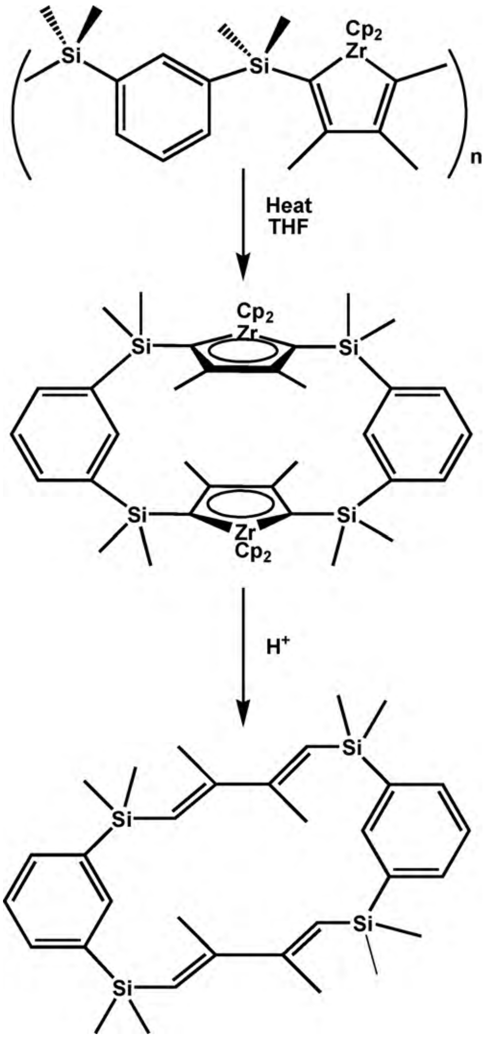


**Fig. 43.** Facile, high yield degradation of zirconocene polymers to form macrocycles [88].

The first successful synthesis of a borole was reported by Eisch et al. in 1969 [89]. The transmetallation of 1,1-dimethyl-2,3,4,5-tetraphenylstannole with $PhBCl_2$ gave pentaphenylborole (**67**) as an air- and moisture-sensitive, deep-blue solid. Another approach used was the lithiation of 1,4-dibromo-tetraphenylbuta-1,3-diene and subsequent treatment with $PhBBr_2$ (Fig. 45). The predicted antiaromatic character of pentaphenylborole was realized by the reactivity towards oxidizing agents such as $O_2$ and $H_2O_2$ or alkynes, the latter leading to the corresponding Diels–Alder product. A more detailed study by the same group revealed the unusually strong Lewis-acidity; upon coordination of $CH_3CN$, the C≡N stretch shifts significantly from 2300 to 2370 cm$^{-1}$ in the IR spectrum, exceed-

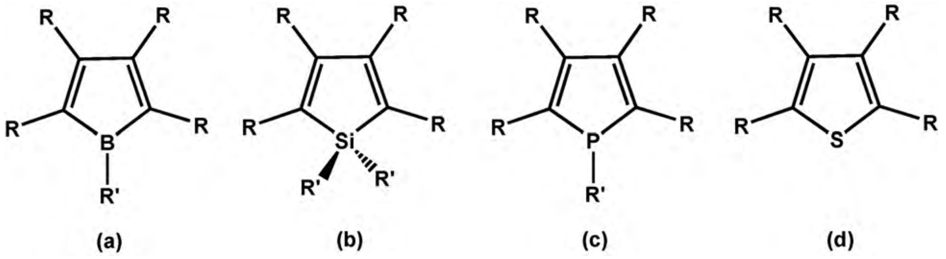


**Fig. 44.** Borole (a), silole (b), phosphole (c) and thiophene (d) structures.

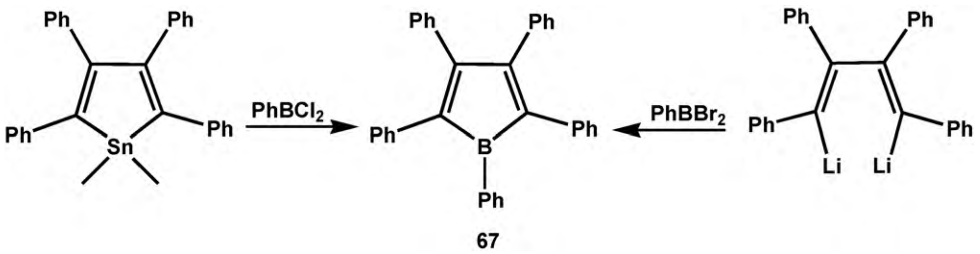


**Fig. 45.** Synthesis of pentaphenylborole (**67**) [89].

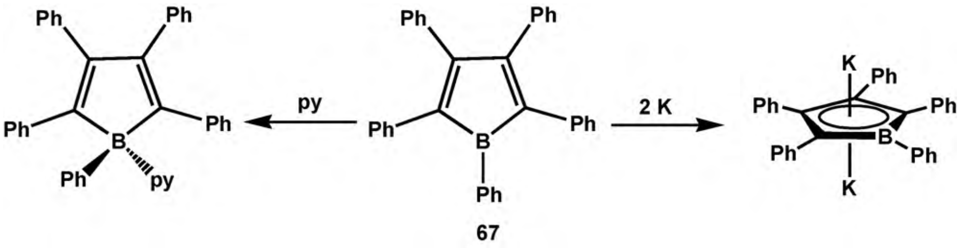


**Fig. 46.** Stabilization of the 4π electron system in pentaphenylborole (**67**) by donor solvent coordination (right) or reduction (left) [90].

ing the effect of $AlCl_3$ (2359 cm$^{-1}$) [90]. According to the authors, this points to a destabilizing effect of the conjugation between the 4π electron system and the empty $p_z$ orbital of the boron, which is decreased if a donor solvent coordinates or reduction occurs to give an aromatic 6π electron heterocycle (Fig. 46). An extended Hückel molecular orbital (EHMO) investigation and SINDO1 studies showed that the ground state of boroles is a singlet state, unlike the cyclopentadienyl cation (II) which exhibits a triplet ground state [90,91].

Schleyer et al. compared the parent borole, $BC_4H_5$, to other $ECH_4$ analogues (E = PH, S, O, $SiH^-$, $SiH^+$, $CH_2$, $CH^+$, $CH^-$, AlH, NH) calculating the magnetic susceptibility, aromatic stabilization energy and the alternating bond lengths [92]. Their results confirmed the antiaromaticity of $BC_4H_5$ and thus the reactivity found for **67**.

However, only in 2008 was the structure of pentaphenylborole (**67**) in the solid state determined by single-crystal X-ray diffraction by Braunschweig and co-workers, who also synthesized and structurally characterized the ferrocenyl derivative **68** (Fig. 47) [93]. ESR, NMR spectroscopic and SQUID magnetic investigations confirmed that the triplet state is not the ground state. The expected alternating bonds of **67** were less pronounced than predicted which was proposed to result from dimer formation in the solid state through CH···B π-donation. Strong Fe···B interactions in **68** also decreased the antiaromaticity of the borole, which can then be seen as an isolated diene system bridged by a boron atom.

A similar observation was made by Yamaguchi et al. for related boroles $ArB(C_4Ph_4)$ (Ar = *p*-$MeC_6H_4$, *p*-$SiMe_3C_6H_4$, *p*-$FC_6H_4$), where the high Lewis-acidity of the boron center and the antiaromaticity favor stabilizing donor–acceptor π interactions [94]. π-interactions between N and B to stabilize the electron deficient boron atom are also operative in $(SiMe_3)_2N$-$B(C_4Ph_4)$, which has been prepared by Braunschweig et al. [95].

The pentakispentafluorophenyl substituted borole **70** was very recently reported by Piers et al., its synthesis involving a zirconacyclopentadiene intermediate (Fig. 48) [96a]. No B···Ar interactions were observed, but dimer formation occurred nevertheless by stacking of the fluorinated rings in staggered conformations as interdigitated propellers. The electron withdrawing substituents increased the Lewis-acidity (**70** > $B(C_6F_5)_3$) and the HOMO–LUMO gap, leading to a blue-shifted absorption at $\lambda_{max}$ = 530 nm compared to **67** ($\lambda_{max}$ = 540 nm). The synthetic route is based in part upon that of Fagan and Nugent [96b], who prepared the crystallographically characterized Diels–Alder dimer of 1-phenyl-2,3,4,5-tetramethylborole *via* direct reaction of a 2,3,4,5-tetramethylzirconacyclopentadiene with $PhBCl_2$.

Boron analogs of the discussed transition metal 2,2′-bph complexes, 2,2′-dibenzoboroles or 9-borafluorenes, have been known

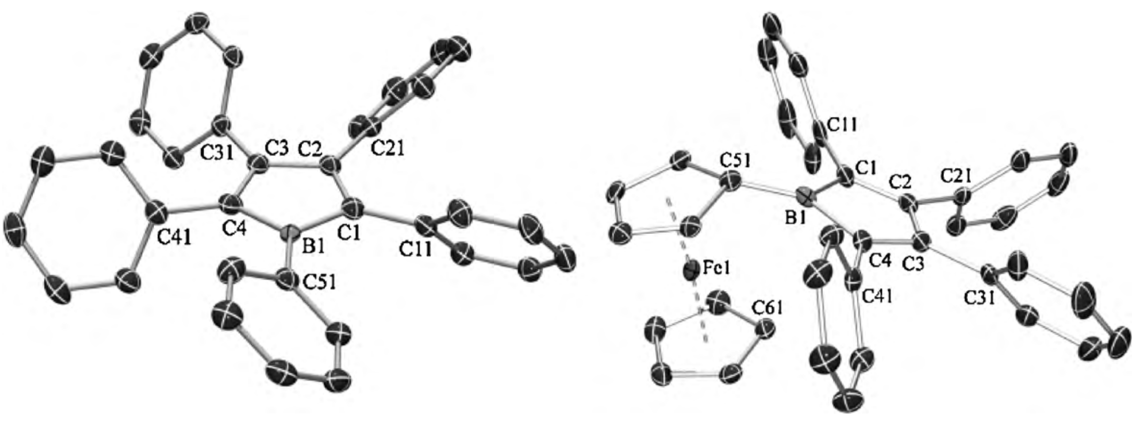


**Fig. 47.** Molecular structures of pentaphenylborole (**67**) (right) and its ferrocenyl derivative (**68**) (left) in the solid state [93].

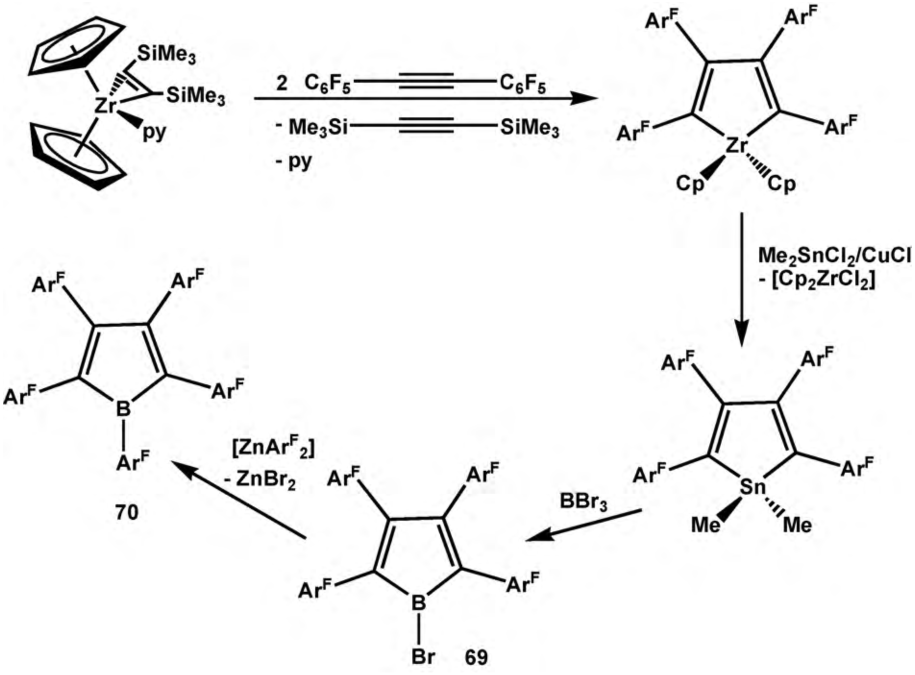


**Fig. 48.** Synthesis of perfluoropentaphenylborole (**70**) ($Ar^F = C_6F_5$) [96].

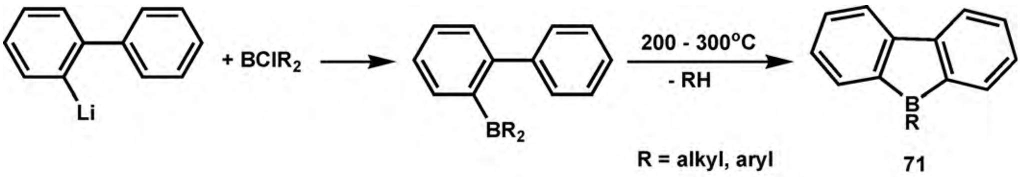


**Fig. 49.** Synthesis of 9-borafluorenes (**71**) [97].

since 1963, when Köster and Benedikt reported on the thermolysis of 2-$BR_2$-biphenyl giving 9-borafluorenes **71** (Fig. 49) [97]. The corresponding 9-chloro-9-borafluorene **72** was obtained when the same reaction was carried out with alkyldichloroboranes.

Piers et al. were interested in the effects of strong Lewis acids on the Zr mediated polymerization of ethylene and prepared perfluorinated analogs of **71**, $(C_{12}F_8)B–R$ [R = Me (**73**), $C_6F_5$ (**74**)], by transmetallation with the corresponding stannole which were structurally characterized by X-ray diffraction studies (Figs. 50 and 51) [98]. Indeed, **73** and **74** proved to be more Lewis acidic than their bis-pentafluorophenyl analogs $MeB(C_6F_5)_2$ and $B(C_6F_5)_3$, respectively.

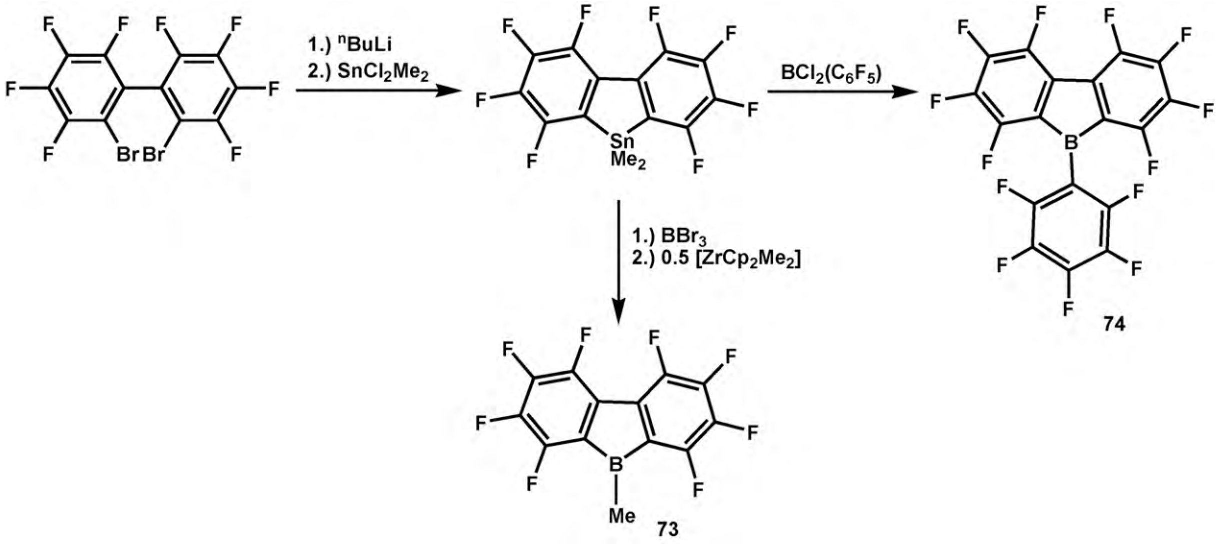


**Fig. 50.** Synthesis of 9-boraperfluorofluorenes **73** and **74** by transmetallation [98].

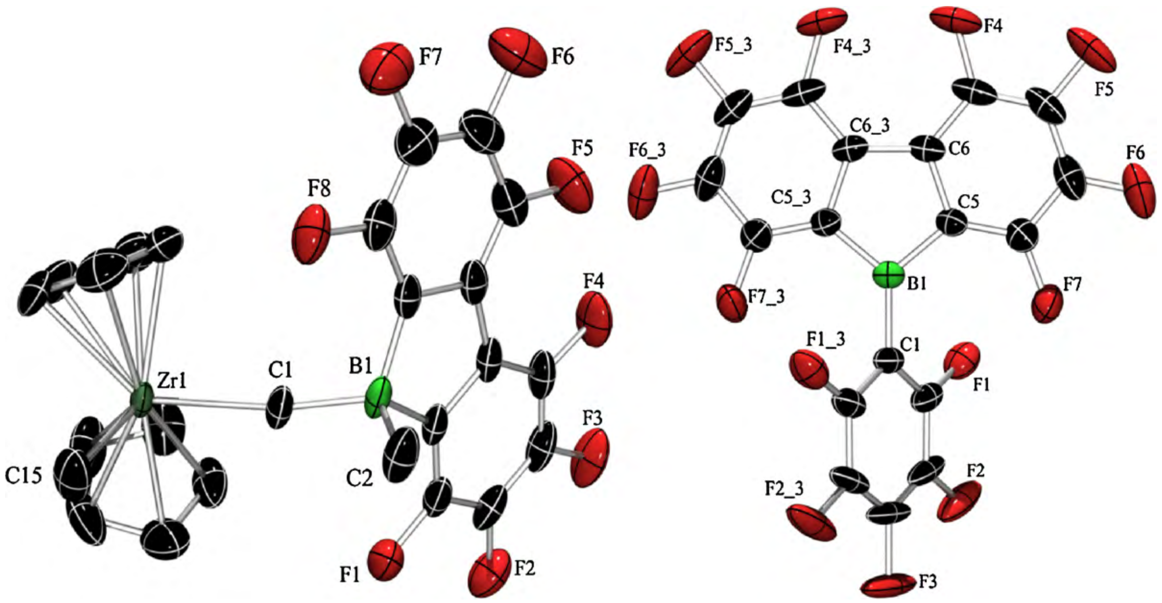
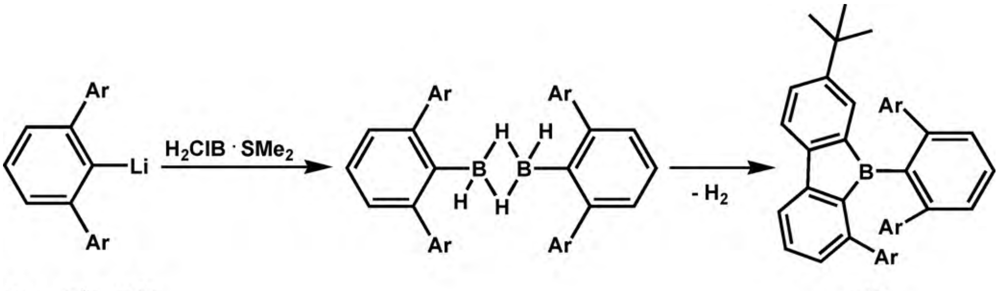


**Fig. 51.** Molecular structures of the cation **73**·$ZrMeCp_2$ (left) and **74** (right) in the solid state [98].



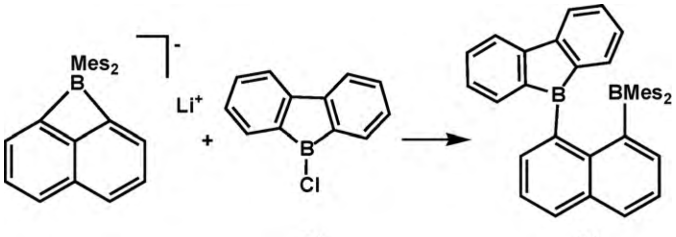
**75**

**Fig. 52.** Intramolecular C–H activation in a base-free terphenyl borane leading to the unsymmetrically substituted dibenzoborole **75** [99].

Unsymmetrically substituted 2,2′-dibenzoboroles have been synthesized by Wehmschulte and co-workers by intramolecular C–H bond activation and $H_2$ extrusion in base-free terphenyl boranes $[ArBH_2]_2$ (Fig. 52) [99]. However, the scope of this reaction type has not yet been explored.

Gabbai et al. synthesized 1-dimesitylboryl-8-(9-borafluorenyl)-naphthalene (**76**), which has been characterized by X-ray diffraction studies (Figs. 53 and 54) and shows an $\eta^1$-coordination of the *ipso*-carbon of one of the Mes groups to the boron atom of the dibenzoborole moiety [100]. Electrochemical reduction generated a radical anion with the unpaired electron delocalized over the two B centers.

Wagner and co-workers investigated boroles and 9-borafluorenes as redox switchable Lewis acids and measured the redox potentials in $FcBR_2$-Lewis base adducts (Fc = ferrocenyl). A direct through space interaction between filled Fe(d) orbitals and the vacant B(p) orbital similar to the one described by Braunschweig et al. in **68** was found in the molecular structure in the solid state of the ferrocenyl derivative **77**, which was prepared by reaction of chloromercury ferrocene $[Fe(C_5H_4HgCl)(Cp)]$ with **72** (Fig. 55) [101]. The formal electron deficiency of the B center is stabilized by pπ conjugation with the Cp ring and by σ interactions with the Fe d orbitals.



**72** **76**

**Fig. 53.** Synthesis of 1-$BMes_2$-8-(9-borafluorenyl)-naphthalene (**76**) [100].

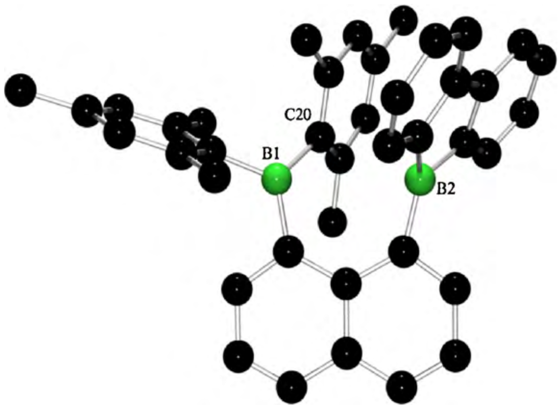


**Fig. 54.** Molecular structure of 1-$BMes_2$-8-(9-borafluorenyl)-naphthalene (**76**) [100].

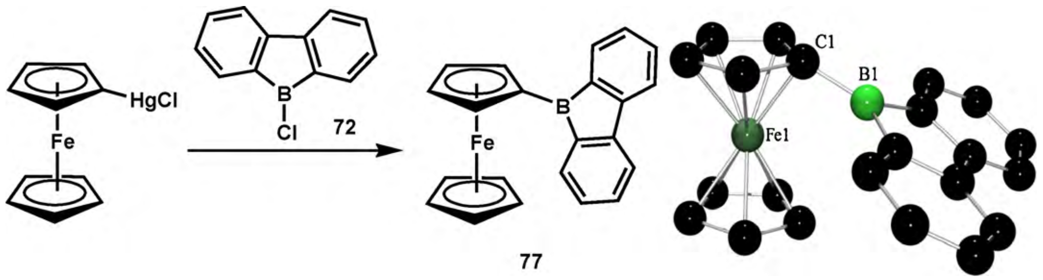


**Fig. 55.** Synthesis and molecular structure in the solid state of [Fe($C_4H_4B(C_{12}H_8)$)(Cp)] (**77**) [101].

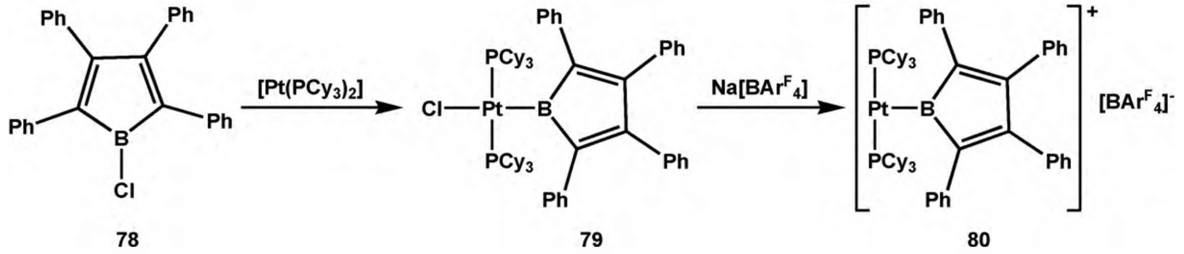


**Fig. 56.** Oxidative addition of **78** to [Pt($PCy_3$)$_2$] and subsequent chloride abstraction from **79** forming **80** [102].

Very recently, the oxidative addition of 1-chloro-2,3,4,5-tetraphenylborole (**78**) to [Pt($PCy_3$)$_2$] has been achieved by Braunschweig et al. (Fig. 56), giving the first metal-*B*-substituted borole **79** [102]. The reaction was accompanied by a color change from blue to dark red, indicating a change in the electronic structure of the borole moiety. Subsequent treatment of **79** with Na[$BAr^F{}_4$] led to the formation of the cationic, 14-electron, T-shaped complex **80**. The structures have been confirmed for both products by single-crystal X-ray analysis (Fig. 57). The $BC_4$ core remains planar, but the B–C bonds appear to be elongated compared to the unperturbed structure in **78**. An NBO analysis suggests significant 5d(Pt) → 2p(B) back donation, reducing the π delocalization in the borole unit and thus causing the elongation of the B–C bonds. The electron donation from the platinum to the boron atom also leads to a hypsochromic shift in the absorption spectra of **79** ($\lambda_{max}$ = 485 nm) and **80** ($\lambda_{max}$ = 524 nm) compared to pentaphenylborole (**67**, $\lambda_{max}$ = 562 nm), as a result of an increase in energy of the $\pi^*$ orbital of the borole moiety. The $\pi$–$\pi^*$ nature of the transition has been confirmed by TD-DFT calculations.

The first foray to make use of the acceptor properties of boroles in luminescent molecules was undertaken by Yamaguchi and coworkers in 2002 [103]. Their 2,2′-bph-type dibenzoboroles **81** shown in Fig. 58 exhibit weak fluorescence ($\lambda_{max}$ = 514–576 nm, $\Phi_f$ = 0.02–0.09) which is based on p$\pi$–$\pi^*$ conjugation. The transition upon irradiation occurs from the HOMO, which is localized at the biphenyl moiety, to the LUMO, localized at the dibenzoborole unit. Donor solvents, such as DMF, or the addition of fluoride, gave a new blue-shifted emission ($\lambda_{max}$ = 419–478 nm) with high quantum yields of $\Phi_f$ = 0.5–0.9. Apparently, the coordination to the boron center interrupts the conjugation in such a way that the LUMO is then mainly localized at the biphenyl rings with very little contribution of the central borole ring. The anion receptor

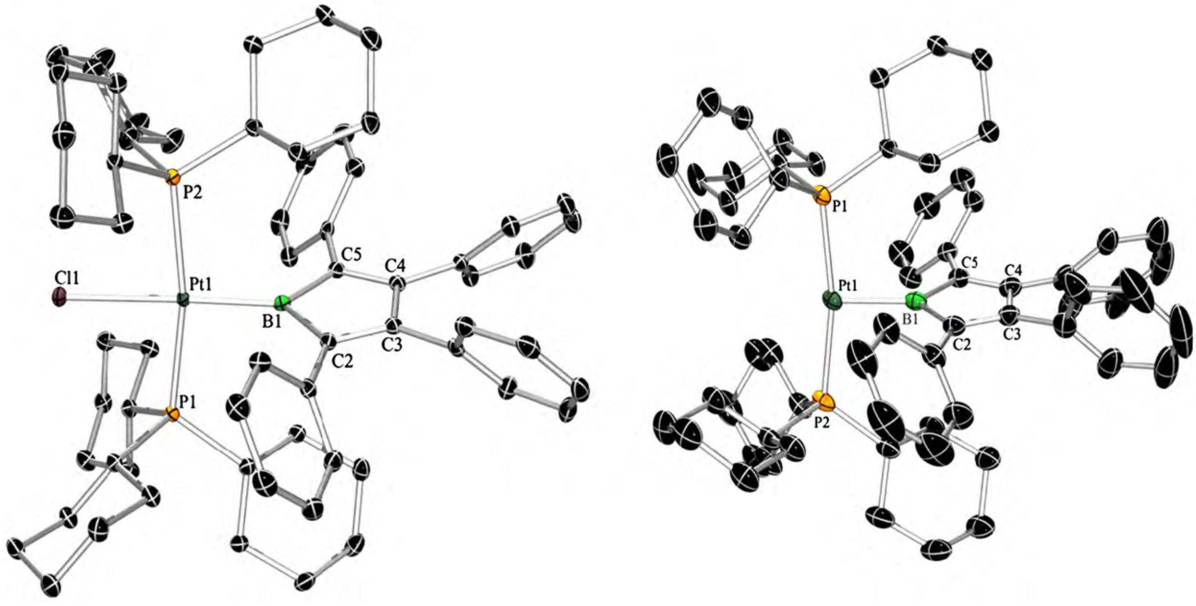


**Fig. 57.** Molecular structures in the solid state of **79** (left) and **80** (right) [102].

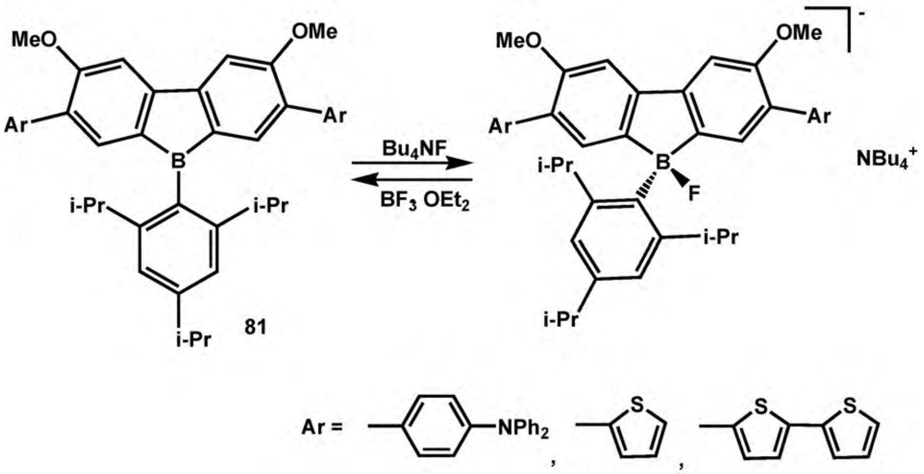


**Fig. 58.** Fluoride coordination to dibenzoboroles **81** [103].

properties in THF solution as well as in thin films of 9-borafluorene-containing polymers have been evaluated *via* photoluminescence quenching measurements by Scherf et al. for future sensing applications [104].

Kang et al. attached large, conjugated systems to the borole unit to obtain a push–pull effect between the donor substituents and the electron accepting borole moiety (Fig. 59) [105]. Thiophene and amine units led to fully conjugated blue-green emitters ($\lambda_{max}$ = 438/534 nm). Again, the $\pi$–$\pi^*$ transition occurs from the HOMO, which is delocalized over the conjugated $\pi$ system, to the LUMO at the boron.

### 4.2. Bis(arylethynyl) siloles

Siloles are interesting main group analogues of metallacycles as they show unique photophysical properties due to the unusual electron deficient nature of the silole ring. As these compounds have been reviewed in detail [106,107], only selected examples will be addressed here. Siloles have an extremely low lying LUMO due to $\sigma^*$–$\pi^*$ conjugation involving the $SiR_2$ $\sigma^*$ orbitals and the ring C–C $\pi^*$ orbitals. Synthesis is straight forward and allows a wide range of substituents to be incorporated. Tamao and co-workers reported a route from bis(phenylethynyl)silane which is first treated with an excess of lithium dihydronapthylide to form 2,5-dilithiosilole. Rearrangement *via* an intramolecular reductive cyclization forms a bis(anion) [108]. This species is the key synthetic building block, allowing a wide range of derivatives to be prepared. If appropriate silane starting materials are used, then substitution directly at the Si heteroatom is possible. The nature of the synthesis can give a highly tuneable series of emissive materials suitable for use in optical applications. For example, 2,5-di(2-pyridyl)silole has been used as an electron transporting layer in organic electroluminescent devices, demonstrating the utility of the electron deficient nature of the siloles [106].

Pagenkopf has used this method in the preparation of luminescent 2,5-bis(phenylethynyl)siloles related to metallacycles previously discussed [109,76]. By exploiting the versatility of, and adapting Tamao's synthetic route, donor–acceptor siloles **83** were prepared (yields of 50% and above were obtained) and the luminescent properties studied (Fig. 60).

All of the compounds that were prepared absorbed and emitted light in the visible region of the electromagnetic spectrum, with the maxima strongly dependent on the push–pull substituents of the chromophore. A bathochromic shift in both absorption and emission occurred as the polarity of the molecule increased, which underlines the charge-transfer in the compounds. The quantum yields for the fluorescence were low to moderate ($\Phi_f$ = 0.004–0.09), depending on the donor and acceptor substituents. These compounds are closely related to the donor–acceptor bis(phenylethynyl)benzenes prepared and studied by Marder et al. [110].

### 4.3. Bis(arylethynyl) phospholes

Phospholes have also been thoroughly studied and have been reviewed [107,111]. However, 2,5-bis(arylethynyl) substituted phospholes are rare, although one might expect similar interesting photophysical properties as found in other $EC_4$ heterocyclic systems. Mathey and co-workers reported for the first time in 1996 the synthesis of the 2,5-bis(phenylethynyl)phosphole **84** by reaction of a 5-lithio-2-phenylethynylphosphole with phenylethynylsulfones (Fig. 61) [112].

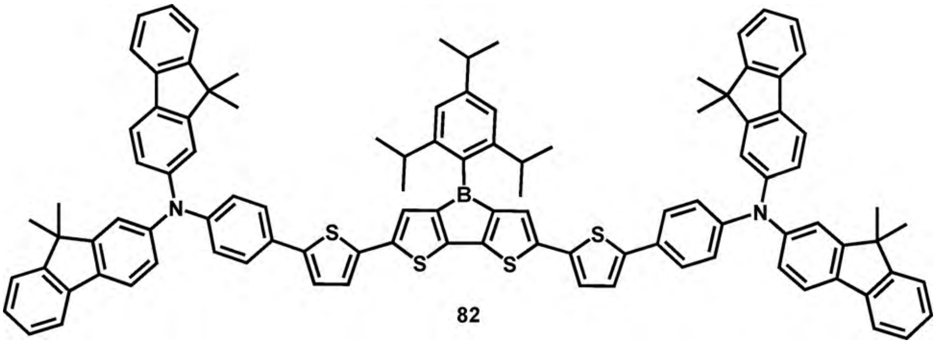


**Fig. 59.** Extended $\pi$-conjugated luminescent borole **82** [105].

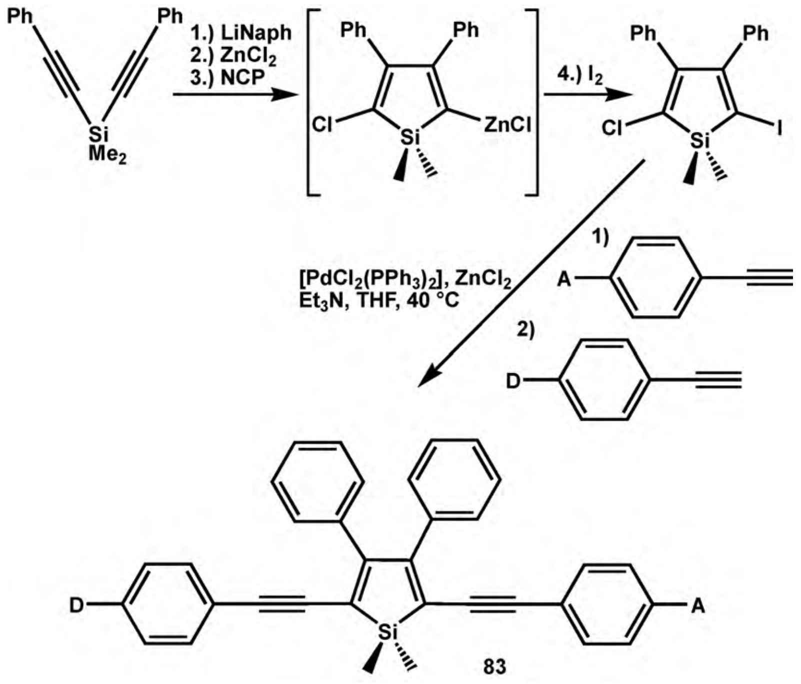


**Fig. 60.** Synthetic route to unsymmetrical 2,5-bis(phenylethynyl)-3,4-diphenyl-siloles **83** [109].

However, no further studies had been undertaken on such systems until recently, when Matano et al. used a ring closing approach *via* a titanacyclopentadiene, which was then reacted with $PhPCl_2$ to give the phosphole **85**. Further Sonogashira cross-coupling reactions with aryl halides afforded the desired 2,5-bis(arylethynyl)phospholes **86** and, after oxidation, **87** was obtained (Fig. 62) [113]. A photophysical investigation showed $\pi \rightarrow \pi^*$ absorption between 398 and 441 nm for **86** and between 418 and 486 nm for **87**. Fluorescence was detected with modest quantum yields ($\lambda_{em}$ = 449–518 nm, $\Phi_f$ = 0.09–0.13) for **86**, while phospholes **87** were very weak emitters ($\lambda_{em}$ = 502–604 nm, $\Phi_f$ = 0.01–0.07). The largest Stokes shift was found for the $NMe_2$ substituted compounds, pointing to a charge transfer from the donor group to the phosphole moiety in the excited state. The general bathochromic shift in the absorption and emission spectra upon oxidation of **86**–**87** suggests an enhancement of the charge transfer.

### *4.4. Bis(arylethynyl) thiophenes*

A number of bis(phenylethynyl)thiophenes (BPETs) have been reported and are of interest due to their luminescence [114–119] and non-linear optical [120–122] properties and also, due to the bent nature of the thiophene moiety, their liquid crystal phase behavior [123–126]. There are a number of routes for the synthesis of BPETs. The most straightforward methods utilize catalytic Sonogashira or Kumada-Tamao cross-couplings of terminal alkynes [114–118] or alkynyl Grignard reagents [127],

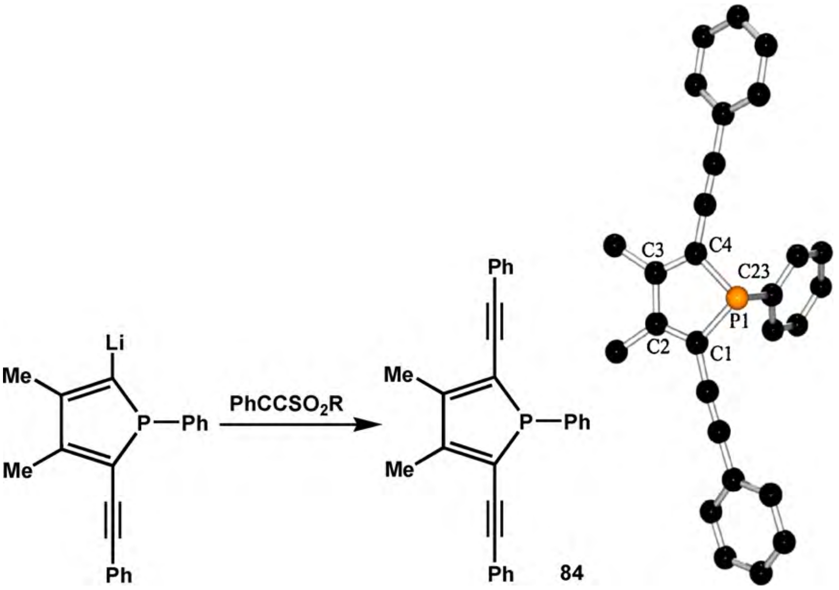


**Fig. 61.** Synthesis and molecular structure in the solid state of **84** [112].

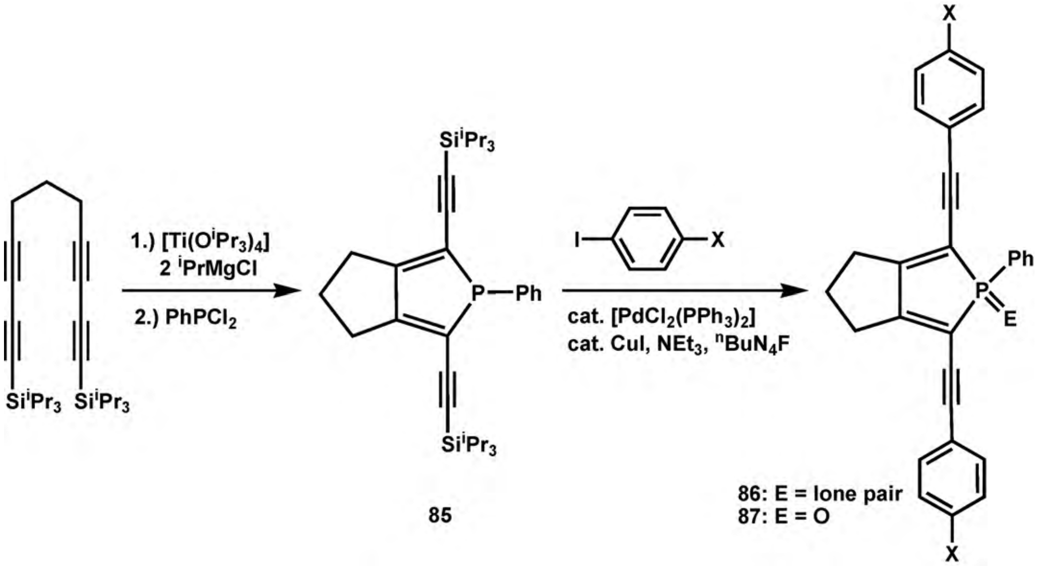


**Fig. 62.** Synthetic route to unsymmetrical 2,5-bis(phenylethynyl)-3,4-diphenyl-siloles **86** and **87** (X = H, $NO_2$, $NMe_2$) [113].

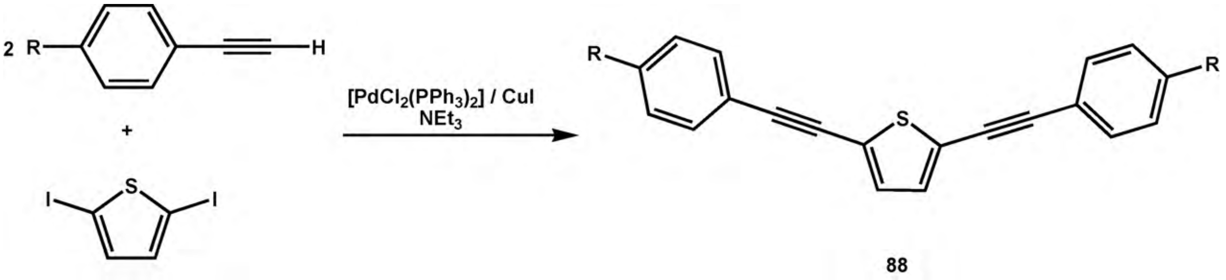


**Fig. 63.** Pd/Cu catalyzed synthesis of bis(phenylethynyl)thiophenes **88** (R = H, Me, OMe, $CF_3$, $NMe_2$, $NO_2$, CN, $CO_2Me$) [118].

respectively, with dihalothiophenes to give BPETs in good yields (Figs. 63 and 64). Pd-catalyzed cross-coupling has also been used to produce BPETs in good yields from triorganoindium compounds and 2,5-dibromothiophene [128].

Other methods have involved longer reaction sequences involving elimination reactions to give BPETs. A one-pot synthesis using benzyl sulfone derivatives and 2-formyl-5-phenylethynylthiophene incorporating two sequential eliminations from the reaction intermediates has been developed, forming symmetrical or unsymmetrical BPETs in good yields [129]. The compound 1,8-diphenyl-1,7-octadiyne-3,6-dione, synthesized in nine steps from 1,4-butanediol, can also be converted to BPET by reaction with bis(triphenyl)tin sulfide in the presence of $BCl_3$ [130].

Only a few studies on the optical properties of 2,5-bis(arylethynyl)thiophenes can be found in the literature. Marder et al. carried out photophysical studies on thiophenes **88** [118]. Absorption maxima for the $\pi \rightarrow \pi^*$ transitions were recorded between 350 and 387 nm, while emission maxima have been observed between 382 and 435 nm, depending on the substituent R at the benzene rings. The photoluminescence occurred with quantum yields of $\Phi = 0.19–0.33$, and lifetimes of $\tau = 0.21–0.40$ ns, indicative of fluorescence.

Eliasson and Norman et al. investigated the one-photon and two-photon excitation of 2,5-bis(arylethynyl)thiophenes experimentally and theoretically, with emphasis on the non-linear optical properties for optical power limiting [131].

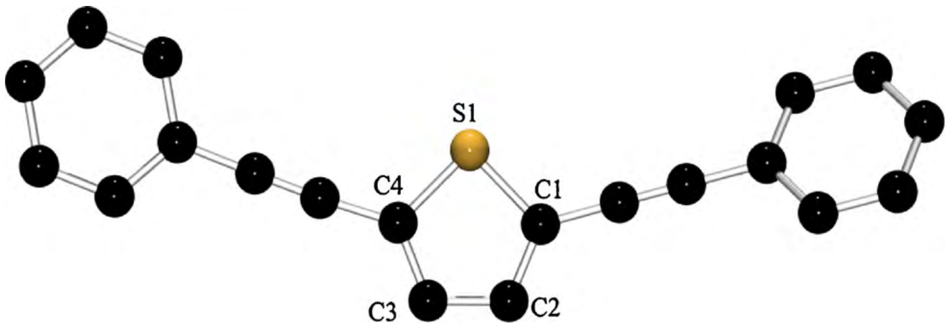


**Fig. 64.** Molecular structure in the solid state of 2,5-bis(phenylethynyl)thiophene (**88**) [118].

## 5. Conclusions

Metallacyclopentadienes and their main group analogues such as boroles, siloles, thiophenes and phospholes display interesting optical properties, which have only recently begun to be exploited. Applications include OLEDs, either as emitting or charge transport layers, depending on the type of compound, and in non-linear optical and two-photon absorbing materials. The metallacyclopentadienes are also intermediates in a number of catalytic processes. Routes to metal-biphenyl complexes are still limited, restricting the development of their chemistry, but those results already reported are encouraging. The recent resurgence of interest in borole chemistry, and the first examples of structurally characterized boroles suggest that major advances will be made in this area in the coming few years.

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## References

[1] (a) F. Hartl, P. Rosa, L. Ricard, P. Le Floch, S. Zalis, Coord. Chem. Rev. 251 (2007) 557;
(b) J. Zhang, X. Wang, G.X. Jin, Coord. Chem. Rev. 250 (2006) 95;
(c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(d) A. Vlcek, Coord. Chem. Rev. 230 (2002) 225;
(e) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[2] (a) A.P. Sadimenko, Adv. Heterocyclic Chem. 95 (2008) 221;
(b) V. Balzani, S. Campagna, Top. Curr. Chem. 280 (2007);
(c) V. Balzani, S. Campagna, Top. Curr. Chem. 281 (2008);
(d) K. Sakai, H. Ozawa, Coord. Chem. Rev. 251 (2007) 21;
(e) H.-L. Kwong, H.-L. Yeung, C.-T. Yeung, W.-S. Lee, C.-S. Lee, W.-L. Wong, Coord. Chem. Rev. 251 (2007) 2188;
(f) A. Vlcek, S. Zalis, Coord. Chem. Rev. 251 (2007) 258;
(g) V. Balzani, G. Bergamini, F. Marchioni, P. Ceroni, Coord. Chem. Rev. 250 (2006) 1254;
(h) B.H. Ye, M.L. Tong, X.M. Chen, Coord. Chem. Rev. 249 (2005) 545;
(i) C. Kaes, A. Katz, M.W. Hosseini, Chem. Rev. 100 (2000) 3553.

[3] (a) M.S. Lowry, S. Bernhard, Chem. Eur. J. 12 (2006) 7970;
(b) H. Yersin, Transit. Met. Rare Earth Compd. III 241 (2004) 1;
(c) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304;
(d) M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 75 (1999) 4.

[4] (a) B. Heller, M. Hapke, Chem. Soc. Rev. 36 (2007) 1085;
(b) H. Bonneman, Angew. Chem. Int. Ed. Engl. 24 (1985) 248.

[5] A. Morneau, B.T. Donovan-Merkert, W.E. Geiger, Inorg. Chim. Acta 300 (2000) 96.

[6] J.J. Eisch, A.M. Piotrowski, K.I. Han, C. Krüger, Y.H. Tsay, Organometallics 4 (1985) 224.

[7] X. Zhang, G.B. Carpenter, D.A. Sweigart, Organometallics 18 (1999) 4887.

[8] M. Retbøll, A.J. Edwards, A.D. Rae, A.C. Willis, M.A. Bennett, E. Wenger, J. Am. Chem. Soc. 124 (2002) 8348.

[9] Z. Hou, A. Fujita, T. Koizumi, H. Yamazaki, Y. Wakatsuki, Organometallics 18 (1999) 1979.

[10] (a) Z. Lu, C.-H. Jun, S.R. de Gala, M.P. Sigalas, O. Eisenstein, R.H. Crabtree, Organometallics 14 (1995) 1168;
(b) Z. Lu, C.-H. Jun, S.R. de Gala, M.P. Sigalas, O. Eisenstein, R.H. Crabtree, J. Chem. Soc., Chem. Commun. (1993) 1877.

[11] C. Perthuisot, B.L. Edelbach, D.L. Zubris, W.D. Jones, Organometallics 16 (1997) 2016.

[12] C. Perthuisot, W.D. Jones, J. Am. Chem. Soc. 116 (1994) 3647.

[13] S. Kumaraswamy, S.S. Jalisatgi, A.J. Matzger, O.S. Miljanic, K.P.C. Vollhardt, Angew. Chem. Int. Ed. 43 (2004) 3711.

[14] B.C. Berris, G.H. Hovakeemian, Y.-H. Lai, H. Mestdaph, K.P.C. Vollhardt, J. Am. Chem. Soc. 107 (1985) 5670.

[15] W.-Y. Yeh, S.C.N. Hsu, S.-M. Peng, G.-H. Lee, Organometallics 17 (1998) 2477.

[16] A. Chehata, A. Oviedo, A. Arévalo, S. Bernès, J.J. García, Organometallics 22 (2003) 1585.

[17] D.A. Vicic, W.D. Jones, J. Am. Chem. Soc. 119 (1997) 10855.

[18] S.A. Gardner, H.B. Gordon, M.D. Rausch, J. Organomet. Chem. 60 (1973) 179.

[19] C.L. Hilton, B.T. King, Organometallics 25 (2006) 4058.

[20] B.L. Edelbach, R.J. Lachicotte, W.D. Jones, J. Am. Chem. Soc. 120 (1998) 2843.

[21] C. Deuschel-Cornioley, A. von Zelewsky, Inorg. Chem. 26 (1987) 3354.

[22] M.R. Plutino, L.M. Scolaro, A. Albinati, R. Romeo, J. Am. Chem. Soc. 126 (2004) 6470.

[23] Y.-H. Chen, J.W. Merkert, Z. Murtaza, C. Woods, D.P. Rillema, Inorg. Chim. Acta 240 (1995) 41.

[24] N. Shimhai, C.N. Iverson, B.L. Edelbach, W.D. Jones, Organometallics 20 (2001) 2759.

[25] S.C. Cohen, A.G. Massey, J. Organomet. Chem. 10 (1967) 471.

[26] M.D. Rausch, L.P. Klemann, J. Chem. Soc., Chem. Commun. (1971) 354.

[27] P. Buchalski, I. Grabowska, E. Kaminska, K. Suwinska, Organometallics 27 (2008) 2346.

[28] (a) R. Uson, J. Vicente, J.A. Cirac, M.T. Chicote, J. Organomet. Chem. 198 (1980) 105;
(b) H.-A. Brune, R. Hohenadel, G. Schmidtberg, U. Ziegler, J. Organomet. Chem. 402 (1991) 179.

[29] T. Agapie, S.J. Schofer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 1304.

[30] C.N. Iverson, R.J. Lachicotte, C. Müller, W.D. Jones, Organometallics 21 (2002) 5320.

[31] M.A. Bennett, K.D. Griffiths, T. Okano, V. Parthasarathi, G.B. Robertson, J. Am. Chem. Soc. 112 (1990) 7047.

[32] A.L. Keen, M. Doster, S.A. Johnson, J. Am. Chem. Soc. 129 (2007) 810.

[33] H. Schwager, S. Spyroudis, K.P.C. Vollhardt, J. Organomet. Chem. 382 (1990) 191.

[34] B.L. Edelbach, D.A. Vicic, R.J. Lachicotte, W.D. Jones, Organometallics 17 (1998) 4784.

[35] C.-H. Jun, Z. Lu, R.H. Crabtree, Tetrahedron Lett. 33 (1992) 7119.

[36] T. Satoh, W.D. Jones, Organometallics 20 (2001) 2916.

[37] B.L. Edelbach, R.J. Lachicotte, W.D. Jones, Organometallics 18 (1999) 4040.

[38] C. Müller, R.J. Lachicotte, W.D. Jones, Organometallics 21 (2002) 1975.

[39] T. Schaub, U. Radius, Chem. Eur. J. 11 (2005) 5024.

[40] C.N. Iverson, W.D. Jones, Organometallics 20 (2001) 5745.

[41] C.B. Blanton, Z. Murtaza, R.J. Shaver, D.P. Rillema, Inorg. Chem. 31 (1992) 3230.

[42] S.R. Stoyanov, J.M. Villegas, D.P. Rillema, Inorg. Chem. 42 (2003) 7852.

[43] M. Maestri, D. Sandrini, V. Balzani, A. von Zelewsky, C. Deuschel-Cornioley, P. Jolliet, Helv. Chim. Acta 71 (1988) 1053.

[44] G.Y. Zheng, D.P. Rillema, J. DePriest, C. Woods, Inorg. Chem. 37 (1998) 3588.

[45] J. DePriest, G.Y. Zheng, N. Goswami, D.M. Eichhorn, C. Woods, D.P. Rillema, Inorg. Chem. 39 (2000) 1955.

[46] G.Y. Zheng, D.P. Rillema, Inorg. Chem. 37 (1998) 1392.

[47] G.Y. Zheng, D.P. Rillema, J.H. Reibenspies, Inorg. Chem. 38 (1999) 794.

[48] Y. Koga, K. Ueno, K. Matsubara, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 4204.

[49] K.R. Lee, M.-S. Eum, C.S. Chui, S.C. Lee, I.J. Kim, Y.S. Kim, Y. Kim, S.-J. Kim, N.H. Hur, Dalton Trans. (2009) 3650.

[50] J.P. Collman, J.W. Kang, W.F. Little, M.F. Sullivan, Inorg. Chem. 7 (1968) 1298.

[51] (a) E. Becker, E. Rüba, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 20 (2001) 3851;
(b) E. Rüba, K. Mereiter, R. Schmid, V.N. Sapunov, K. Kirchner, H. Schottenberger, M.J. Calhorda, L.F. Veiros, Chem. Eur. J. 8 (2002) 3948;
(c) K. Kirchner, M.J. Calhorda, R. Schmid, L.F. Veiros, J. Am. Chem. Soc. 125 (2003) 11721.

[52] (a) R. Schmid, K. Kirchner, J. Org. Chem. 68 (2003) 8339;
(b) J. Le Paih, F. Monnier, S. Dérien, P.H. Dixneuf, E. Clot, O. Eisenstein, J. Am. Chem. Soc. 125 (2003) 11964;
(c) J. Le Paih, S. Dérien, B. Demerseman, C. Bruneau, P.H. Dixneuf, L. Toupet, G. Dazinger, K. Kirchner, Chem. Eur. J. 112 (2005) 1312.

[53] Y. Wakatsuki, T. Kuramitsu, H. Yamazaki, Tetrahedron Lett. 15 (1974) 4549.

[54] V. Gandon, C. Aubert, M. Malacria, Chem. Commun. (2006) 2209.

[55] M. Lautens, W. Klute, W. Tam, Chem. Rev. 96 (1996) 49.

[56] I. Ojima, M. Tzamarioudaki, Z. Li, R.J. Donovan, Chem. Rev. 96 (1996) 635.

[57] U. Rosenthal, V.V. Burlakov, M.A. Bach, T. Beweries, Chem. Soc. Rev. 36 (2007) 719.

[58] E.T. Knight, L.K. Myers, M.E. Thompson, Organometallics 11 (1992) 3691.

[59] H.G. Alt, H.E. Engelhardt, M.D. Rausch, L.B. Kool, J. Organomet. Chem. 329 (1987) 61.

[60] M. Westerhausen, M.H. Digeser, C. Gückel, H. Nörg, J. Knizek, W. Ponikwar, Organometallics 18 (1999) 2491.

[61] D.J. Sikora, M.D. Rausch, R.D. Rogers, J.L. Atwood, J. Am. Chem. Soc. 101 (1979) 5079.

[62] J.L. Atwood, W.E. Hunter, H. Alt, M.D. Rausch, J. Am. Chem. Soc. 98 (1976) 2454.

[63] H. tom Dieck, C. Munz, C. Müller, J. Organomet. Chem. 384 (1990) 243.

[64] H. Suzuki, K. Itoh, Y. Ishii, K. Simon, J.A. Ibers, J. Am. Chem. Soc. 98 (1976) 8494.

[65] B. Clarke, M. Green, F.G.A. Stone, J. Chem. Soc. A (1970) 951.

[66] C.S. Yi, J.R. Torres-Lubian, N. Liu, A.L. Rheingold, I.A. Guzei, Organometallics 17 (1998) 1257.

[67] Y. Yamada, J. Mizutani, M. Kurihara, H. Nishihara, J. Organomet. Chem. 637–639 (2001) 80.

[68] L.J. Canoira, J.L. Davidson, G. Douglas, K.W. Muir, J. Organomet. Chem. 362 (1989) 135.

[69] T.V. Harris, J.W. Rathke, E.L. Muetterties, J. Am. Chem. Soc. 100 (1978) 6966.

[70] R. Usón, J. Vicente, M.T. Chicote, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1983) 1131.

[71] C. Bianchini, A. Mell, M.M. Peruzzini, A. Vacca, F. Vizza, Organometallics 10 (1991) 645.

[72] H. Yamazaki, K. Yasufuku, Y. Wakatsuki, Organometallics 2 (1983) 726.
[73] T. Shimura, A. Ohkubo, K. Aramaki, H. Uekusa, T. Fujita, S. Ohba, H. Nishihara, Inorg. Chim. Acta 230 (1995) 215.
[74] Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, J. Am. Chem. Soc. 105 (1983) 1907.
[75] M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Inorg. Chim. Acta 250 (1996) 129.
[76] J.P. Rourke, A.S. Batsanov, J.A.K. Howard, T.B. Marder, Chem. Commun. (2001) 2626.
[77] A. Steffen, M.G. Tay, A.S. Batsanov, J.A.K. Howard, A. Beeby, K.Q. Vuong, X.-Z. Sun, M.W. George, T.B. Marder, Angew. Chem. Int. Ed. 49 (2010) 2349.
[78] A.F. Hill, A.D. Rae, M. Schultz, A.C. Willis, Organometallics 26 (2007) 1325.
[79] M. Horáček, I. Císařová, J. Kubišta, A. Spannenberg, K. Dallmann, U. Rosenthal, K. Mach, J. Organomet. Chem. 689 (2004) 4592.
[80] V.V. Burlakov, A. Ohff, C. Lefeber, A. Tillack, W. Baumann, R. Kempe, U. Rosenthal, Chem. Ber. 128 (1995) 967.
[81] U. Rosenthal, P.-M. Pellny, F.G. Kirchbauer, V.V. Burlakov, Acc. Chem. Res. 33 (2000) 119.
[82] D.P. Hsu, W.M. Davis, S.L. Buchwald, J. Am. Chem. Soc. 115 (1993) 10394.
[83] L. Pu, T. Hasegawa, S. Parkin, H. Taube, J. Am. Chem. Soc. 115 (1993) 2545.
[84] M. Kurashina, M. Murata, T. Watanabe, H. Nishihara, J. Am. Chem. Soc. 125 (2003) 12420.
[85] J.-C. Lee, A. Nishio, I. Tomita, T. Endo, Macromolecules 30 (1997) 5205.
[86] H. Nishihara, T. Shimura, A. Ohkubo, N. Matsuda, K. Aramaki, Adv. Mater. 5 (1993) 752.
[87] T. Shimura, A. Ohkubo, N. Matsuda, I. Matsuoka, K. Aramaki, H. Nishihara, Chem. Mater. 8 (1996) 1307.
[88] S.S.H. Mao, F.-Q. Liu, T.D. Tilley, J. Am. Chem. Soc. 120 (1998) 1193.
[89] J.J. Eisch, N.K. Hota, S. Kozima, J. Am. Chem. Soc. 91 (1969) 4575.
[90] J.J. Eisch, J.E. Galle, S. Kozima, J. Am. Chem. Soc. 108 (1986) 379.
[91] E.J.P. Malar, K. Jug, Tetrahedron 42 (1986) 417.
[92] P.v.R. Schleyer, P.K. Freeman, H. Jiao, B. Goldfuss, Angew. Chem., Int. Ed. Engl. 34 (1995) 337.
[93] H. Braunschweig, I. Fernandez, G. Frenking, T. Kupfer, Angew. Chem. Int. Ed. 47 (2008) 1951.
[94] C.-W. So, D. Watanabe, A. Wakamiya, S. Yamaguchi, Organometallics 27 (2008) 3496.
[95] H. Braunschweig, T. Kupfer, Chem. Commun. (2008) 4487.
[96] (a) C. Fan, W.E. Piers, M. Parvez, Angew. Chem. Int. Ed. 48 (2009) 2955;
    (b) P.J. Fagan, W.A. Nugent, J.C. Calabrese, J. Am. Chem. Soc. 116 (1994) 1880.
[97] R. Köster, G. Benedikt, Angew. Chem. Int. Ed. 2 (1963) 323.
[98] P.A. Chase, W.E. Piers, B.O. Patrick, J. Am. Chem. Soc. 122 (2000) 12911.
[99] (a) R.J. Wehmschulte, M.A. Khan, B. Twamley, B. Schiemenz, Organometallics 20 (2001) 844;
    (b) R.J. Wehmschulte, A.A. Diaz, M.A. Khan, Organometallics 22 (2003) 83.
[100] J.D. Hoefelmeyer, S. Sole, F.P. Gabbai, Dalton Trans. (2004) 1254.
[101] L. Kaufmann, H. Vitze, M. Bolte, H.-W. Lerner, M. Wagner, Organometallics 27 (2008) 6215.
[102] H. Braunschweig, C.-W. Chiu, K. Radacki, P. Brenner, Chem. Commun. (2010) 916.
[103] (a) S. Yamaguchi, T. Shirasaka, S. Akiyama, K. Tamao, J. Am. Chem. Soc. 124 (2002) 8816;
    (b) A. Wakamiya, K. Mishima, K. Ekawa, S. Yamaguchi, Chem. Commun. (2008) 579.
[104] V.D.B. Bonifacio, J. Morgado, U. Scherf, J. Polym. Sci. Part A: Polym. Chem. 46 (2008) 2878.
[105] S. Kim, K. Song, S.O. Kang, J. Ko, Chem. Commun. (2004) 68.
[106] S. Yamaguchi, K. Tamao, J. Organomet. Chem. 653 (2002) 223.
[107] M. Hissler, P.W. Dyer, R. Réau, Coord. Chem. Rev. 244 (2003) 1.
[108] K. Tamao, S. Yamaguchi, M. Shiro, J. Am. Chem. Soc. 116 (1994) 11715.
[109] A.J. Boydston, Y. Yin, B.L. Pagenkopf, J. Am. Chem. Soc. 126 (2004) 3724.
[110] (a) P. Nguyen, Z. Yuan, L. Agocs, G. Lesley, T.B. Marder, Inorg. Chim. Acta 220 (1994) 289;
    (b) P. Nguyen, G. Lesley, T.B. Marder, I. Ledoux, J. Zyss, Chem. Mater. 9 (1997) 406;
    (c) M. Biswas, P. Nguyen, T.B. Marder, L.R. Khundkar, J. Phys. Chem. A 101 (1997) 1689.
[111] (a) A.N. Hughes, C. Srivanav, J. Heterocyclic Chem. 7 (1970) 1;
    (b) A.N. Hughes, D. Kleemola, J. Heterocyclic Chem. 13 (1976) 1;
    (c) F. Mathey, Chem. Rev. 88 (1988) 429;
    (d) A.P. Sadimenko, Adv. Heterocyclic Chem. 79 (2001) 115;
    (e) M. Hissler, P.W. Dyer, R. Reau, Top. Curr. Chem. 250 (2005) 127;
    (f) L.D. Quin, Curr. Org. Chem. 10 (2006) 43;
    (g) M.G. Hobbs, T. Baumgartner, Eur. J. Inorg. Chem. (2007) 3611;
    (h) J. Crassous, R. Reau, Dalton Trans. (2008) 6865;
    (i) Y. Matano, H. Imahoria, Org. Biomol. Chem. 7 (2009) 1258.
[112] S. Holand, F. Gandolfo, L. Ricard, F. Mathey, Bull. Soc. Chim. Fr. 133 (1996) 33.
[113] Y. Matano, M. Nakashima, H. Imahori, Angew. Chem. Int. Ed. 48 (2009) 4002.
[114] J.G. Rodríguez, A. Lafuente, L. Rubio, J. Esquivias, Tetrahedron Lett. 45 (2004) 7061.
[115] J.G. Rodríguez, J. Esquivias, A. Lafuente, L. Rubio, Tetrahedron Lett. 62 (2006) 3112.
[116] S.-S. Sun, A.J. Lees, J. Am. Chem. Soc. 122 (2000) 8956.
[117] T.S. Jung, J.H. Kim, E.K. Jang, D.H. Kim, Y.-B. Shim, B. Park, S.C. Shin, J. Organomet. Chem. 599 (2000) 232.
[118] J.S. Siddle, R.M. Ward, J.C. Collings, S.R. Rutter, L. Porrès, L. Applegarth, A. Beeby, A.S. Batsanov, A.L. Thompson, J.A.K. Howard, A. Boucekkine, K. Costuas, J.F. Halet, T.B. Marder, New J. Chem. 31 (2007) 841.
[119] A. Beeby, K.S. Findlay, S.R. Rutter, P. Matousek, A.W. Parker, M. Towrie, in preparation.
[120] P. Lind, C. Lopes, K. Öberg, B. Eliasson, Chem. Phys. Lett. 387 (2004) 238.
[121] P. Lind, A. Eriksson, C. Lopes, B. Eliasson, J. Phys. Org. Chem. 18 (2005) 426.
[122] R. Vestberg, C. Nilsson, C. Lopes, P. Lind, B. Eliasson, E. Malmstrom, J. Polym. Sci. Part A, Polym. Chem. 43 (2005) 1177.
[123] S.H. Eichhorn, A.J. Paraskos, K. Kishikawa, T.M. Swager, J. Am. Chem. Soc. 124 (2002) 12742.
[124] G. Heppke, D. Moro, Science 279 (1998) 1872.
[125] H.-F. Hsu, C.-H. Kuo, C.-F. Chen, Y.-H. Lin, L.-Y. Husng, C.-H. Chen, K.-O. Cheng, H.-H. Chen, Chem. Mater. 16 (2004) 2379.
[126] K. Kishikawa, M.C. Harris, T.M. Swager, Chem. Mater. 11 (1999) 867.
[127] K. Sanechika, T. Yamamoto, A. Yamamoto, Bull. Chem. Soc. Jpn. 57 (1984) 752.
[128] M.A. Penz, I. Perez, J.P. Sestelo, L.A. Sarandeses, Chem. Commun. (2002) 2246.
[129] A. Orita, F. Ye, G. Babu, T. Ikemoto, J. Otera, Can. J. Chem. 83 (2005) 716.
[130] F. Freeman, D.S.H. Kim, J. Org. Chem. 57 (1992) 1722.
[131] P. Lind, M. Carlsson, B. Eliasson, E. Glimsdal, M. Lindgren, C. Lopes, L. Boman, P. Norman, Mol. Phys. 107 (2009) 629.