CHEMICAL REVIEWS

Review

Peripheral Covalent Modification of Inorganic and Organometallic Compounds through C#C Bond Formation Reactions

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Chem. Rev., **2008**, 108 (10), 4185-4207 • DOI: 10.1021/cr8002592 • Publication Date (Web): 09 September 2008

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Chem. Rev. **2008,** *108,* 4185–4207

Peripheral Covalent Modification of Inorganic and Organometallic Compounds through C−C Bond Formation Reactions

Tong Ren*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received August 9, 2007

Contents

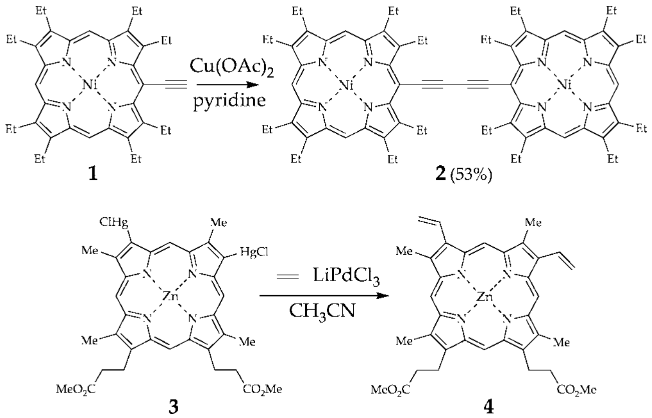
1. Introduction

More than a century after the founding of coordination chemistry by Alfred Werner,[1] inorganic chemistry has branched into organometallics, bioinorganic, polymer, and solid state/materials chemistry. A common feature of the new frontiers of inorganic chemistry is the increasing degree of complexity of ligands and the rich functionalities of the resultant compounds. The desire to achieve complex inorganic species of either novel functionality or intricate topology provides stimulus for new synthetic strategies with improved efficiency and selectivity. One of the emerging strategies invokes the formation of C−C bond at the coordinated ligands distant from the metal center. This approach takes advantage of Pd-catalyzed cross-coupling reactions that have been explored extensively by organic chemists with well-defined catalysts and the scope of substrates.[2,3] Successful peripheral modifications include the Sonogashira, Suzuki, Negishi, Heck, and Stille reactions. Alternatively, peripheral C−C bond formation can also be achieved through homocoupling reactions such as the Glaser reaction[4] and the olefin metathesis reaction.[5]

The earliest example of peripheral modification appears to be the work of Schlögl and Steyrer,[6] where the series of $\mathrm{Fc-(C{\equiv}C)_{2\mathit{m}}-Fc}$ ($m = 1-4$) type compounds was prepared from the oxidative coupling of $\mathrm{Fc-(C{\equiv}C)_{\mathit{m}}H}$ with excess $\mathrm{Cu(OAc)_2}$ in pyridine/MeOH (Eglinton conditions). The other early example was based on the nickel complex of octaethylporphyrin (Ni(OEP)): the *meso*-bromovinyl compound was converted to the *meso*-acetylene derivative (**1**), which was converted to a butadiyne-bridged dimer (**2**) under the Eglinton conditions (Scheme 1).[7] The pioneering exploration of peripheral cross-coupling is probably attributed to those of Smith and co-workers,[8,9] where the β-olefinated porphyrins (**4**) were prepared from the β-mercurated porphyrins (**3**) under Heck coupling conditions (Scheme 1).

While the reports on peripheral C−C bond formation were sparse early on, this area exploded in the 1990s with major efforts on metalloporphyrins and metal-bipy/terpy compounds. To date, the peripheral modification approach becomes omnipresent in all areas of inorganic chemistry, and notable applications range from the formation of robust molecular scaffolds to the syntheses of metal-bioconjugates under mild conditions. This review is organized by the types of reactions in the following order: Sonogashira and Cadiot−Chodkiewicz, Suzuki and Negishi, Heck, Stille, and oxidative/reductive homocoupling reactions. The peripheral olefin metathetic reactions were recently covered in the excellent review by Bauer and Gladysz[10] and will not be included here. Finally, the subject of this review should not be confused with the activation of small molecules via metal coordination—a topic key to homogeneous catalysis that has

Scheme 1. Early Examples of Peripheral C−C Bond Formation Reactions



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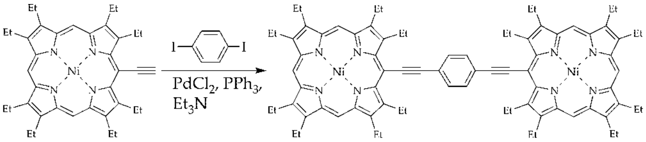
* E-mail: tren@purdue.edu. Tel.: 1-765-494-5466. Fax: 1-765-494-0239.

10.1021/cr8002592 CCC: \$71.00

Tong Ren received his B.S. and M.S. in chemistry in China (1981 and 1984) and his Ph.D. in inorganic chemistry from Texas A&M University under the supervision of F. Al Cotton (1990). He held postdoctoral appointments at Texas A&M with Cotton (1991) and at MIT with Stephen J. Lippard (1991−1993). He was an assistant professor at Florida Institute of Technology (1993−1998) and an associate professor at the University of Miami (1998−2005), and he has been a full professor at Purdue University since 2005. Research interests in his laboratory include organometallic molecular wires, metal−biomolecule conjugates, and mitigation of hazardous chemicals.

been discussed in numerous monographs and reviews. It is worthwhile to mention that a two-volume set under the title of "Reactions of Coordinated Ligands" provides a good overview of the activation of ligands with reactive sites typically at either the α- or β-positions.[11,12]

Scheme 2. Sonogashira Reaction on Ni(OEP)



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2. Sonogashira and Cadiot−Chodkiewicz Reactions

The Sonogashira reaction (also known as Heck−Cassar−Sonogashira−Hagihara reaction)[13−15] refers to the cross-coupling between a terminal alkyne and an aryl halide in the presence of catalytic amounts of Pd(II)/Pd(0), Cu(I), and base. The reaction involves a series of intermediate steps such as alkynyl transmetalation (Cu to Pd) and reductive elimination to afford the final product. The detailed description of mechanistic aspects of the Sonogashira reaction can be found in reviews and monographs.[4,16,17]

$$\mathrm{ArX + HC{\equiv}CR \xrightarrow[Base]{Pd^{2+},\ Cu^{+}} ArC{\equiv}CR} \qquad (1)$$

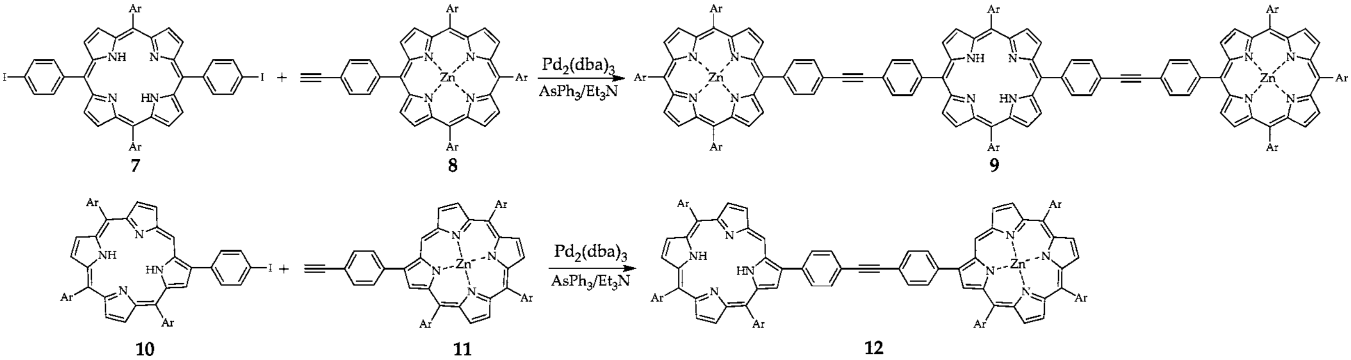
2.1. Modification of Metalloporphyrins

The earliest attempt of Sonogashira modification on porphyrin appeared in a 1993 publication by Arnold and co-workers, where the cross-coupling between Ni(OEP) bearing a *meso*-ethyne substitutent (**5** in Scheme 2) and 1,4-diiodobenzene (or 1,3-diiodobenzene) resulted in dimers of Ni(OEP) bridged by 1,4- (**6**) or 1,3-diethynylbenzene.[18] In a later report, cross-coupling reactions between compound **5** and either an I−R or an I−bridge−I type substrate were explored, and many bridged dimers of Ni(OEP) were prepared.[19]

Shortly after Arnold's initial report, Lindsey and co-workers disclosed the preparation of a dendritic Zn−tetraphenylporphyrin pentamer from the cross-coupling between a Zn−tetraphenylporphyrin (TPP) bearing an iodo substituent on each of the phenyls and 4 equiv of TPP containing only one ethyne substituted phenyl.[20] Subsequent efforts from Lindsey's group include (i) cross-coupling between a TPP with one 4′-iodophenyl and a TPP with 4′-ethynylphenyl to form a dimer[21,22] and (ii) cross-coupling between H_2(TPP) bearing 4′-iodophenyl at both the 5- and 15-positions (**7** in Scheme 3) and 2 equiv of Zn(TPP) bearing a peripheral ethyne (**8**) to yield a linear trimer (**9**).[23−25] The formation of a TPP dimer (**12** in Scheme 3) via the cross-coupling between two β-substituted porphyrins (**10** and **11**) was realized by Lindsey and Balasubramanian.[26] Photodyads linked by a phenylene−ethyne unit were also reported.[27] The Cu-free Sonogashira conditions (as noted in Scheme 3) were always used to prevent both Cu occupation of free base TPP and the Glaser-type homocoupling side reaction. Aided with analytical size-exclusion chromatography and MALDI-TOF MS data, a mechanism was proposed to account for the byproducts detected under the Cu-free conditions.[28] More recently, Martensson and co-workers further explored Cu-free reaction conditions, especially the effects of bases and solvents, and prepared Au(III)-free base porphyrin dyads under the optimized conditions.[29]

The laboratory of Therien prepared Zn-porphyrins bearing one or two ethynes at either the *meso*- or β-positions from the respective bromo precursors and, subsequently, the dimer and trimer bridged by acetylene at the *meso*-positions.[30−32] Using a 5,15-dibromo precursor, 4-dimethylaminophenylethyne and 4-nitrophenylethyne were placed on the *meso*-positions through the sequential Sonogashira couplings to yield *push−pull* porphyrins (Scheme 4, compound **13**).[33] Symmetric bis(4-X-phenylethyne) compounds were similarly

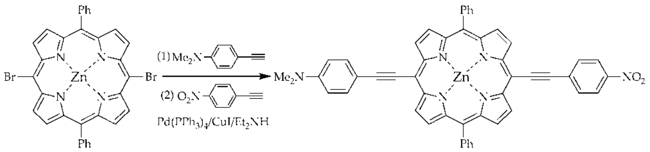
Scheme 3. Sonogashira Modification of TPP at *meso*- and β-positions



7 8 9

10 11 12

Scheme 4. Sonogashira Modification of TPP at *meso*- and *β*-positions



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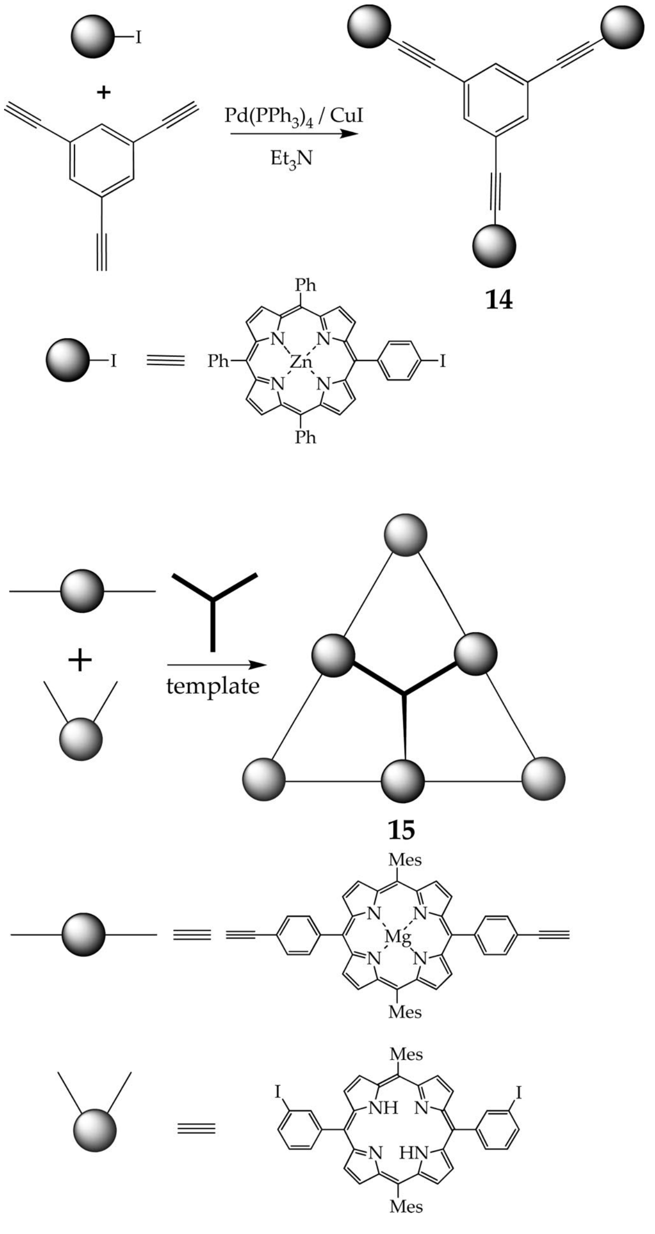
Scheme 5. Preparation of Supramolecular Arrays via Sonogashira Coupling



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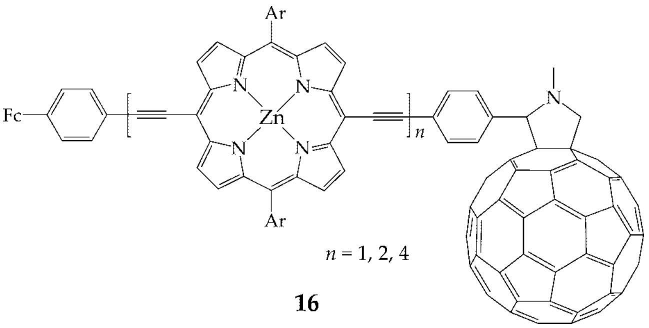
Scheme 6. Ferrocene−Fullerene Dyad



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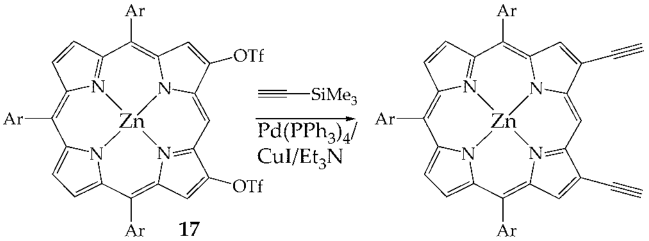
Scheme 7. Sonogashira Coupling with Triflate Substituents



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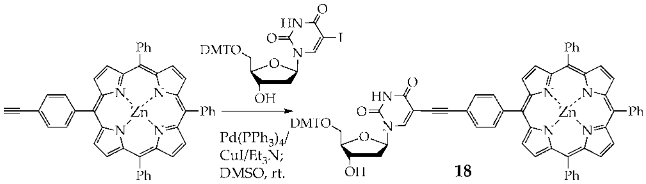
prepared with X = NMe$_2$, OMe, F, H, and NO$_2$.[34] More recently, Therien and co-workers extended their Sonogashira modification to construct linear Zn-porphyrin oligomers bridged by ethyne at *meso*-positions,[35] linear triads of Ru(terpy)$_2$−Zn(Porp)−acceptor,[36] and those of nitrophenyl or nitro-oligothiophene as the acceptor.[37,38] In addition, porphyrin dimers bridged by a single ethyne at either (*meso*,*meso*-), (*meso*,*β*-), or (*β*,*β*-) positions undergo a cocatalyzed [2 + 2 + 2]-cycloaddition reaction to afford cofacial porphyrin dimers and oligomers.[39−41]

Modifications of metalloporphyrins via Sonogashira coupling have been studied by many other groups. Shultz and co-workers reported a detailed study of the formation of a porphyrin dimer through the reaction between 5-iodo-substituted 10,15,20-trimesitylporphyrin Zn(II) and 1,1′-di(ethynyl)methylenecyclohexane (an *iso*-ene-diyne),[42] and they noticed that the yields of Sonogashira coupling were dramatically increased through the in situ desilylation of 1,1′-bis(trimethylsilylethynyl)methylenecyclohexane. Using 5,15-diiodo-10,20-dimesitylporphyrin Zn(II) as the linear linker, Gossauer and co-workers prepared both the symmetric and unsymmetric trimers of a 1,3,5-triethynylbenzene core (Scheme 5, compound **14**) and a hexameric porphyrin dendrimer of an extended trigonal core.[43] Lindsey and co-workers developed two sets of building blocks: 5,15-(4-ethynylphenyl)-10,20-dimesitylporphyrin as the linear linker, and 5,15-(3-iodophenyl)-10,20-dimesitylporphyrin as the 60 deg linker. Two building blocks cross-coupled in the presence of a trigonal template (trinitrile) to afford a hexameric macrocycle (Scheme 5, compound **15**).[44] Sanders and co-workers later extended the strategy to a slightly different triad of Zn(II)-porphyrin.[45]

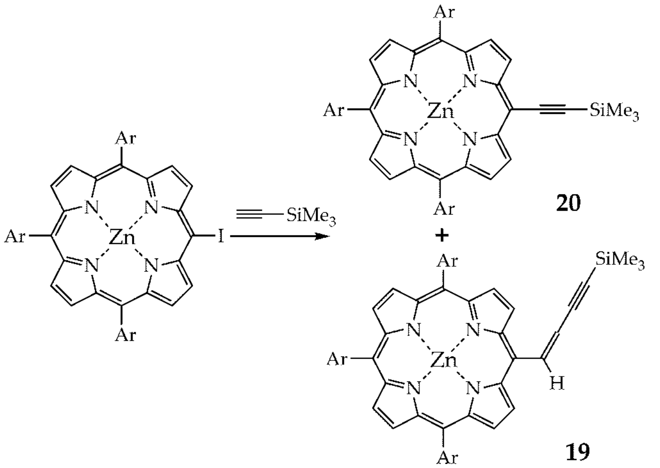
Metalloporphyrins are often introduced as the chromophore in photonic wires via Sonogashira coupling. Odobel and co-workers prepared a Zn(II)−phthalocyanine (donor)−Sn(II) porphyrin (acceptor) dyad spanned by oligo(phenyleneethynylene) using stepwise cross-coupling reactions.[46] Similarly, Anderson and co-workers applied successive cross-couplings to prepare dyads of ferrocene (donor)−fullerene (acceptor) linked by butadiyne−Zn(porp) oligomers (**16** in Scheme 6),[47] where the excitation at Zn(porp) initiated the charge transfer from ferrocene to fullerene.

Other porphyrin modifications via Sonogashira coupling include the following: (i) *meso*-grafting of ferrocenylethyne through the reaction between 5,15-dibromo-10,20-diphenylporphyrin Ni(II) and ferrocenylacetylene;[48] (ii) *meso*-grafting of phenyleneethyne;[49] (iii) grafting of triarylamine at two *trans*-*meso*-positions;[50] (iv) modification of Zn-porphyrin with *meso*-perfluoroalkyl with *meso*-ethynyl appendage;[51] (v) preparation of linear trimer and symmetric pentamer of Zn-porphyrin with ethyne as *meso*-bridges;[52] (vi) formation of Zn(II) TPP-21-thiaporphyrin dyads of phenylethynylene linkages;[53] (vii) attachment of an ami-

Scheme 8. Formation of Zn–Porphyrin Nucleoside Conjugate



Scheme 9. Formation of Eneyne Product



dinium group through an ethyne bridge at either the *meso*- or *β*-position;[54] (viii) preparation of Zn(II) porphyrin–perinaphthothioindigo conjugate via coupling imidazolylethynyl onto the *meso*-positions of Zn(porphyrin);[55,56] and (ix) introduction of thiophene appendage at the *meso*-position of Ni-porphyrin.[57] Osuka and co-workers prepared *β*,*β*′-diethyne Zn(porphyrin) from *β*,*β*′-bis(triflate) Zn(porphyrin) (**17** in Scheme 7), an unusual starting material for Sonogashira coupling.[58] Stultz and co-workers prepared the conjugate of 5-iodouridine and 5-(4′-ethynylphenyl)-10,15,20-triphenylporphyrin Zn(II) (compound **18** in Scheme 8), which was converted to the corresponding phosphoramidite and incorporated into single-stranded DNA.[59]

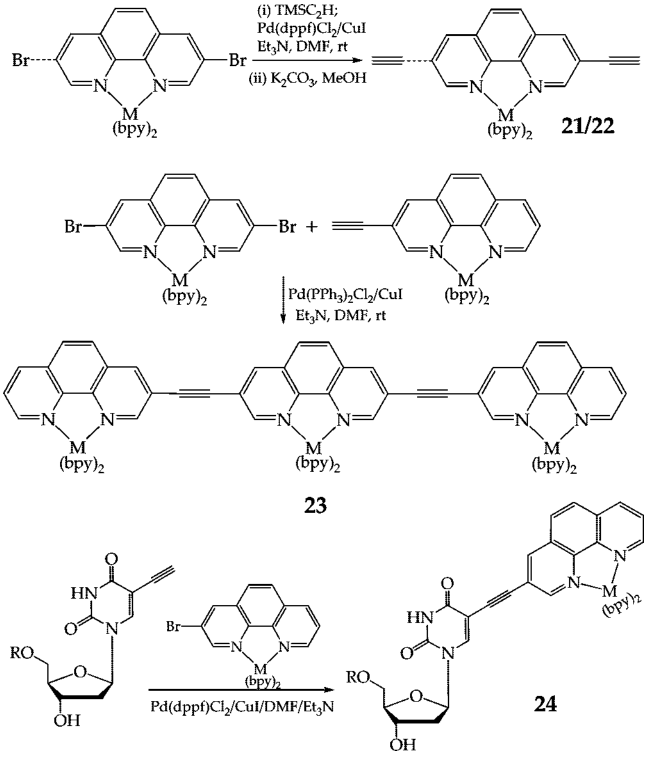
While the Sonagashira coupling method results in expected products in good yield, formation of byproduct is frequently observed but rarely subjected to a thorough analysis. Lin and co-workers reported the attachment of *N*-methylated pyridylethynyl at the *meso*-positions of Zn-porphyrins,[60] and the surprising modification of 2-pyridineacetyl at the *meso*-position of Ni(II)-porphyrin during the Sonogashira coupling reaction.[61] Yeh and co-workers found that the cross-coupling between 5-iodo-10,15,20-triarylporphyrin Zn(II) and HC≡CSiMe$_3$ in large excess (10–50-fold) resulted in a *meso*-eneyne product (**19** in Scheme 9) in addition to the expected *meso*-ethyne derivative (**20**), and the ratio between compounds **19** and **20** depends on the nature of Pd catalysts.[62]

Feasibilities of Sonogashira coupling on the periphery of metallophthalocyanine have been demonstrated, including the formation of zinc–phthalocyanine–estradiol conjugates,[63] bis(zinc(II) phthalocyanine) bridged by perylenediimide,[64] and the dyad of zinc phthalocyanine and tin porphyrin with oligo(phenyleneethynylene) bridge.[46]

2.2. Modification of Compounds Bearing Bipyridine/Terpyridine and Analogous Ligands

Transition metal complexes of 2,2′-bipyridine (bipy), 2,2′:6′,2”-terpyridine (terpy), and related ligands have attracted tremendous interest during the last three decades,[65] and the peripheral covalent modification has been recognized as an efficient tool for the formation of functional conjugates and hierarchical assembly based on metal bipy/terpy species. The first example was from Tor and co-workers, who demonstrated the modification of 3-bromo-1,10-phenanthroline that was coordinated to a [M(bipy)$_2$]$^{2+}$ fragment (M = Ru or Os) under the Sonogashira conditions to yield the corresponding 3-ethyne derivative (compound **21** in Scheme 10).[66–68] Complexes containing 3,8-dibromo-1,10-phenanthroline were similarly modified to yield the corresponding 3,8-diethyne derivatives (**22**), and the reaction between 3,8-dibromo-1,10-phenanthroline complex and 2 equiv of complex **21** resulted in linear trimer **23**. The same cross-coupling strategy was extended to the reactions between 5-(ethynyl)deoxyuridines and [Ru(bipy)$_2$(3-BrPhen)]$^{2+}$, which afforded the Ru-containing nucleosides (**24** in Scheme 10).[69] More recently, Sonogashira modification of Ru complexes based on 4,7-dibromo-1,10-phenanthroline ligand was described by Tor's group, where interesting dual emissions at room temperature were uncovered.[70] Hocek and co-workers have reported similar modification of 2′-deoxyadenosine by a series of Ru(bipy)$_3$ compounds.[71]

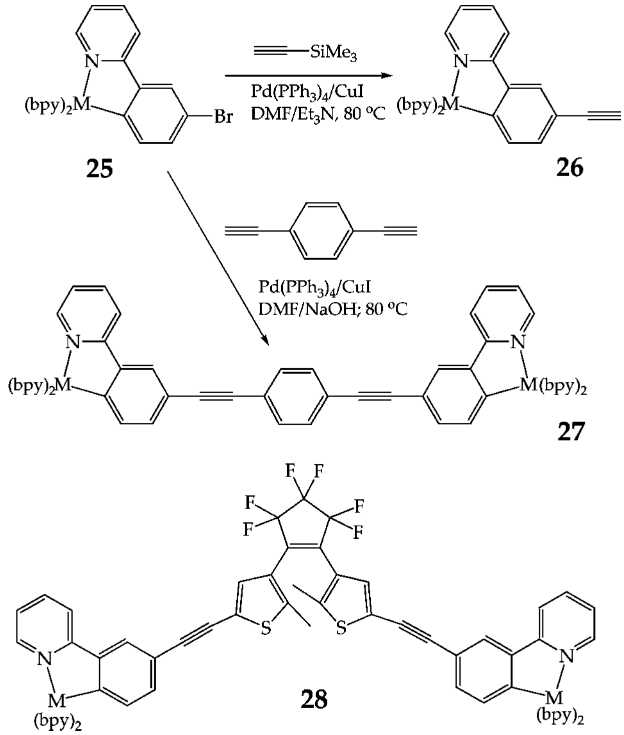
Scheme 10. Modification of 3-Br-phen Ligands



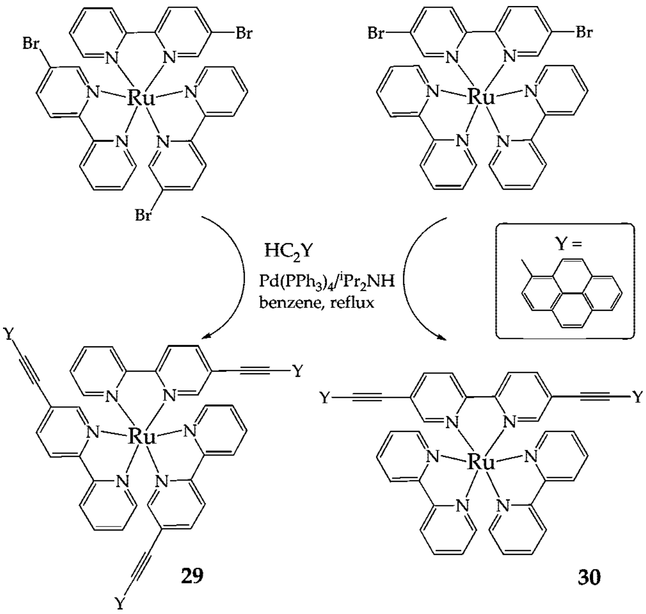
Coudret and Launay investigated the cross-coupling reactivity of [Ru(bipy)$_2$L]$^+$ (**25** in Scheme 11), where L is a cyclometallated 5-bromo-2-phenylpyridine. Complex **25** cross-couples with either a terminal ethyne or a HC≡C–Ar–C≡CH to yield either a 5-ethyne monomer (**26**) or a bridged dimer (**27**), respectively.[72–74] A bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene bridge was similarly introduced between two units of [Ru(bipy)$_2$L]$^+$ (**28**), and photomodulation of the electronic-coupling between two Ru centers was demonstrated.[75] It was also demonstrated that a thio-acetal capped OPE can be appended to complex **25** using iterative Sonogashira coupling reactions.[76]

Ziessel and co-workers prepared many Ru-bipy and Ru-terpy compounds bearing one or multiple pyrenylethynyl

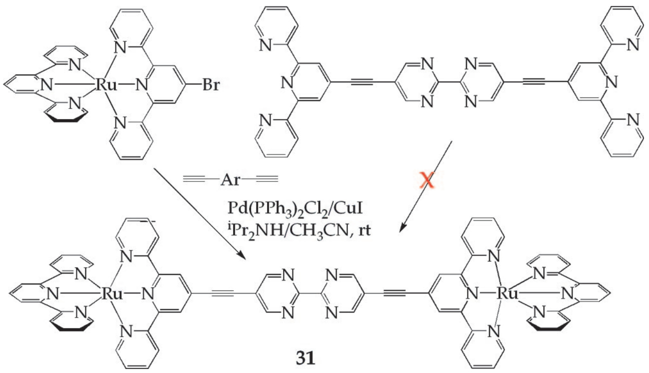
Scheme 11. Modification of 5-Bromo-2-phenylpyridine Complex



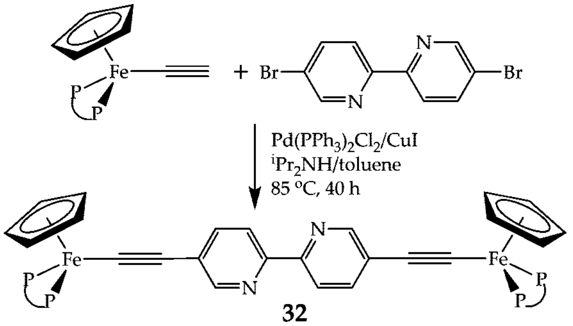
Scheme 12. Pyrenylethyne Modification of Coordinated 5-Br-bipy



Scheme 13. Bis-Ru(terpy)$_2$ via Cross-Coupling



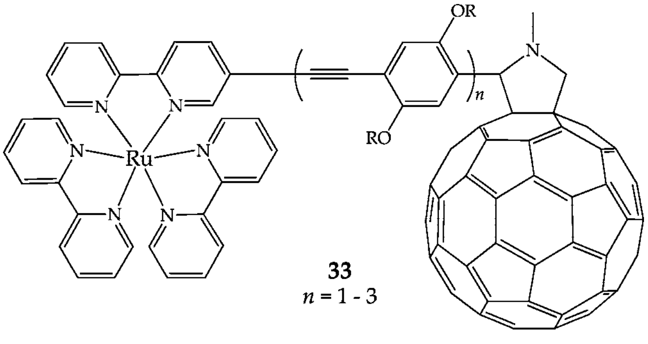
Scheme 14. Modification of bipy by Organometallic Alkyne



substituents. A frequently encountered problem is the low solubility of free bipy or terpy bearing pyrenylethyne, which prevents the formation of Ru complexes. The Sonogashira coupling was extensively utilized in two types of combinations: (i) reaction between a Ru species bearing either 5-Brbipy, 5,5′-Br$_2$bipy, or 4′-Br-terpy and pyrenyl-1-ethyne; and (ii) Ru species bearing 5-ethynylbipy or 5,5′-(diethynyl)bipy and 1-bromopyrene.[77,78] Ziessel and co-workers reported the attachment of pyrenylethynyl to either Ru(5-Brbipy)$_3^{2+}$ or Ru(bipy)$_2$(5,5′-Br$_2$bipy)$^{2+}$ under Sonogashira conditions to yield complexes **29** or **30** (Scheme 12), respectively.[79] Neither complex could be prepared from the corresponding bipy ligands bearing pyrenylethynyl because of their poor solubility. A similar difficulty was experienced in the attempt of preparing complex **31** (Scheme 13) by reacting bis-terpyridines bridged by rigid spacers with Ru species with labile sites,[80] which was circumvented with a cross-coupling between 2 equiv of Ru(terpy)(4′-Br-terpy) and the diethynyl containing bridges (Scheme 13). More recently, Ru(terpy)$_2$ species with pyrenylethynyl pendants at 5- and 5″-positions were prepared from the cross-coupling of Ru(5,5′-dibromo-terpy)$_2$ or Ru(5,5″-dibromo-terpy)(terpy) and pyrenylethyne.[81] Similar grafting of pyrenylethynyl was also achieved with 5,6-dibromo-1,10-phenanthroline bound to Ru.[82] Further extending this strategy, Ru-bridge-Os-bridge-Ru triad was prepared from the ethynyl capped Ru(bipy)$_3$ unit and diiodo functionalized Os(bipy)$_3$ unit,[83] and Ru(bipy)$_3$ unit of extended thiophene arms was prepared by diiodo functionalized Ru(bipy)$_3$ and ethynyl-capped thiophene moiety.[84] More recently, the collaboration between the groups of Lapinte and Ziessel led to the preparation of CpFe(P−P)(σ-C≡C−) modification of both 2,2′-bipy and 4,4″-terpy ligand (compound **32** in Scheme 14), which coordinate to Mo(CO)$_4$ and Ru(terpy) fragments, respectively, to yield novel heterometallic arrays.[85] Benniston and co-workers also prepared dimers of Ru(terpy)$_2$ bridged with either an extended ethynylnaphthalene using either cross-coupling and homocoupling reactions[86] or dyads with biphenyl linkers of controlled torsion angles.[87]

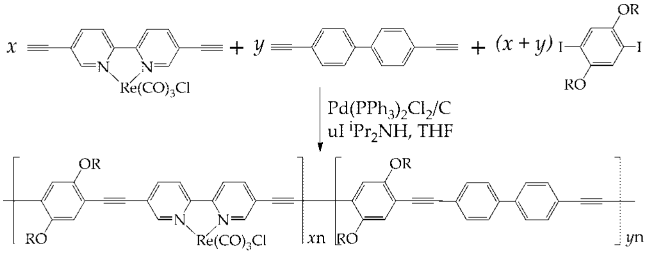
Sonogashira coupling was also used to graft a terpy unit onto a dithiolene bridged Fe$_2$(CO)$_6$ moiety, and the subsequent complexation of the terpy to Ru afforded a photoactive iron hydrogenase model.[88] Subsequently, a Ru(bipy)$_3^{2+}$ unit was appended through cross-coupling to a triarylphosphine bound to Fe$_2$(CO)$_6$.[89] Taking advantage of the selectivity of cross-coupling reactions, Odobel and co-workers constructed photodyads (**33** in Scheme 15) of Ru(bipy)$_3^{2+}$ and fullerene with OPE bridges.[90] A related photodyad based on the combination of porphyrins and Ru(terpy)$_2^{2+}$ was also reported.[91]

Scheme 15. OPE-linked Photo Dyads of Ru(bipy)$_3$ and Fullerene



33
n = 1 - 3

Scheme 16. Preparation of Metallo-Main-Chain Polymers



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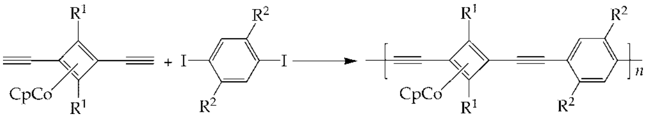
Scheme 17. Sonogashira Copolymerization of π-Carboxylic Complexes

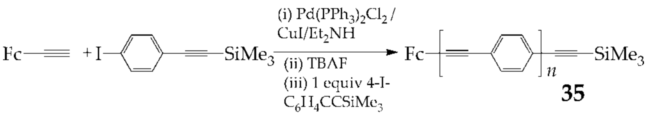


Polymers and dendrimers based on metallomonomers can be prepared using the Sonogashira coupling. Copolymerizations of metal (M = Ru and Re) complexes containing 5,5′-diethynyl-2,2′-bipyridine with 1,4-diiodobenzene under the Sonogashira conditions yielded metal-containing rigid rod poly(heteroaryleneethynylene)s (**34** in Scheme 16).[92,93] Similarly, tricarbonyl(arene)chromium was incorporated into the main chain of PPE by copolymerizing η^6-(1,4-diethynylbenzene)Cr(CO)$_3$ and 1,4-diiodobenzene.[94] Chan and co-workers used Sonogashira coupling to append OPEs onto Pt(II) Schiff base complex to yield phosphorescent dyes.[82] Osawa, Wakatsuki, and co-workers reported a unique and elegant approach of metallodendrimer synthesis: the cross-coupling between M(bipy')$_3$ (bipy' is the bipy ligand bearing 1-ethynylbenzene-4-I substituent at both 5 and 5′ positions) and Ru(4′-ethynylterpy)$_2$ to afford both the first- and second-generation dendrimers in over 60% isolated yields.[95]

2.3. Modification of π-Coordinated Carbocyclic Ligands

These reactions frequently involved η^5-cyclopentadienyl (Cp), η^4-cyclobutene, and η^6-benzene. The early work of Bunz and Altmann demonstrated the copolymerization of (η^4-1,3-diethynylcyclobutene)(η^5-cyclopentadienyl)cobalt with 1 equiv of 1,4-diiodobenzene in the presence of PdCl$_2$(PPh$_3$)$_2$, CuI, and piperidine (Scheme 17).[96] Subsequently, carbon-rich scaffolds of interesting topology such as "butterfly" were prepared from (η^4-tetraethynylcyclobutene)(η^5-cyclopentadienyl)cobalt using Sonogashira coupling reactions in succession.[97]

Scheme 18. Synthesis of Fc-OPE via Sonogashira Reaction



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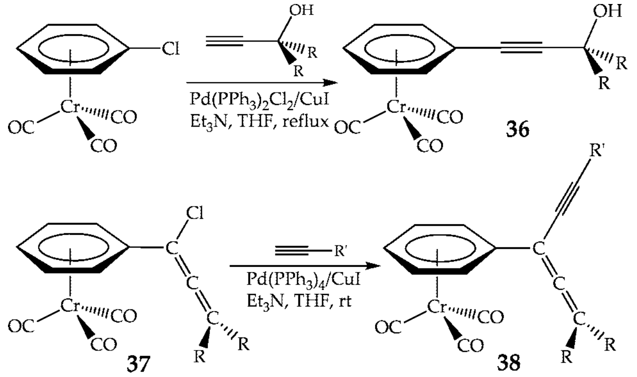
Scheme 19. Modification of (η^6-Benzene)Cr(CO)$_3$



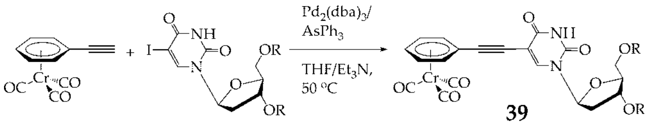
36 **37** **38**

Another early example is the synthesis of ferrocene capped OPE (**35** in Scheme 18) by Sita and co-workers, where the OPE chain off the ferrocene center was extended by an iterative sequence of Sonogashira coupling and deprotection reactions.[98] The same methodology was used to prepare Fc$-$(C$\equiv$CC$_6$H$_4$)$_n-$SR by Sita[98] and others with n up to 6,[99] and these oligomers prove to be useful probes for the study of intramolecular electron transfer. Lin and co-workers adopted the similar protocol to prepare a series of Fc$-$(C$\equiv$CC$_6$H$_4$)$_n-$4-py and investigated the ability of these rigid species as *N*-donor ligands.[100] Recently, Sita and co-workers extended the work to Fc-capped OPEs containing a pyridyl unit in the backbone.[101]

Similar to the Fc-containing species, compounds containing η^6-benzene ligand can also be modified using Sonogashira coupling, and most of these studies came from the laboratory of Muller. The initial success was based on the modification of (η^6-chlorobenzene)Cr(CO)$_3$ with HC$\equiv$CSiMe$_3$ in the presence of Pd(PPh$_3$)$_2$Cl$_2$, CuI, and Et$_3$N, and the resultant η^6-(ethynyl)benzene species was further cross-coupled with either η^6-chlorobenzene species to yield an ethyne-bridged dimer or various iodobenzenes to afford the corresponding derivatives.[102] Subsequently, modification with propargyl group yielded (η^6-propargylbenzene)Cr(CO)$_3$ (**36** in Scheme 19), and the chloroallenyl species (**37**) underwent a further Sonogashira modification to yield the exotic ynallenyl arene derivative (**38**).[103] Subsequent studies include (i) conversion of η^6-(1,4-diethynyl)benzene compound to the corresponding η^6-(1,4-diphenyleneethynyl)benzene species[104] and (ii) conversion of (η^6-chlorobenzene)-Cr(CO)$_2$(PPh$_3$) to the corresponding (η^6-ethynylbenzene) species.[105]

Conjugates between 2′-deoxyuridine and (η^6-arene)M-(CO)$_3$ were prepared using Sonogashira coupling method as well.[106] The authors noted that both the conventional homogeneous conditions such as Pd(PPh$_3$)$_2$Cl$_2$/CuI/Et$_3$N/THF and the use of resin "Amerlite IRA-67" as the weak base only led to intractable reaction mixtures. The use of Pd$_2$(dba)$_3$/AsPh$_3$/Et$_3$N/THF conditions resulted in the formation of the expected conjugate (**39** in Scheme 20) in good yield (76%).

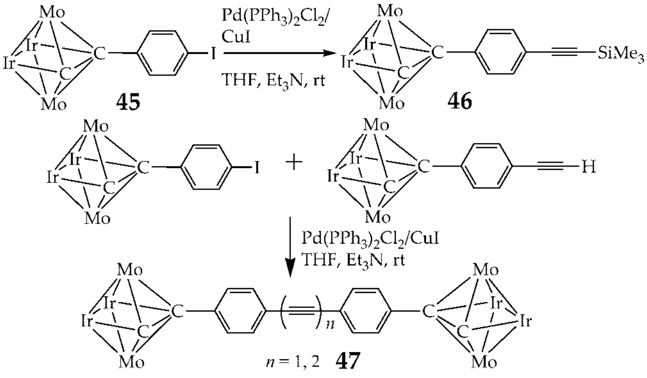
Scheme 20. Conjugate with Uridine



2.4. Modification of Polynuclear Compounds

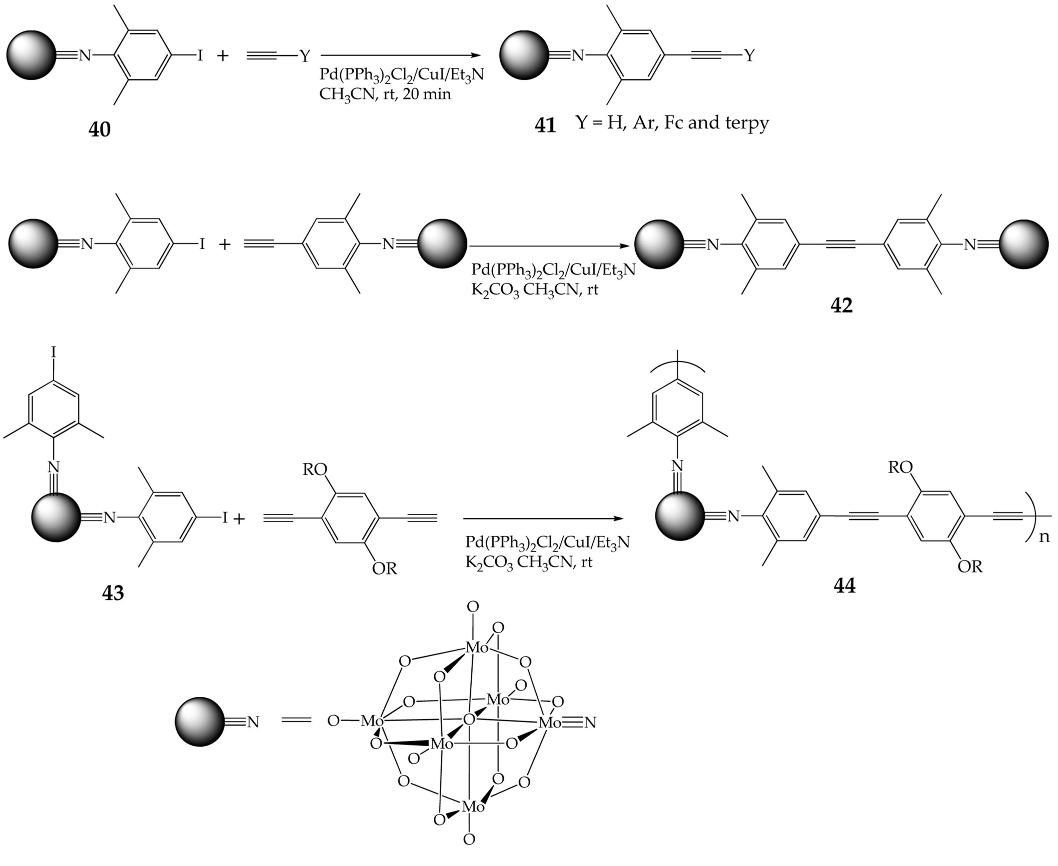
Cross-coupling and homocoupling reactions on the periphery of di- and polynuclear species remain sparse, and one of the limiting factors is the structural integrity of metallo species under the coupling reaction conditions. Using polyoxometalate $[Mo_6O_{19}]^{2-}$ as the starting point, one or two M=O functionalities can be transformed to Mo=NAr.[107] With 4-IPh as the Ar (compound **40** in Scheme 21), a number of derivatives bearing a C≡CY group (Y = Ar' and H, **41**) were prepared via the Sonogashira coupling.[108] The dimeric polyoxo species, termed "dumbbells" (**42**), can be achieved using one of two approaches: (i) the cross-coupling between compounds **40** and **41** (Y = H) and (ii) the cross-coupling between 2 equiv of **40** and 1,4-diethynebenzene.[109] Subsequently, the cross-coupling reactions between iodo-bearing polyoxometalate and appropriate ethynes afforded derivatives bearing ferrocenyl, terpyridine, and enantiomerically pure 1,1′-binaphthyl functionalities, and these compounds exhibited interesting redox and optical activities.[110−112] The polyoxo ion bearing two Mo=NPh-4-I in *cis*-positions (**43**) was also prepared, and it reacts with 1,4-diethynebenzene in 1:1 molar ratio to afford a mixture of zigzag oligomers with *n* around 18 (**44**).[113] The degree of polymerization could be increased by extending the aryleneethynyl bridges, and these rigid rod materials were found to be excellent active species for single-layer photovoltaic cells.[114]

Scheme 22. Sonogashira Couplings on Mo_2Ir_2 Clusters



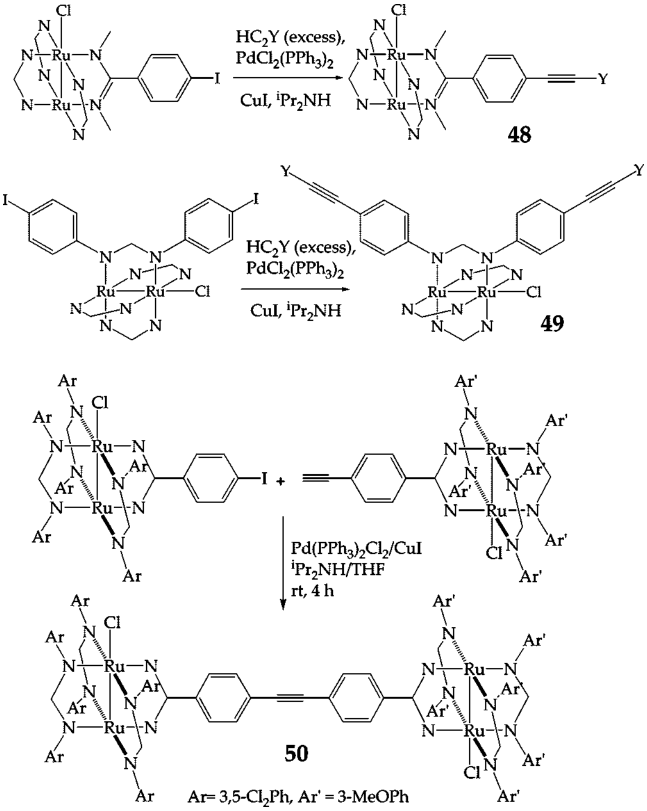
Humphrey and co-workers prepared Mo_2Ir_2 clusters containing a (μ_4-η^2-C≡C)C_6H_4−4-I ligand (compound **45** in Scheme 22), which was converted under Sonogashira conditions to the corresponding $[Mo_2Ir_2]$(μ_4-η^2-C≡C)C_6H_4-4-C≡$CSiMe_3$ (**46**).[115] Cross-coupling between compounds **45** and **46** (desilylated) resulted in both the expected ethyne-bridged dimer and butadiyne-bridged dimer (**47**) as byproducts of Cu(I) promoted oxidative coupling.[115] Similar reactions were carried out with (μ_4-η^2-5-C≡C)C_4H_2S-2-I (C_4H_2S is 2,5-substituted thiophene) replacing (μ_4-η^2-C≡C)C_6H_4-4-I, resulting in the cluster $[Mo_2Ir_2]$(μ_4-η^2-5-C≡C)C_4H_2S-2-C≡$CSiMe_3$. Upon desilylation, the latter compound can be either homodimerized to yield the butadiyne bridged dimer of Mo_2Ir_2 cluster or cross-coupled with the 2-I species to yield the ethyne-bridged dimer.[116] Cross-coupling reactions between the μ_3-bromocarbyne on a Co_3 cluster with various W- or Ru-bound polyyne were also successful under Sonogashira conditions.[117]

Scheme 21. Sonogashira Couplings with Polyoxo Anion Building Blocks

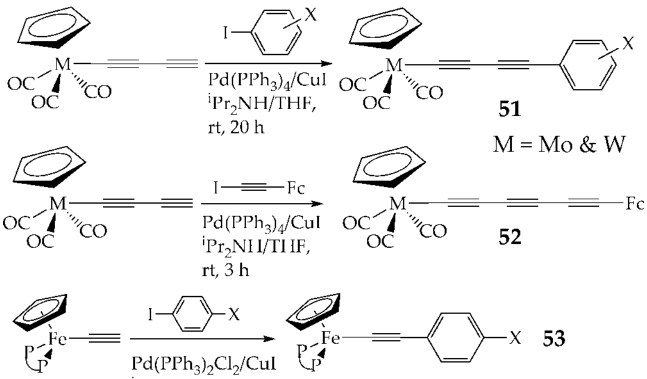


Another set of robust compounds is based on diruthenium paddlewheel motifs developed in our laboratory, namely, $Ru_2L_2L'_2$ and Ru_2L_3L' type compounds,[118] where the ancillary ligand L is either *N,N'*-di(3-methoxyphenyl)-formamidinnate (DmAniF) or *N,N'*-di(3,5-dichlorophenyl)-formamidinate ($D(3,5\text{-}Cl_2Ph)F$), and L' is an iodo-containing ligand, either *N,N'*-dimethyl-4-iodobenzamidinate (DMBA-I) or *N,N'*-di(4-iodophenyl)formamidinate (D(4-IPh)F). Two types of Sonogashira reactions with a Ru_2 substrate are presented in Scheme 23. The initial attempt was based on $Ru_2(DmAniF)_3(DMBA\text{-}I)Cl$, which cross-coupled with $HC\equiv CY$ ($Y = SiMe_3$ and Fc) to afford the corresponding $Ru_2(DmAniF)_3(DMBA\text{-}C\equiv CY)Cl$ (**48**) in modest yields.[119] Concurrent Sonogashira couplings on $Ru_2(DmAniF)_2(DMBA\text{-}I)_2Cl$ resulted in $Ru_2(DmAniF)_2(DMBA\text{-}C\equiv CFc)_2Cl$ in decent yield.[120] Similarly, both $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)Cl$ and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}I)_2Cl$ underwent Sonogashira coupling to afford, respectively, $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}C\equiv CY)Cl$ and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_2(DMBA\text{-}C\equiv CY)_2Cl$ with yields better than those of DmAniF auxiliary ligands.[121] The improved yields are attributed to the electron deficiency of $D(3,5\text{-}Cl_2Ph)F$ ligand, which renders $Ru_2(D(3,5\text{-}Cl_2Ph)F)_{4\text{-}x}(DMBA\text{-}I)_xCl$ type compounds better substrates for cross-coupling reactions. $Ru_2(DArF)_{4\text{-}x}(D(4\text{-}IPh)F)_xCl$ ($x = 1$ (**49**) and 2) type compounds also underwent Sonogashira coupling reaction under similar conditions. Furthermore, heterodimer of Ru_2 compound of a single ethyne bridge (**50**) was obtained from the coupling reaction between $Ru_2(DmAniF)_3(DMBA\text{-}I)Cl$ and $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}C\equiv CH)Cl$.[122] Sonogashira coupling reactions using *trans*-$(RC\equiv C)_2[Ru_2(DmAniF)_3(DMBA\text{-}I)]$ as the Ru_2-substrate were also attempted but failed to yield the expected products. Instead, Ru_2-species free of axial alkynyl ligands were detected as the main byproduct.[119]

Scheme 23. Sonogashira Couplings on Ru_2 Compounds



Scheme 24. Extension of M-σ-polyynyl



2.5. Modification of Metal-Bound Alkynyl Ligands

The first of such reactions was reported by Bruce and co-workers, where a W-σ-butadiynyl compound cross-coupled with either iodobenzene or $IC\equiv CFc$ to yield complexes of an extended conjugated backbone (**51** and **52** in Scheme 24).[123−125] Lapinte, Paul, and co-workers successfully cross-coupled $Cp^*Fe(dppe)(\sigma\text{-}C\equiv CH)$ with IAr (Ar as phenyl bearing either electron-donating or -withdrawing substituent) to yield the corresponding $Cp^*Fe(dppe)(\sigma\text{-}C\equiv CAr)$ (**53** in Scheme 24),[126−129] and these compounds provide the basis for a subsequent comprehensive study of the linear free energy relationship (LFER) in metal−acetylide compounds.[130] Alternatively, it is also possible to modify a Ru-bound phenylacetylide with a 4-iodo substituent as demonstrated by Humphrey and co-workers,[131] and this method was key to the convergent synthesis of alkynylbis(bidentate phosphine)ruthenium dendrimers from a 1,3,5-triiodobenzene core.[132]

2.6. Cadiot Reaction

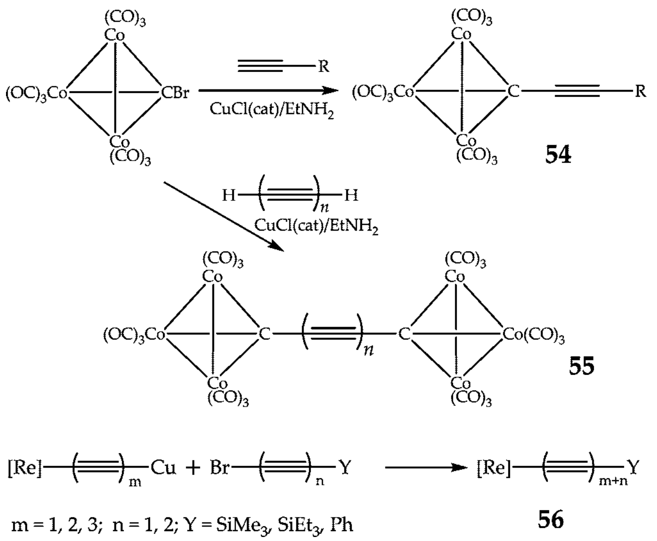
The Cadiot−Chodkiewicz reaction (Cadiot reaction for short) refers to the cross-coupling reaction between a cuprous acetylide and a haloacetylene and is either stoichiometric or catalytic (eq 2).[4,17]

$$RC\equiv CCu + BrC\equiv CR' \xrightarrow{\text{pyridine}} RC\equiv C-C\equiv CR' \qquad (2)$$

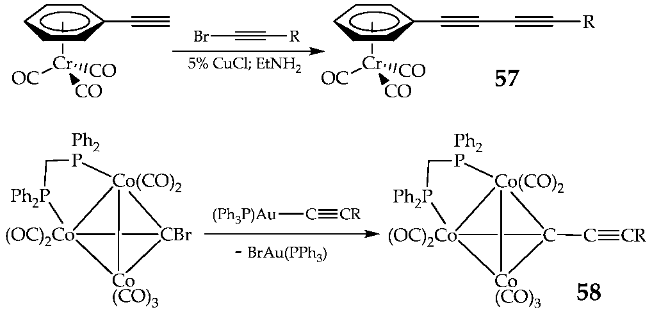
It is an effective alternative to the Sonogashira coupling. Robinson and co-workers demonstrated the utility of *catalytic* Cadiot reaction in the syntheses of both a Co_3 cluster bearing an ethyne (**54** in Scheme 25) and two Co_3 clusters bridged by a polyyndiyl chain (**55**).[133] Gladysz and co-workers prepared $^{134}{-}\sigma\text{-}(C\equiv C)_{m+n}Y$ (**56**, $^{134} = \eta^5\text{-}Cp^*Re(NO)(PPh_3)$) from a *stoichiometric* Cadiot reaction between $^{134}{-}(C\equiv C)_mCu$ and $Br(C\equiv C)_nY$.[134−137] Yam and co-workers utilized *catalytic* Cadiot reaction to prepare a number of $Re(CO)_3({}^tBu_2bpy)(C_6Y)$ type compounds from $Re(CO)_3({}^tBu_2bpy)(C_4H)$ and BrC_2Y.[138]

In addition to the modification of σ-alkynyl ligands, Cadiot reaction has also been performed with the alkynyl functional groups on π-bonded carbocyclic ligands. Muller and co-workers cross-coupled a Cr compound of η^6-(ethynyl)benzene with a number of BrCCR in the presence of $EtNH_2$ and a catalytic amount of CuCl to yield the Cr derivatives bearing η^6-(butadiynyl)benzene (compound **57** in Scheme 26) and studied NLO properties of these derivatives.[139,140] Bunz and co-workers used a *stoichiometric* Cadiot reaction to either convert 1,2-diethynylfer-

Scheme 25. Caddiot Extension of M-σ-polyynyl



Scheme 26. Other Cadiot Couplings



rocene to 1,2-di(butadiynyl)ferrocene[141] or append 1,2-diethynylbenzene to cobound diethynylcyclobutadiene and 1,2-diethynylferrocene.[142] Gleiter and co-workers also utilized *stoichiometric* Cadiot reaction to extend the olygyne chain off the Cp-ring coordinated to a Co center.[143] Bruce and co-workers developed a Cadiot-like reaction for the extension of metal carbon chains: the μ_3-bromocarbyne on a Co_3 cluster reacts with various terminal alkynes capped by $Au(I)PAr_3$ in the presence of Cu(I)−Pd(0) catalysts, and the reactions appear to be driven by the elimination of $BrAu(PAr_3)$ moiety (Scheme 26).[144−146] Similar chain-extension chemistry was successfully carried out with Ru_3/Os_3 clusters.[147] Reactions of metal−polyynyl capped by $AuPAr_3$ with $I{-}(C{\equiv}C)_m{-}I$ resulted in remarkable C_{14}-bridged dimers of monuclear Ru complex and Co_3 cluster.[148]

3. Suzuki and Negishi Reactions

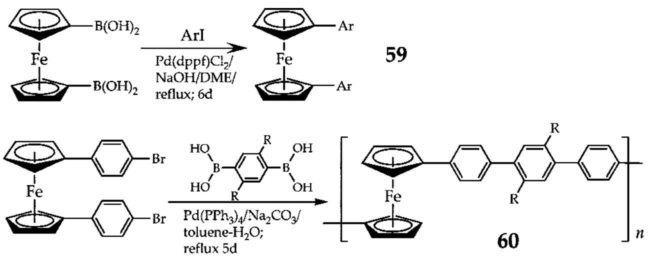
The Suzuki−Miyaura (Suzuki for short) coupling refers to the cross-coupling of an organoboron compound with an organic halide compound in general,[149−151] and it is most frequently practiced in the form of biphenyl formation shown in eq 3.

$$\mathrm{ArB(OH)_2 + XAr'} \xrightarrow[\text{Base}]{\mathrm{Pd^{2+},\ Cu^{+}}} \mathrm{Ar{-}Ar'} \qquad (3)$$

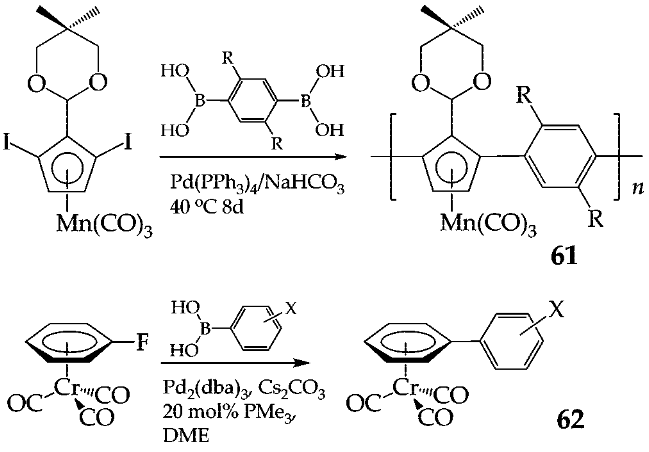
3.1. Suzuki Reactions of Organometallic Species

The early examples of the Suzuki reaction at the ligand sphere appear to be those of Knapp and Rehahn: ferrocene-1,1′-dibronic acid reacted with a number of aryl halides in the presence of $Pd(PPh_3)_4$ and Na_2CO_3(aq) to yield 1,1′-diarylferrocene (**59** in Scheme 27), which could also be

Scheme 27. Suzuki Coupling on Ferrocene



Scheme 28. Suzuki Coupling on Other Metallocenes



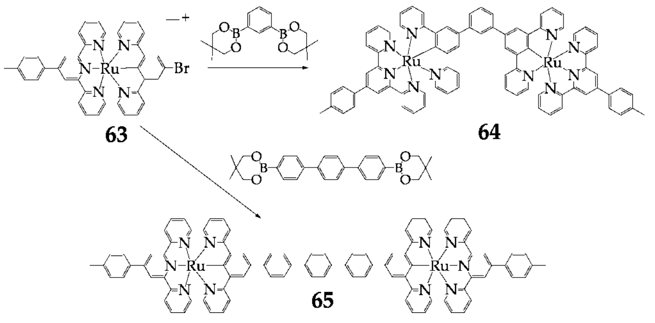
prepared from the reaction between 1,1′-dihaloferrocene (halogen = Br and I) and phenyleneboronic acid.[152] Similarly, 1,1′-di(4-bromophenyl)ferrocene and 1,4-phenylene−diboronic acid reacted under the same Suzuki conditions to yield ferrocene−terphenyl copolymer (**60**).[153,154] Similarly, the reactions between ferrocenylboronic acid and 1,3-dihalo-5-X-benzene (X = donor or acceptor substituent) in the presence of $Pd(dppf)Cl_2$ and refluxing DME resulted in the corresponding 1,3-diferrocenyl-5-X-benzene in ca. 60% yield.[155] Interestingly, the reactions between ferrocenylzinc chloride and 1,3-dihalobenzene under the Negishi conditions (see section 4.5 below) failed to yield 1,3-diferrocenylbenzene.

Bunz and co-workers investigated the utility of Suzuki coupling in the formation of metallo olio(phenylene) species: $[Cp^*Ru(\eta^6\text{-}1,4\text{-}Br_2C_6H_4)]^+$ reacted with phenyl boronic acid to yield a Ru-bound terphenyl;[156] and 2,5-diiodo cymantrenes reacted with 1,4-phenylenedoboronic acid to yield a highly polydisperse 1:1 copolymer (**61** in Scheme 28).[157] (η^6-Fluorobenzene)tricarbonylchromium(0) underwent Suzuki coupling with various substituted phenylboronic acids to afford the corresponding biphenyl derivatives (**62**) in 60−80% yields.[158] Similarly, η^6-(5-bromonaphthalene)tricarbonylchromium was derivatized using Suzuki coupling to yield planar chiral derivatives.[159] The Suzuki coupling method was also used to graft ferrocenyl onto electron-rich oligo(phenothazine)s.[160]

3.2. Suzuki Reactions of Bipy/Terpy Complexes

Collin, Sauvage, and co-workers investigated reactions between [Ru(ttpy)(L)]+ (**63** in Scheme 29, ttpy = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine), L = 1-bromo-3,5-dipyridyl benzene, and diboronic esters to yield a diruthenium species bridged by oligo(phenylene) linkers (**64** and **65**) in the presence of $Pd(PPh_3)_4$ (10 mol %) and Na_2CO_3 (aq) in refluxing dimethyl ether (DME).[161] Suzuki coupling has been utilized in both

Scheme 29. Suzuki Coupling on $[Ru(ttpy)(L)]^+$

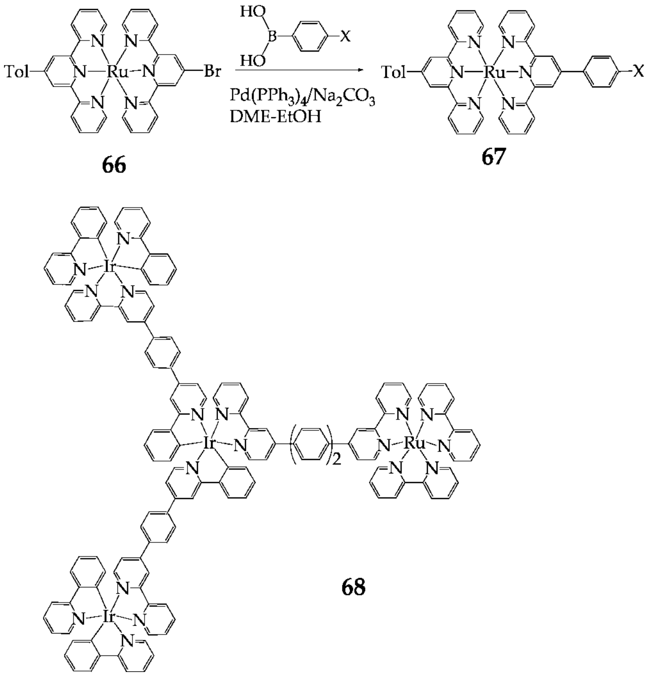


63

64

65

Scheme 30. Suzuki Coupling with $Ru(terpy)_2$



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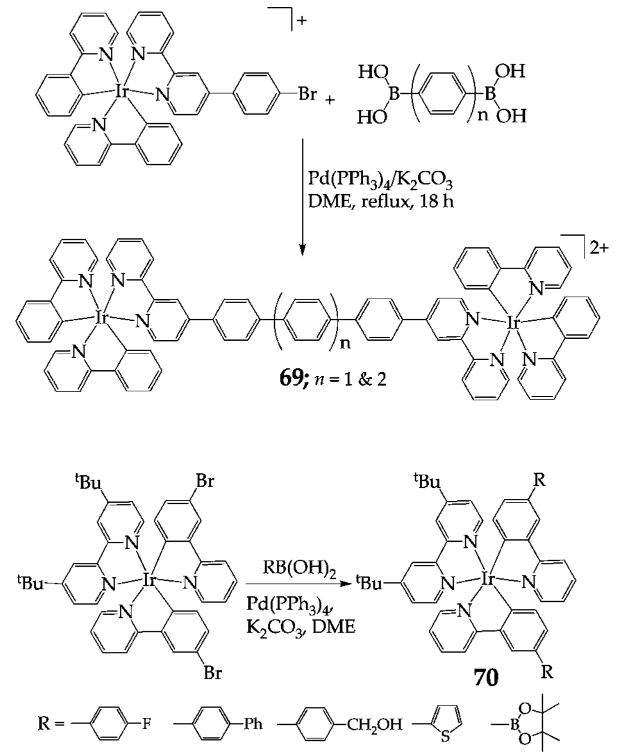
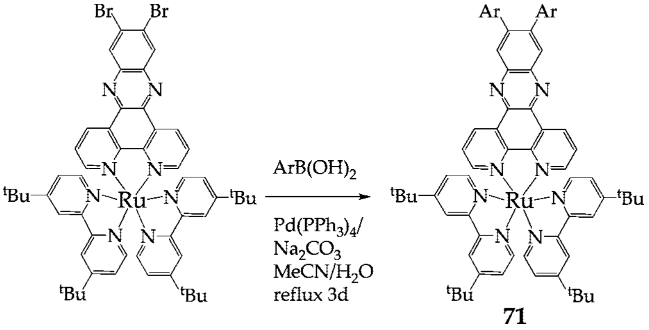
Scheme 31. Suzuki Coupling with Ir-bound bipy



69; $n = 1$ & 2

70

Scheme 32. Extension of Ru-bound Ligand via Suzuki Coupling



71

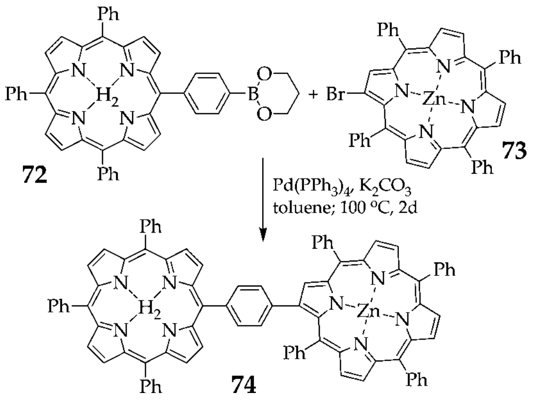
appending an oligo(phenylene) to a metal−bipy/terpy complex and bridging two or more metal−bipy/terpy units with oligo(phenylene)s. Kelch and Rehahn prepared the copolymer of $Ru(terpy)_2$ and terphenyl through the coupling of 1,4-phenylene diboronic acid and bis[4′(*p*-bromophenyl)-2,2′:6′,2″-terpyridine]Ru(II).[162] Williams and co-workers examined Suzuki coupling reactions based on both $Ru(terpy)_2$ complexes bearing a phenylboronic acid unit at the 4′ position with an aryl halide and a $Ru(terpy)_2$ complex bearing a 4′-Br (**66** in Scheme 30) with an arylboronic acid, and they found that both approaches yielded the expected derivative (**67**) with the latter type giving better results.[163,164] Similar modification was carried on $Ir(III)(terpy)_2$ type complexes subsequently.[165] Using two iterations of bromination/Suzuki coupling sequence, a Y-shape Ir_3Ru assembly (**68** in Scheme 30) was achieved, and the energy gradient of Ir_2 to Ir(center) to Ru was demonstrated.[166]

De Cola and co-workers prepared oligo(phenylene)-linked dinuclear Ir(III) compounds (**69** in Scheme 31) from the Suzuki reactions between $[Ir(ppy)_2(bpy\text{-}ph\text{-}Br)]^+$ (ppy = 2-phenylpyridinate, and bpy-ph-Br = 4-(*p*-bromo)phenyl-2,2′-bipyridinate) and diboronic acids.[167] The same Suzuki coupling approach enabled the preparation of oligo(phenylene) bridged $Ru(bipy)_3{}^{2+}$ dimers with n up to 5 in yields of 70−80%.[168] Interestingly, $Os(bipy)_3{}^{2+}$ dimers were only obtained in very low yields using the peripheral approach.[168] Leung and co-workers used the Suzuki coupling reaction between $[Ir(Brppy)_2({}^tBubpy)]^+$ (ppy = 2-(4′-Br-phenyl)pyridine and ^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) and a number of alkyl/aryl boronic acids to yield the corresponding $[Ir(Rppy)_2({}^tBubpy)]^+$ derivatives (**70** in Scheme 31).[169] The same type of chemistry also enabled the insertion of Ir(III) center into the main chain of poly(9,9′-alkylfluorene).[170] Rau and co-workers demonstrated the grafting of aryl groups at the 11 and 12 positions of dipyridophenazine (dppz) in $[Ru(tbbpy)_2(dppz\text{-}Br_2)]^{2+}$ to provide $[Ru(tbbpy)_2(dppz\text{-}Ar_2)]^{2+}$ (**71** in Scheme 32).[171] The authors concluded that, while the peripheral modification does not enhance the synthetic yield compared with the preparation of **71** from modified dppz ligand directly, it provides access to the type **71** complex bearing aryl substituents that are less thermally robust. Recently, Suzuki coupling between $Ru(bipy)_3$ complexes bearing a phenylboronic acid unit and bromoadenine was demonstrated.[71]

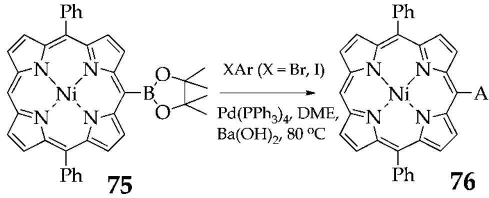
3.3. Suzuki Reactions of Metalloporphyrins

The Suzuki coupling protocol has been frequently invoked for the modification of metalloporphyrins. Chan and Zhou provided the first demonstration of the formation of a heterodimer (**74** in Scheme 33) by coupling a free-base

Scheme 33. Porphyrin Dimerization via Suzuki Coupling



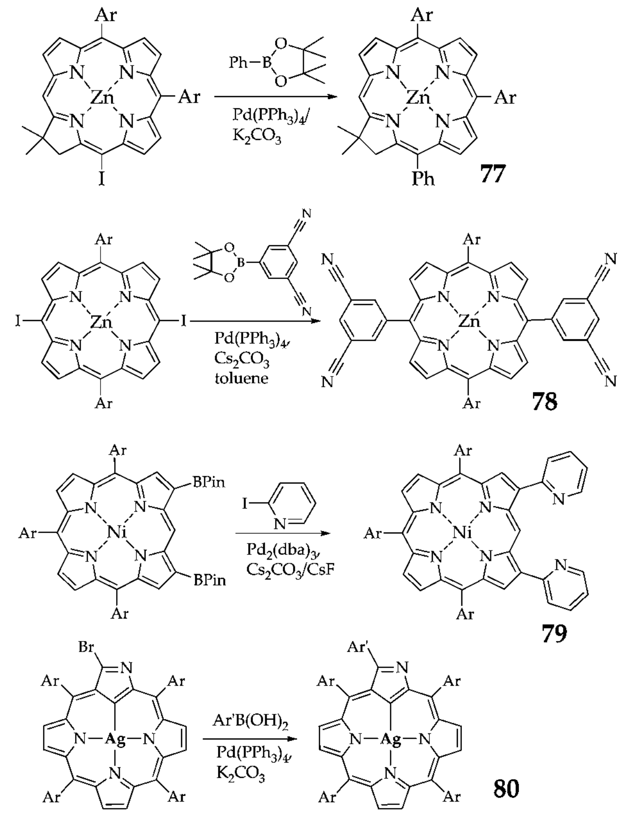
Scheme 34. Reactions of "Suzuki Porphyrin"



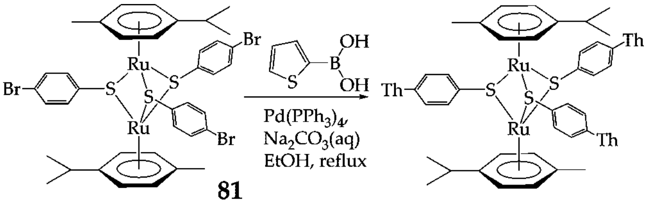
TPP—boronate (**72**) with a Zn(β-BrTPP) (**73**).[172] Therien and co-workers introduced a pinacolborane substituent at the 5-position of (10,20-diphenylporphyrinato)Zn(II) to yield a "Suzuki porphyrin" (**75** in Scheme 34), which reacted with various haloarenes to yield the corresponding *meta*-arylated Zn(II)(porphyrin) (**76**).[173,174] The same "Suzuki porphyrin" was subsequently used for the construction of push—pull Zn(II)(porphyrin)s by Therien.[37] Alternatively, 5-(4-bromophenyl)porphyrin Zn reacted with quinone—oligo(phenylene)—boronic acid to yield a Zn(porp)—quinone dyad bridged by oligo(phenylene).[175] The "Suzuki porphyrin" approach was also adopted by other groups. Osuka and co-workers cross-coupled a Suzuki porphyrin and a free-base porphyrin bearing one or two *meta*-Br substituents to yield the corresponding porphyrin dimer or trimer.[49,176] Cross-coupling of Mg(II)(5,10,15,20-tetrabromoporphine) with various arylboronic acids resulted in the fully *meta*-arylated porphyrins in 50—70% yields.[177] Lindsey and co-workers prepared various Zn(II) porphyrin dyads bridged by both the imino and bis(dipyrrinato)metal linkers from a Suzuki porphyrin.[178,179] Nocera and co-workers prepared both the "Pacman" and "Hangman" porphyrins from a Suzuki porphyrin as well.[180,181] Using the analogs of Therien's Suzuki porphyrin, Diederich et al. prepared a number of dendritic metalloporphyrins as the mimics of hemoglobin.[182]

The utilities of Suzuki coupling have been expanded beyond simple *meso*- or β-modification. It was used to graft thioether capping groups onto the linear oligomers of Zn(II) porphyrins by Osuka,[183] to introduce a *meso*-substituent into 5,10-diaryl chlorins (**77** in Scheme 35) and oxoclorins by Lindsey,[184] and to prepare the copolymers of fluorene and Pt(II)(TPP) by Cao.[185] In a very elaborate study by Diederich and co-workers,[186] the Suzuki coupling was used repeatedly for introducing a 3-siloxybenzyl substituent at the *meso*-position of Zn(II)(5,15-diarylporphyrin) scaffolds, which was subsequently converted to a malonate pendant and eventually led to the formation of various porphyrin—fullerene dyads. Diederich and co-workers also used the Suzuki coupling approach to append *meso*-3,5-dicyanophenyl to Zn(II)-porphyrins (**78** in Scheme 35).[187] Osuka prepared a Ni(II)-porphyrin bearing 2-pyridyl pendants on the adjacent β-positions (**79**) from the corresponding Suzuki porphyrin and demonstrated the "pincer" capacity of the resultant porphyrin through the formation of a Pd complex.[188] The *N*-confused Ag(I)-porphyrin (**80**) can be similarly functionalized at the β-position using the Suzuki coupling.[189] The peripheral modification via Suzuki coupling was recently extended to the [26]-hexaphyrin Au(I)$_2$ compounds[190] and Zn—phthalocyanine bearing an oligo(phenylene) pendant.[191]

Scheme 35. Other Suzuki Modifications of Porphyrin



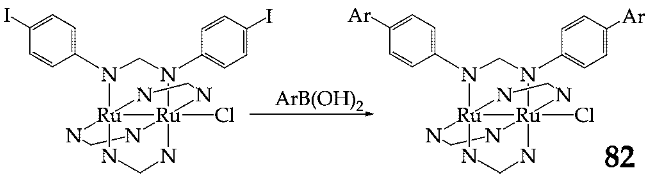
Scheme 36. Suzuki Ru-bound Thiolate Ligands



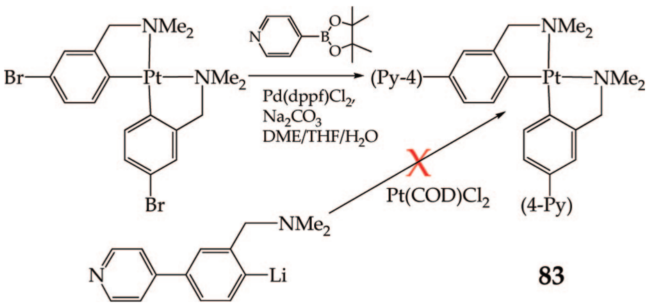
3.4. Suzuki Reactions of Di- And Polynuclear Complexes

Modifications of di- and polynuclear compounds using the Suzuki protocol are rare. Süss-Fink, Chérioux, and co-workers cross-coupled $[Ru_2(\eta^6\text{-}p\text{-Me-}C_6H_4\text{-}^iPr)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{-Br})_3]^+$ (**81** in Scheme 36) with 2/3-$(B(OH)_2)C_4H_3S$ in the presence of $Pd(PPh_3)_4$ and Na_2CO_3.[192] Similar couplings between $[Ru_2(\eta^6\text{-}p\text{-Me-}C_6H_4\text{-}^iPr)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{-Br})_2(\mu\text{-H})]^+$ and $[(Cp^*Rh)_2(\mu_2\text{-S-}p\text{-}C_6H_4\text{-Br})_3]^+$ with 2/3-$(B(OH)_2)C_4H_3S$ were successfully executed by Süss-Fink and co-workers subsequently.[193,194] Our laboratory also explored the utility of the Suzuki method with various diruthenium substrates.[195] The initial attempt of the reaction between $Ru_2(DmAniF)_3(D4\text{-}IPhF)Cl$ and $PhB(OH)_2$ in the presence of $Pd(OAc)_2$, K_2CO_3 under the reflux of aqueous tetrahydrofuran (THF) resulted in the degradation of the diruthenium species. The combination of *trans*-$PdCl_2(PPh_3)_2$, ^tBuOK, and

Scheme 37. Suzuki Modification of Ru$_2$ Compounds



Scheme 38. Suzuki Modification of Pt-bound *C*,*N*-ligand



THF solvent resulted in the expected Suzuki derivative Ru$_2$(DmAniF)$_3$(D(4-Ar-Ph)F)Cl (**82** in Scheme 37). The optimized conditions were also successfully applied to the reactions with Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-IPh)F)Cl as the Ru$_2$ substrate. In addition, the Ru$_2$(DArF)$_3$(D(4-IPh)F)(σ-CCPh) type compounds also underwent Suzuki coupling to yield the corresponding derivatives in satisfactory yields. It is noteworthy that the free ligand HD(4-IPh)F either decomposed or became the dehalogenated derivative under various Suzuki coupling conditions, reaffirming the necessity of the peripheral modification reaction. Another example demonstrating the necessity of peripheral reactions was reported by van Koten and co-workers,[196] where the *C*,*N*-*ortho*-chelated aminoaryl Pt(II) complex reacted with 4-pyridyl boronic acid under Suzuki conditions to yield the pyridyl functionalized derivative (**83** in Scheme 38), while the attempt to prepare complex **83** from the lithium salt of the pyridyl functionalized ligand failed.

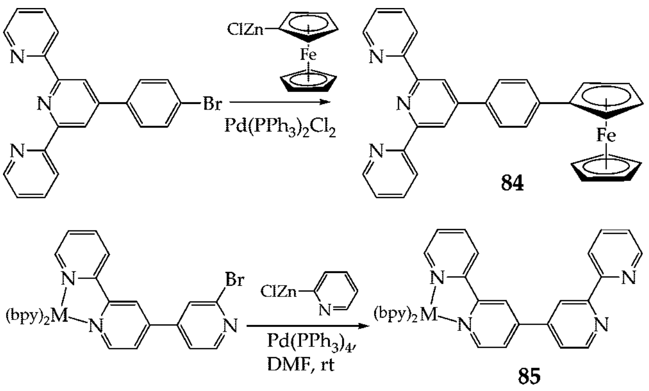
3.5. Negishi Reaction

The Negishi coupling method is broadly defined as the cross-coupling reaction between an organic halide and an organometal including Zn, Al, or Zr with either a Pd or Ni catalyst.[197,198] The most frequently practiced Negishi conditions invoke organozinc and Pd catalyst (eq 4).

$$\mathrm{RZnBr} + \mathrm{XR'} \xrightarrow{\mathrm{Pd^{2+},base}} \mathrm{R{-}R'} \qquad (4)$$

Sauvage and co-workers prepared ferrocenyl modified terpyridine ligand (**84** in Scheme 39) from the reaction of 4′-(4-bromo-phenyl)-terpy and Zn-modified ferrocene.[199] Similarly, the reactions between ClZnFc and RBr under the Negishi conditions resulted in the functionalized ferrocenes with R as pyridine-containing organic moieties.[200,201] Cannon and co-workers prepared polymers containing Fc in the main chain from the reactions between 1,1′-bis(4-bromophenyl)-ferrocene and dizinc reagents.[202] Using the Negishi conditions, Hanan and co-workers reacted 2-Br−Zn−pyrdine with a 2″-bromo-2,2′:4′,4″-terpyridine that is coordinated to a Ru center to generate the second bipy-like chelate (**85** in Scheme 39).[203] Under the Negishi conditions, Therien succeeded in introducing aryl/alkyl groups at the β-position of TPP.[204] Dinh and Gladysz carried out a comprehensive study on the preparation of “heavy fluorous” cyclopentadienyl complexes $\{[\eta^5\text{-C}_5\text{H}_{5\text{-}x}(\text{CH}_2\text{CH}_2\text{R}_{f8})_x]\text{Re(CO)}_3\}$ from the reactions between $[(\eta^5\text{-C}_5\text{H}_{5\text{-}x}\text{Br}_x)\text{M(CO)}_3]$ and IZn(CH$_2$CH$_2$R$_{f8}$), where M = Mn or Re, x = 3 or 4, and $\text{R}_{f8} = -(\text{CF}_2)_7\text{CF}_3$.[205] In the case of x = 5, the singly dehalogenated complex $\{[\eta^5\text{-C}_5\text{H}(\text{CH}_2\text{CH}_2\text{R}_{f8})_4]\text{M(CO)}_3\}$ was the predominant product.[205]

Scheme 39. Negishi Modification of bipy and terpy



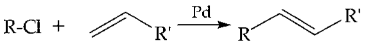
In addition to the aryl−aryl formation reaction, the Negishi protocol was also employed for the cross-couplings of ArI and ClZnC≡CR to yield the corresponding ArC≡CR,[100,206] where R is either ferrocenyl or [5]trovacenyl. In a recent example, FcC≡CZnCl successfully reacted with penta(4-bromophenyl)cyclopentadienyl that is bound to a Ru center to enable the grafting of ferrocenylethyne, whereas the Sonogashira conditions failed to produce the desired product.[207] The homocoupling byproducts, which are often encountered in Sonogashira-type coupling reactions because of the use of CuI cocatalyst, are notably absent from the reactions employing the Negishi conditions.

Negishi cross-coupling was successfully applied to the Ru$_2$L$_3$L′ type compounds with the ancillary ligand L as D(3,5-Cl$_2$Ph)F and L′ as either D(4-IPh)F or DMBA-I. As shown in Scheme 40, Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(D(4-IPh)F)Cl reacted with 4−8 equiv of BrZnC$_6$H$_4$-4-OCH$_3$ in the presence of Pd(DPEphos)Cl$_2$ at room temperature to afford the corresponding biphenyl products (**86** in Scheme 40) in 80−90% yields.[208] In comparison with the Suzuki modification on the same Ru$_2$ species,[195] Negishi coupling is very mild and expedient (1−2 h). *trans*-(PhC≡C)$_2$[Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(DMBA-I)], a substrate of poor thermal tolerance, was converted to the corresponding biphenyl products under the Negishi conditions in good yields, further demonstrating the advantage of mild reaction conditions. Finally, *trans*-(PhC≡C)$_2$[Ru$_2$(D(3,5-Cl$_2$Ph)F)$_3$(DMBA-I)] reacted with BrZnCH=CH$_2$ to yield the corresponding vinyl derivative (**87** in Scheme 40) under conditions (room temperature in 2 h) much milder than those required for the Heck coupling reactions.

4. Heck Reactions

The Heck reaction generally refers to the Pd-catalyzed coupling of either aryl halide or alkenyl halide with an alkene (eq 5) and has been one of the most frequently used cross-coupling techniques in organic chemistry.[209,210] On the other hand, examples of the peripheral Heck reaction are quite limited and dominated by both the modification of metalloporphyrins and the synthesis of conjugated polymers containing metal units.

The first attempt of peripheral Heck reactions was reported in the work of Smith and co-workers, where Zn/Cu porphy-



(5)

rins bearing a β-HgCl group (**88** in Scheme 41) react with methyl acrylate in the presence of $LiPdCl_3$ to yield acrylated porphyrins (**89**).[8,9] This approach was subsequently utilized as a general method to introduce unsaturated organic groups at the β-position of Zn porphyrins.[211] This chemistry was reinvestigated recently with 5,15-diarylporphyrin-M(II) (M = Zn and Ni), where the preferential mercuration at the β^B-position led to β^B-acrylate derivatives.[212] Interestingly, Zn(II) vinyl porphyrins reacted with 5-chloromercuriuridine under very similar Heck conditions, which resulted in the *trans*-olefin bridged uridine−porphyrin conjugates (**90** in Scheme 41) with *gem*-bridged conjugates as the minor product.[213]

Heck coupling reactions between β-bromo-functionalized Zn-porphyrins and either styrene or 1,4-divinylbenzene resulted in olefin substituted Zn-porphyrins or the bridged Zn-porphyrin dimer.[214] Subsequently, Heck coupling of β-bromo-functionalized Zn-porphyrin with internal olefin was demonstrated.[215] Conversely, bis(β-vinyl)-porphyrin was successfully cross-coupled with a number of aryl bromides,[216] and the method was useful in the synthesis of porphyrin based discotic liquid crystals.[217] A very detaile d study of Heck-type reactions between bis(*meso*-bromo)metalloporphyrin and various terminal olefins was reported by Arnold and co-workers, where the expected olefinated products (**91** in Scheme 42) were obtained in 70% or better yields.[218] The authors also noticed (i) the presence of the dehalogenated byproduct (**92** in Scheme 42) with 5,15-dibromoporphyrin substrate and (ii) the coexistence of *E*/*Z* products with strong acceptor −CN. In an attempt to cross-couple a *meso*-bromo-Ni(II)-porphyrin and a *meso*-vinyl-Ni(II)-porphyrin, the new C−C bond was formed at the β-position adjacent to the *meso*-position occupied originally by the bromo substituent (**93** in Scheme 42). To account for the unexpected product, the authors proposed the *meso*-to-β-migration of PdL_2Br moiety after the insertion into the C−Br bond.

Yu and co-workers demonstrated that metalloporphyrins bearing two *meso*-styryl groups (**94** in Scheme 43) reacted with 1,4-diiodoarene to yield hybrid porphyrin−phenylene-vinylene copolymers (**95**).[219,220] Subsequently, copolymers containing either Ru(II) (**96** in Scheme 43) or Co(II) moiety in the main chain were similarly prepared.[221−224] The same approach was extended to prepare very complex copolymers that contain both metalloporphyrin and metallophthalocyanine in the backbone and oligo(phenylene vinylene) as the bridges.[225] Chan and co-workers also investigated the copolymerization of Ru(II) and Re(I) compounds of 3,8-dibromo-1,10-phenanthroline with 1,4-divinylbenzene and 1,4-dibromo-2,5-dioctoxybenzene under the Heck conditions.[226]

Heck-type reactions on diruthenium species were examined in our laboratory, and a dependence on conditions was experienced with Ru_2 substrates.[227] With $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(D(4\text{-}IPh)F)Cl$ (**97** in Scheme 44) as the substrate, the reaction was most efficient with $Pd(OAc)_2$ as the catalyst and Et_3N as both the base and solvent. With $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)Cl$, the combination of $Pd(OAc)_2$ and nBu_4NOAc (Jeffrey conditions)[228,229] was found to be the most effective. Diruthenium species bearing axial phenylacetylide ligands, i.e., $Ru_2(D(3,5\text{-}Cl_2Ph)F)_3(DMBA\text{-}I)(\sigma\text{-}C{\equiv}CPh)_2$ (**98** in Scheme 44), were successfully cross-coupled with various olefins in the presence of $Pd(dba)_2$, KF, and $^nBu_4NCl$ at room temperature.

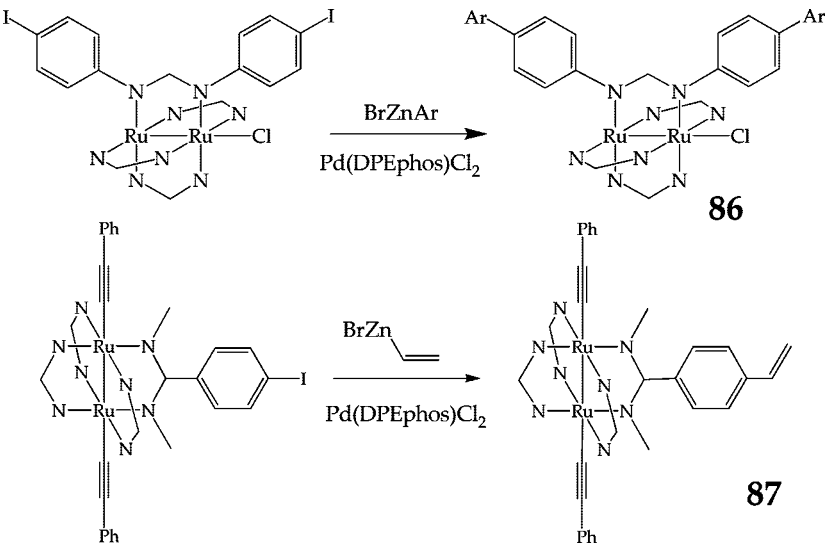
5. Stille Reactions

The Stille reaction generally refers to the carbon−carbon bond formation reaction through the cross-coupling of an organic halide with an organotin agent (eq 6)[210,230] and is frequently employed for the introduction of olefin functionality.

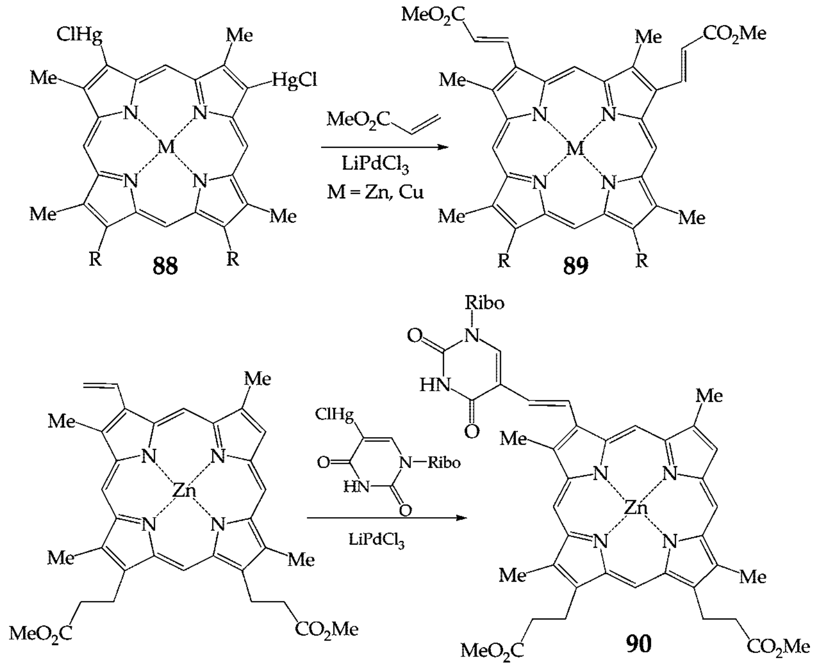
$$RSnMe_3 + XR' \xrightarrow{Pd(0)} R{-}R' \tag{6}$$

The first elaboration of the peripheral Stille coupling reaction came from the work of Therien and co-workers,[204,231] where 5,15-dibromo-10,20-diphenylporphyrinzinc(II) reacted smoothly with Bu_3SnR to afford the alkylated derivatives in very high yields (**99** in Scheme 45). Subsequently, 2 equiv of 5-bromo-15-aryl-10,20-diphenylporphyrinzinc(II) reacted with linear rigid spacers bearing $-SnBu_3$ group on both ends to afford Zn(II) porphyrin dimers of well-defined distances (**100** in Scheme 45).[232] The reaction of 5-bromo-10,15,20-triphenylporphyrinzinc(II) with tributylstannylcyclobutenedione resulted in the corresponding *meso*-squaryl-porphyrin.[233]

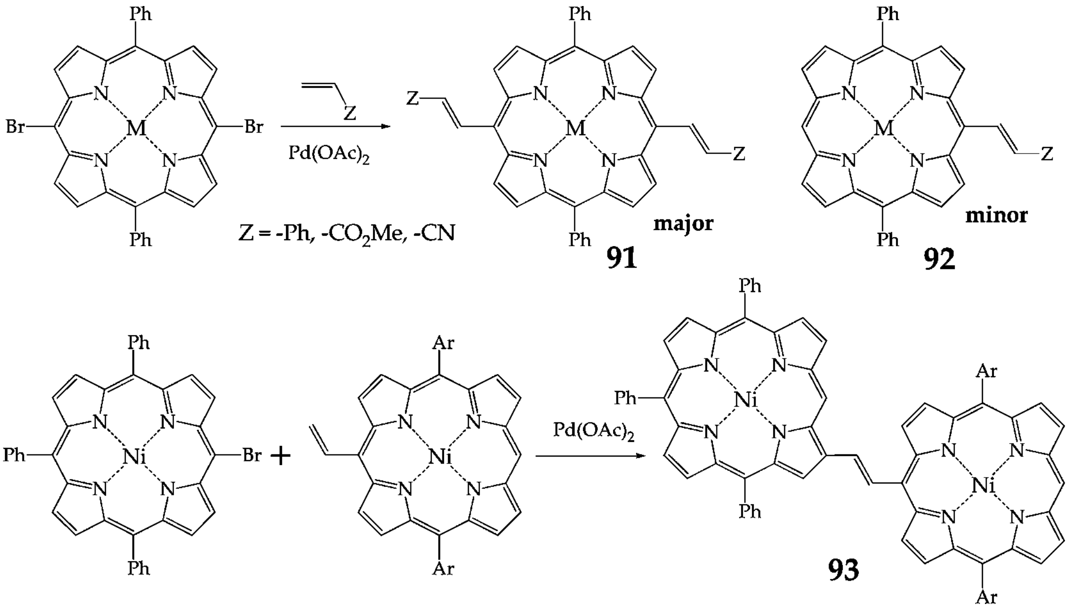
Scheme 40. Negishi Modification of Ru_2 Compounds



Scheme 41. Heck Reaction of Mercurated Substrates



Scheme 42. Heck Reaction of *meso*-bromo-Porphyrins

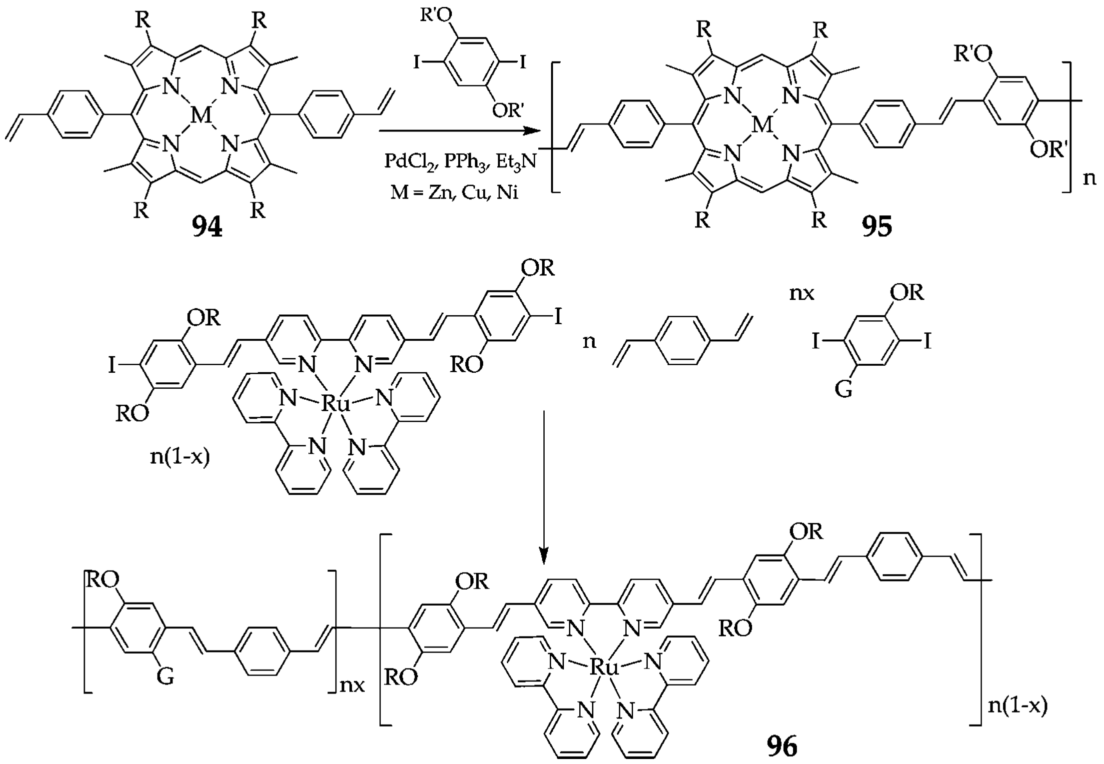


Odobel and co-workers explored the synthesis of highly conjugated Zn(II)-porphyrin dimers using the Stille coupling. The reaction of 5-iodo-10,15,20-triarylporphyrinzinc(II) with tributylstannylbutadienyl acetal provides the porphyrin derivative of butadienyl acetal appendage (**101** in Scheme 46), which was further reacted with bipyridine bisphosphonate to yield the dimer.[234] Similar to the aforementioned approach of Therien, 5-iodo-10,15,20-triarylporphyrinzinc(II) reacts with bis(tributylstannyl)quarterthiophene, resulting in the oligo-thiophene bridged dimer.[235] A dimer of Zn(II)-porphyrin bridged by a single vinylene at the *meso*-positions was prepared using the Stille coupling, whereas attempted McMurry and Wittig couplings failed.[236] Odobel and co-workers also prepared a Zn(II)−phthalocyanine−Sn(II) porphyrin dyad spanned by oligo(phenyleneethynylene) through *meso*-ethylene linkers using stepwise Stille coupling reactions.[46]

An important theme of metalloporphyrin chemistry is the utility as antitumor agents. In this vein, Smith and co-workers prepared several 2,3-dialkynyl-5,10,15,20-tetraphenylporphyrin-Ni(II) (**102** in Scheme 47) from a 2,3-dibromo-Ni(II)TPP using the Stille coupling and studied the Bergman cyclization of these metalloenediynes.[237] The same type compounds were also investigated by Zaleski.[238] In a more detailed follow-up, octobromo derivative of Ni(TPP) was converted to the corresponding octo-phenylethynyl species (**103** in Scheme 47) along with the partially dehalogenated species containing only five or six phenylethynyl substituents.[239] The *N*-confused Ag(I) porphyrins can be arylated at the β-position using the Stille coupling with both the yields and selectivity being better than those from the Suzuki coupling.[189]

The Stille coupling reaction has also been utilized extensively in the peripheral modification of metal bipyridine/

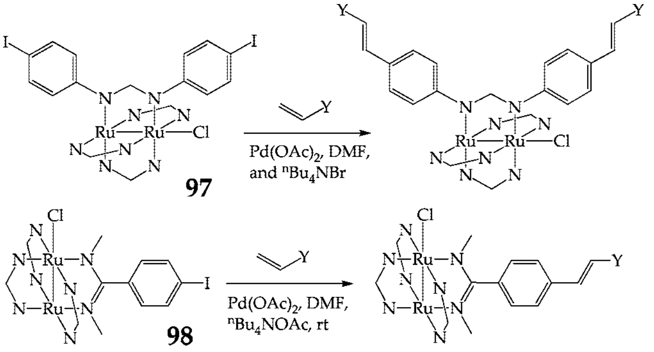
Scheme 43. Synthesis of Metallopolymers via Heck Coupling



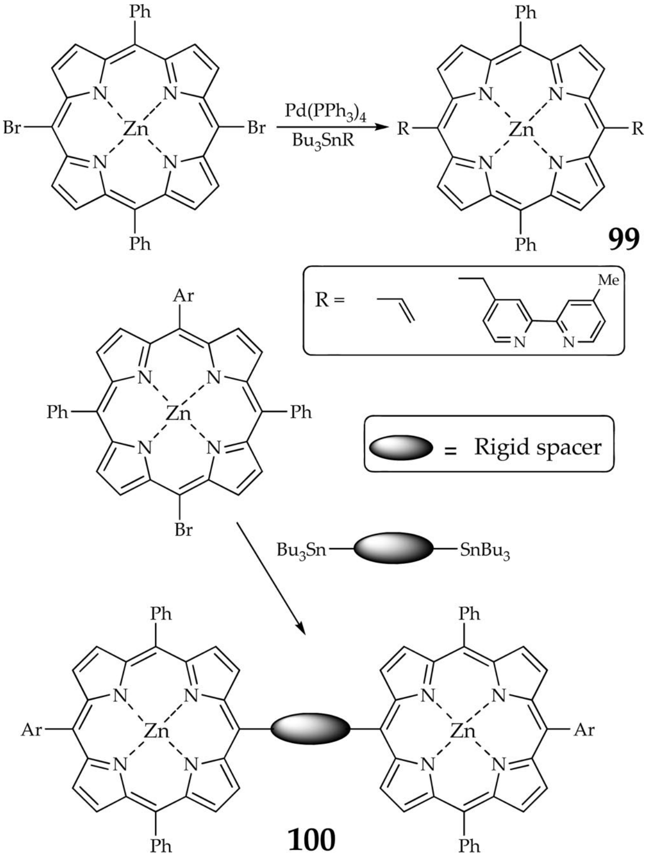
terpyridine complexes. Sauer and co-workers demonstrated that a Ru(bipy)$_3$ unit bearing a Bu$_3$Sn substituent cross-couples with either a 5-bromo-terthiophene or a 4-bromo-Ru(bipy)$_3$ to yield the terthiophene attached Ru(bipy)$_3$ or a 4,4-dimer of Ru(bipy)$_3$.[240] Guillerez and co-workers prepared co-oligomers of Ru(bipy)$_3$ and tetrathiophene (**104** in Scheme 48) using the Stille reaction between Me$_3$Sn capped tetrathiophene and Ru(bipy)$_2$(5,5′-dibromo-bipy) in good yield, while the metalation of an oligomer containing a free 2,2′-bipy did not yield the desired Ru-containing oligomer.[241] Bichromic compounds composed of a Ru(bipy)(terpy) unit linked with a chromophore (ANT) were achieved using the Stille coupling between Ru(bipy)(4′-Brterpy) and ANT-SnMe$_3$.[242]

Bunz and co-workers used the Stille coupling extensively to modify metal bound η^4- and η^5-carbocyclic ligands. Star-shaped tricarbonyl(cyclobutadiene)iron and cymantrene compounds were prepared from the reactions between the corresponding periodo precursors and R(C≡C)$_2$SnMe$_3$ in modest yields.[243] Bis- and tris-ethynylated cymantrene and tricarbonyl(cyclobutadiene)iron compounds were similarly prepared in good yields,[244,245] and the iron-containing tris-compound was successfully dimerized. Tamm and co-workers attached a 1,3,5-cycloheptatrien-2-yl group to (η^5-C$_5$H$_4$I)Mn(CO)$_3$ using the Stille coupling (Scheme 49).[246] Similarly, [(η^6-C$_6$H$_5$Cl)Mn(CO)$_3$]+ reacted with Bu$_3$SnAr in the presence of Pd$_2$(dba)$_3$ to yield the [(η^6-C$_6$H$_5$Ar)-Mn(CO)$_3$]+ type compounds (Ar = Ph and thiophene).[247] Modification of (η^6-C$_6$H$_5$X)Cr(CO)$_3$ (X = F and Cl) through

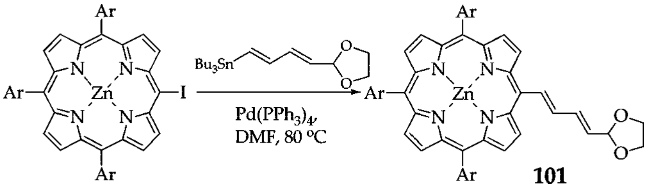
Scheme 44. Heck Coupling of Ru$_2$ Substrates



Scheme 45. Stille Coupling of *meso*-bromo-Porphyrins



Scheme 46. Stille Coupling of *meso*-iodo-Porphyrin



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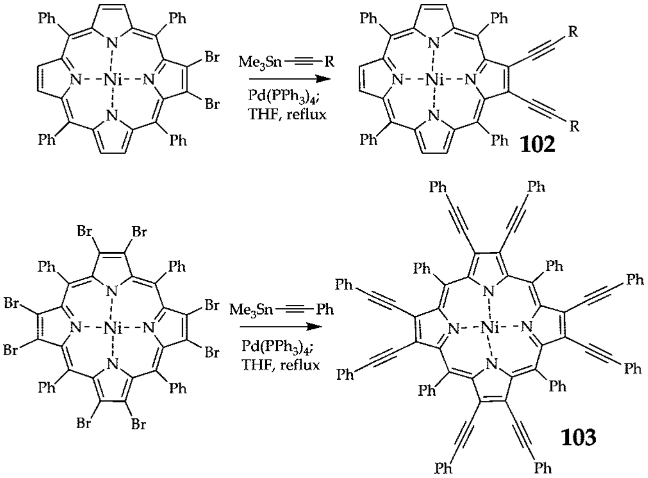
Scheme 47. Porphyrin Ene-diynes from Stille Coupling



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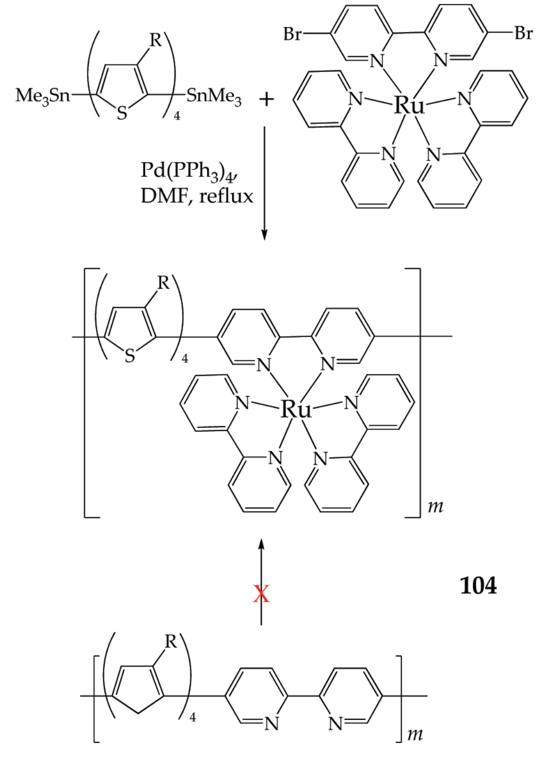
Scheme 48. Ru-thiophene Oligomers via Stille Coupling



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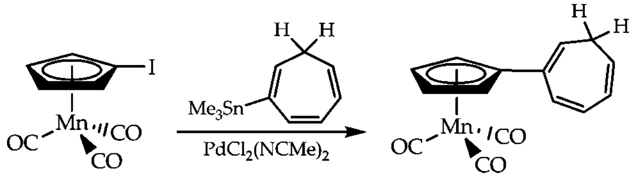
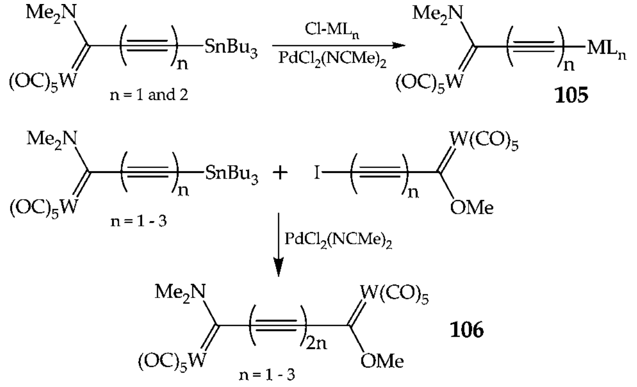
Scheme 49. Modification of Carbocyclic Ligand via Stille Coupling



Scheme 50. Stille Coupling for Carbon-Rich Organometallics



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106

the attachment of vinyl and thiophene group via the Stille coupling was also achieved.[158,248]

The Stille coupling is also a useful tool in the preparation of carbon-rich organometallic compounds. Fischer and coworkers developed W-(alkynyl)carbenes bearing $-SnBu_3$ capping group, which cross-couples with a variety of M−Cl species under Stille conditions to yield interesting bi- (**105** in Scheme 50) and trimetallic compounds.[249−251] The coupling between a W-(alkynyl)carbene bearing $-SnBu_3$ and the other bearing iodo group resulted in alkyndiyl bridged bis(carbene) compounds (**106** in Scheme 50).[252] Reaction between $Me_3SnCCSnMe_3$ and $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_4I)$ in the presence of $Pd(dppf)Cl_2$ resulted in ethyndiyl bridged ditrovacenes.[206]

6. Oxidative and Reductive Homocouplings

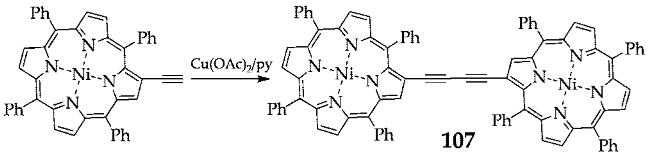
Typical organic homocoupling reactions include the Wurtz, Ullmann, and Glaser types.[253] The first two are reductive in nature and require harsh reaction conditions, which limit their utility in peripheral modifications. Oxidative coupling of two terminal acetylene in the presence of $Cu(I)/O_2$ or a stoichiometric amount of Cu(II), the Glaser reaction (eq 7), is one of the most useful methods in constructing oligoyne scaffolds.[4] There are also sparse examples of other oxidative/reductive homocouplings that proceed at ambient conditions, which will be discussed in section 7.2.

6.1. Glaser-Type Reactions

$$2\ R{-}{\equiv}\ \xrightarrow[-\ H_2O]{Cu(I)/O_2}\ R{-}{\equiv}{-}{\equiv}{-}R \qquad (7)$$

As mentioned in the Introduction, the first peripheral Glaser reaction was conducted in the 1960s by Schlogl and co-workers, where various Fc-$(C{\equiv}C)_m$H ($m = 1-4$) were dimerized by $Cu(OAc)_2$ in pyridine/MeOH (Eglinton conditions).[6,254] The oxidative coupling of Fc-(C≡C)H and Fc-$(C{\equiv}C)_2$H was reinvestigated by Marder,[255] and that of Fc-$(C{\equiv}C)_3$H was investigated by Adams.[256] Another early application of the Glaser reaction for peripheral modification was the work of Johnson and co-workers, who converted *meso*-bromovinyl-*β*-octaethylporphyrin Ni(II) to the corresponding *meso*-ethynyl derivative with NaH, and the latter was converted to a butadiyne-bridged dimer (see Scheme 1) upon oxidation with $Cu(OAc)_2$ in pyridine (Eglinton conditions).[7] Later on, Arnold examined similar reactions with *β*-ethyne substituted Ni(II)TPP and Ni(II)OEP and demonstrated the formation of *β*,*β*′-butadiyndiyl bridged porphyrin dimer (**107** in Scheme 51).[257] Zn(II)-porphyrins bearing

Scheme 51. Glaser Coupling Ni-porphyrin-β-ethyne



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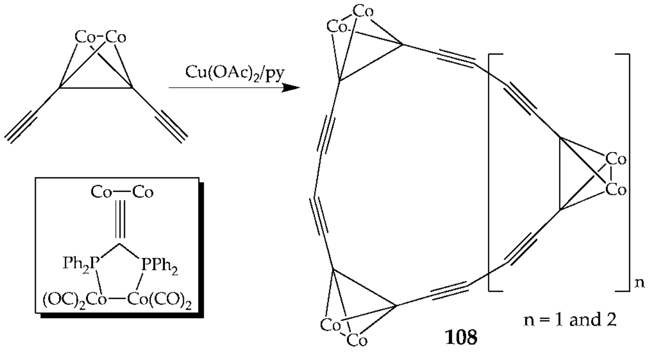
Scheme 52. Formation of Carbomacrocycles via Glaser Coupling



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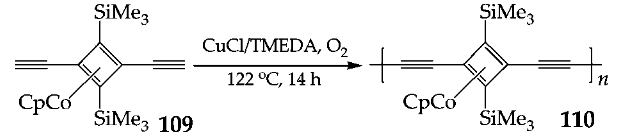
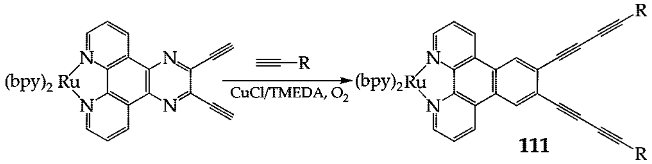
Scheme 53. Polymerization via Glaser Coupling



109 **110**

Scheme 54. Extension of Ethyne to Butadiyne via Glaser Coupling



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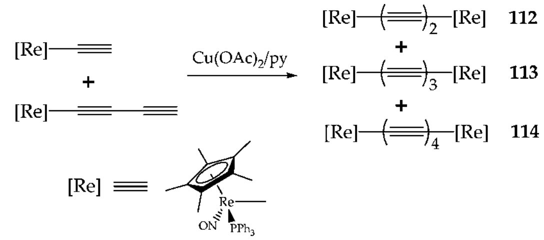
Scheme 55. Glaser Coupling of Re-σ-polyyne



112 **113** **114**

meso-ethyne were successfully dimerized through aerobic oxidation in the presence of CuCl/TMEDA (Hay conditions).[258]

The Glaser coupling has also been applied to nonporphyrin metal complexes bearing peripheral ethynes. Treating a hexatriyne with a $Co_2(CO)_4$(dppm) unit bound to the C3−C4 bond under Eglinton conditions ($Cu(OAc)_2$/py), Diederich and co-workers successfully obtained both cyclo[18]carbon and cyclo[24]carbon stabilized by the Co_2 units (**108** in Scheme 52), and the former compound was characterized by X-ray crystallography.[259] Bunz and Altmann oxidatively coupled (η^4-2,4-diethynyl-1,3-bis(trimeythylsilyl)cyclobutene)(η^5-cyclopentadienyl)cobalt (**109** in Scheme 53) under Hay conditions at 122 °C over 14 h to yield polymers of broad molecular weight distribution (**110**).[260] By shortening the reaction time and lowering the reaction temperature, they were able to isolate shorter oligomers from dimer to nonamer on preparative high-performance liquid chromatography (HPLC).[261] Subsequently, the similar Co monomers bearing 2,4-dibutadiynyl were polymerized under Hay conditions at room temperature.[262] Oxidative coupling of *cis*-diethynyl Co monomer (η^4-3,4-diethynyl-1,2-bis(trimeythylsilyl)cyclobutene)(η^5-cyclopentadienyl)cobalt) under the Hay conditions resulted in a mixture of cyclic trimers and cyclic tetramers.[263] Bunz and co-workers used Vogt conditions ($Cu(OAc)_2/CH_3CN$) to construct the butterfly-shaped carbon-rich frameworks with a Co−cyclobutadiene core.[264] Also prepared using the Glaser coupling are the oligoalkyne-bridged (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt dimer[143] and trovacene dimers.[206] Faust and Ott achieved the extension of ethynyl pendant to butadiynyl (**111** in Scheme 54) of a pyrazino[2,3-f][1,10]phenanthroline that is coordinated to a $Ru(bipy)_2^{2+}$ fragment under Hay conditions.[265]

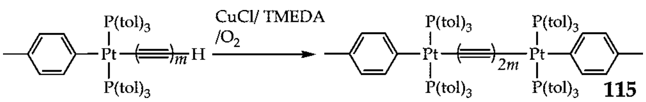
The most notable application of oxidative coupling strategies is the synthesis of polyyndiyl bridged bimetallic compounds from mononuclear σ-polyynyl compounds, and the approach is necessitated by the extreme instability of organic polyynes. The laboratory of Gladysz was among the earliest to adapt this approach and has provided ample examples of synthetic approaches leading to extended systems over the years. The first example involves the dimerization of $^{134}-C\equiv C-H$ under Eglinton conditions to yield $^{134}-C\equiv C-C\equiv C-^{134}$, where ^{134} is ($\eta^5$-Cp*)Re(NO)-($PPh_3$).[266] Subsequently, the oxidative coupling of a mixture of $^{134}-C\equiv C-H$ and $^{134}-C\equiv C-C\equiv C-H$ led to the formation and isolation of the $^{134}-(C\equiv C)_m-^{134}$ series with m = 2, 3, and 4 (**112**−**114** in Scheme 55).[267,268] Mononuclear $^{134}-(C\equiv C)_lH$ compounds with l = 3−5, prepared from $^{134}-C\equiv C-C\equiv C-H$ using the Cadiot−Chodkiewicz reaction, were similarly dimerized to yield the $^{134}-(C\equiv C)_{2\,L}-^{134}$ series.[137,269]

The shorter members of the $^{134}-(C\equiv C)_m-^{134}$ series yielded very delocalized monocations and are, hence, excellent models of organometallic molecular wires.[270−272] However, the monocation $\{^{134}-(C\equiv C)_m-^{134}\}^+$ became very unstable with $m \equiv 4$ and could not be detected, even at low temperature.[137] Speculating that the monocation undergoes fast reaction through the open polyyndiyl chain, $[Re']-(C\equiv C)_4-[Re']$ was prepared through the oxidative coupling of $[Re']-(C\equiv C)_2H$, where the PPh_3 was replaced by $PPh_2(CH_2)_6CH{=}CH_2$ in [Re′].[273] The pendant terminal olefin was subsequently dimerized upon the treatment of the Grubbs first-generation catalyst to provide a flexible hydrocarbon chain encircling the polyyndiyl chain. Alternatively, $H(C\equiv C)_2-[Re''](PPh_2(CH_2)_nPPh_2)[Re'']-(C\equiv C)_2H$ was prepared first, then subjected to oxidative coupling.[274] However, the voltammetric characterization of the latter compounds did not reveal added stability for the cationic species due to the addition of the encircling hydrocarbon chain.[274]

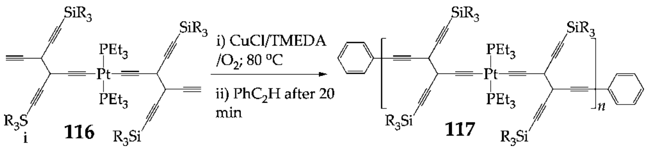
The other series of metal capped polyyndiyl compounds developed in the laboratory of Gladysz is based on Pt-$(PAr_3)_2(\sigma\text{-Ar})$ ([Pt]) type compounds. Initially, $[Pt]-(C\equiv C)_mH$ was homocoupled under the Hay conditions (CuCl/TMEDA, O_2) to yield $[Pt]-(C\equiv C)_{2m}-[Pt]$ (m = 2−4).[275−277] In the course of this study, the Glaser-type reaction was also utilized for the chain extension to yield a longer $[Pt]-(C\equiv C)_mH$. More recently, the Glaser coupling of $[Pt]-(C\equiv C)_mH$ with m = 6 and 7 resulted in remarkable diplatinum compounds spanned by C_{24} and C_{28} bridges (**115** in Scheme 56), respectively.

Bruce and co-workers investigated the dimerization of various metal−polynyl species under the Hay conditions,

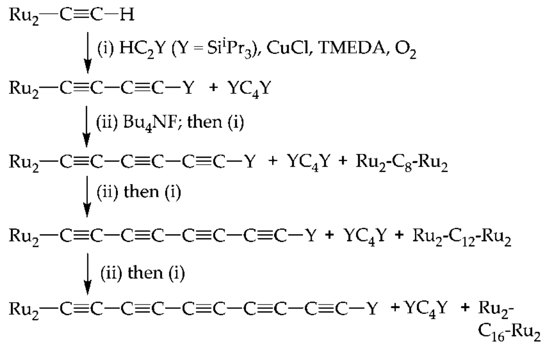
Scheme 56. Glaser Coupling of Pt-σ-polyyne



Scheme 57. Pt-σ-Eneyne Oligomer via Glaser Coupling



Scheme 58. Synthesis of Extended $Ru_2(ap)_4(C_{2k}Y)$

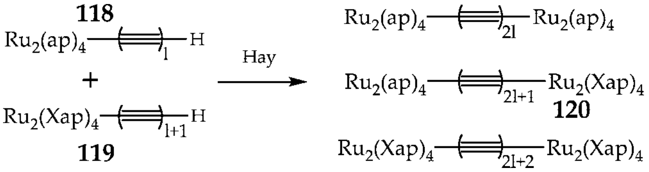


including $CpW(CO)_3(C\equiv C)_2H$[123,124] and $Ar_3PAu(C\equiv C)_2$-H.[278] Syntheses of butadiyndiyl bridged dirhenium species and octatetrayndiyl bridged diplatinum complex from the oxidative coupling of the corresponding "half" molecules were reported by Yam and co-workers.[279,280] Lapinte and Coat described the homocoupling of $Cp^*Fe(dppe)(C\equiv C)_2H$ under the Eglinton conditions to yield $[Cp^*Fe(dppe)]_2(\mu$-$(C\equiv C)_4)$.[281] Akita, Moro-oka, and co-workers reported the preparation and structural characterization of the $Fp^*-(C\equiv C)_{2m}-Fp^*$ series from $Fp^*-(C\equiv C)_mH$ under the Hay conditions, where $m = 2$ and 3 and $Fp^* = Cp^*Fe(CO)_2$.[282,283] Rigaut and co-workers prepared $[Ru]-(C\equiv C)_6-[Ru]$ ($[Ru] = Ru(dppe)_2Cl$) from the coupling of $[Ru]-(C\equiv C)_3H$ under the Eglinton conditions.[284] In an elegant and remarkable example, Diederich and co-workers polymerized bis(tetraethynylethene)Pt monomer (**116** in Scheme 57) under the Hay conditions, and the resultant polymer (**117**) has a remarkably small polydispersity index (M_w/M_n) of 1.06.[285]

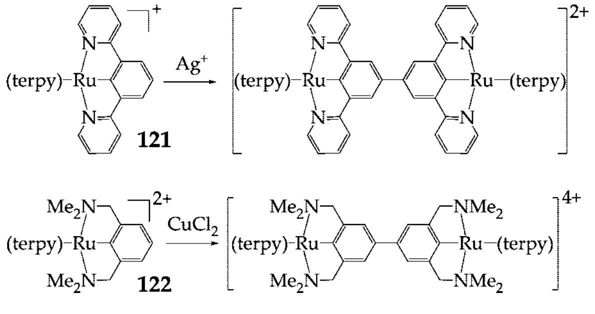
Lehn and co-workers prepared a selectively desilylated bisalkynyl compounds *trans*-$(Me_3SiC_4)-Ru_2(DPhF)_4-(C_4H)$ (DPhF is *N*,*N*′-diphenylformamidinate), which was homocoupled under the modified Hay conditions (CuCl/py/O_2) to yield *trans*-$[(Me_3SiC_4)-Ru_2(DPhF)_4]_2(\mu$-$C_8)$.[286] Our laboratory has explored extensively the utility of Glaser coupling in both the formation of $[Ru_2]-(C\equiv C)_{2m}-[Ru_2]$ type compounds with $m \equiv 2$ and the synthesis of $[Ru_2]-(C\equiv C)_mR$ type compounds with $m \equiv 3$, where $[Ru_2]$ is either $Ru_2(ap)_4$ or $Ru_2(Xap)_4$, ap is 2-anilinopyridinate, and Xap is an aniline-substituted ap. Using the strategy described in Scheme 58, $Ru_2-(C\equiv C)_mY$ was extended by one acetylene unit at a time under the Hay conditions, and the Ru_2-polyynyls with m up to 6 have been obtained in this fashion.[287,288] As experienced in the aforementioned studies by Gladysz, the use of HC≡CY in large excess is the key to suppress the formation of homocoupling product $[Ru_2]-(C\equiv C)_{2m}-[Ru_2]$ and, hence, maximize the yield of $Ru_2-(C\equiv C)_{m+1}Y$.

While the preparation of $Ru_2-(C\equiv C)_mY$ type compounds has been tedious, the preparation of $[Ru_2]-(C\equiv C)_{2m}-[Ru_2]$ type dimer from $Ru_2-(C\equiv C)_mH$ is fairly straightforward under either the Hay or Eglinton conditions.[208,289,290] It is clear that $[Ru_2]-(C\equiv C)_m-[Ru_2]$ type compounds with an *odd m* cannot be accessed in this fashion. A *brute force* approach adapted by us involves subjecting a mixture of $[Ru_2(ap)_4](C\equiv C)_lH$ (**118** in Scheme 59) and $[Ru_2(Xap)_4]$-$(C\equiv C)_{l+1}H$ (**119**, Xap = 2-(3,5-dimeoxyanilino)pyridinate or 2-(3-isobutoxyanilino)pyridinate) to oxidative coupling under the Hay conditions. The significant difference in solubility between $Ru_2(ap)_4$ and $Ru_2(Xap)_4$ type compounds enables the separation of $Ru_2(ap)_4-(C\equiv C)_{2L+1}-Ru_2(Xap)_4$ (**120**) from the symmetric products, and compounds of $l =$ 2 and 3 have been successfully prepared.[288]

Scheme 59. Synthesis of $Ru_2-(C_{2l+1})-Ru_2$ VIb Other Oxidative and Reductive Couplings



Scheme 60. Oxidative Coupling of Aromatic C−H Bonds

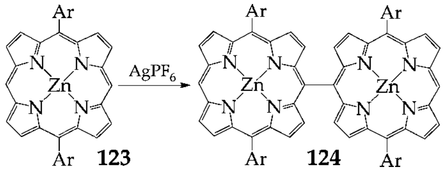


6.2. Other Oxidative and Reductive Couplings

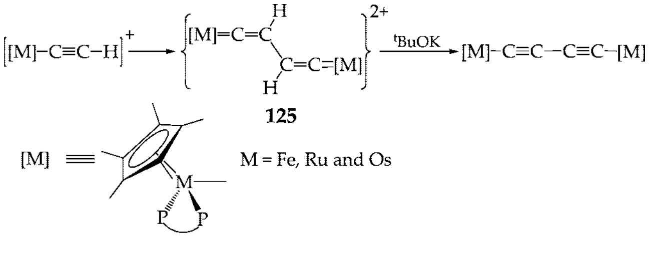
Facile C−C bond formation can also be achieved through oxidative coupling of aromatic C−H functionality of cyclometalated ligand. The first of such examples was reported by Sauvage, where $[Ru(terpy)(dpb)]^+$ (**121** in Scheme 60, Hdpb is di(*o*-pyridyl-1,3-benzene)) was dimerized through the C−C bond formation at the 5′ position of the benzene ring of dpb upon treatment with Ag^+ in large excess.[291] This work was later extended to the Os analog, and the authors speculated that the C−C bond formation was preceded by the formation of 5′ radical.[292] van Koten and co-workers demonstrated that bis(dimethylaminomethyl)aryl Ru(II) complexes (**122** in Scheme 60) can also be dimerized through the formation of C4−C4′ bond with $CuCl_2$ as the oxidant and the concurrent conversion of Ru(II) to Ru(III).[293,294] The latter feature contrasts the earlier finding of [Ru(terpy)-(dpb)]+ dimerization, where the oxidation state of Ru remained the same. The later study revealed that the Ru(III) dimer could be reduced to either the corresponding Ru(II) dimer with hydrazine or the cleaved monomer (**122**) with ascorbic acid.[295] In addition to the aforementioned Ru-based examples, Espinet and co-workers reported the formation of tetrapalladia species via double oxidative coupling of aromatic C−H bonds in a dimeric orthopalladated amido complex.[296]

Similarly, oxidation of 5,15-diarylporphyrin Zn(II) (**123** in Scheme 61) by Ag^+ led to the *meso,meso* C−C bond formation and initial isolation of porphyrin dimer (**124**), trimer, and tetramer by Osuka and co-workers.[297] Subsequent studies by both Osuka's and other groups revealed that the

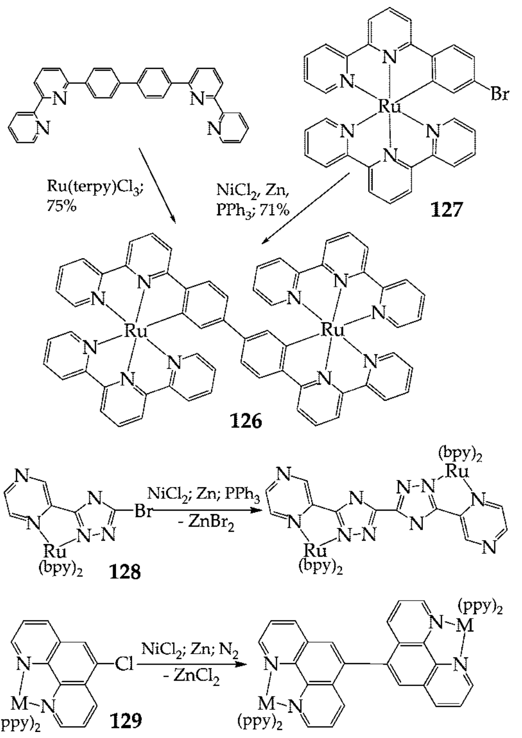
Scheme 61. Oxidative Coupling of Porphyrin C−H Bonds



Scheme 62. Dimerization of Metal−Polyynyl via Vinylidene



Scheme 63. Dimerization via Semmelhack Reaction



same coupling can be achieved either by using 2,3-dichloro-5,6-dicyanoquinone (DDQ) as the oxidant[298,299] or electrochemically.[300,301] The coupling chemistry via Ag+ oxidation has proliferated since the original publication and allows a geometric growth of $\{Zn(porp)\}_n$ polymers with n up to 1024 (2^{10}).[183]

While the Glaser coupling is the predominant pathway to dimerize metal-σ-polyynyl species, some other approaches are also possible. Work from Lapinte's laboratory revealed that the electron-richness of a Cp*Fe(dppe) fragment renders both easy access to $[Cp^*Fe(dppe)(C\equiv CH)]^+$ and its facile conversion to a vinylidene linked dimer $[Cp^*Fe(dppe)(=C=CH)-(HC=C=)(dppe)FeCp^*]^{2+}$ (**125** in Scheme 62), and the latter was deprotonated by a strong base to yield $[Cp^*Fe(dppe)]_2[\mu\text{-}(C\equiv C)_2]$.[302,303] Similar dimerizations were reported for $Cp^*M(dppe)(C\equiv CH)$ (M = Ru and Os) by Bruce and co-workers.[304,305] Alternatively, a carbon-localized radical could be produced by the deprotonation of $[(RC\equiv C)Mn(dmpe)_2(C\equiv CH)]^+$, which proceeds to form the C_4-bridged dimer.[306,307]

Although very rare, it is also possible to achieve peripheral C−C bond formation, reductively, using the Semmelhack reaction,[308,309] which is a much milder alternative to the Ullman reaction. Constable reported the preparation of the dimer of Ru(terpy)(*C,N,N*-pbpy) (**126** in Scheme 63, Hpbpy is 6-phenyl-2,2′-bipyridine) from the reduction of Ru(terpy)(*CNN*-4-bromo-pbpy) (**127**) by $NiCl_2/Zn/PPh_3$ in a yield of 71%, which is comparable to that of direct metalation of the dimerized ligand with $Ru(terpy)Cl_3$ (75%).[310] Vos and co-workers reported the preparation of Ru(II) complex containing pyrazin-2-yl-3-(5-bromo-1,2,4-triazole) (**128** in Scheme 63) and its subsequent reductive dimerization in the presence of Zn, $NiCl_2$, and PPh_3.[311] Griffiths and co-workers produced bimetallic species (M = Ir, Ru, and Os) through the reductive coupling of mononuclear complexes of 5-chloro-1,10-phenanthroline (**129** in Scheme 63) by a mixture of Zn and $NiCl_2$.[312]

7. Conclusions

Among many possible advantages of peripheral modifications, three stand out. First, the excellent regio- and chemoselectivity offered by cross-coupling reactions enables precise hierarchical assemblies, and this has been reflected in the preparations of supramolecules **14** and **15** and photodyad/triad **33** and **68**. Second, formation of a polydentate ligand from the modification of a *coordinated* ligand facilitates the subsequent formation of multinuclear complexes, while direct metalation of the polydentate ligand failed because of the poor solubility. This approach is often adapted in the synthesis of bipy and terpy complexes, and the advantage is evident in the preparation of compounds **29**−**32**. Third, the mild conditions of cross-coupling and homocoupling reactions allow the preparation of both metal−biomolecule conjugates and compounds of extended carbon-rich fragments such as **108**, **115**, and **117**.

Advantages of peripheral reactions have been recognized in areas beyond C−C bond formation reactions. For instance, C−X (X = N, S, O) bond formation at the periphery of metalloporphyrins under the cross-coupling conditions was recently demonstrated.[313,314] Covalent modification of MOFs (metal-organic-frameworks) and its impact on the uptake of gas molecules have also been explored recently.[315−317] The peripheral C−C bond formation approach may also become a powerful tool for both main group chemistry and semiconductor device fabrication, as demonstrated by recent examples of Heck and Suzuki modifications of *para*-octaiodophenylsilsesquioxane[318] and secondary functionalization of Si(111) surfaces via Heck coupling and olefin metathesis,[319] respectively. It is clear that the cross-coupling chemistry has already received considerable attention from the inorganic community. It is the hope of the author that this review will stimulate further interest in peripheral modification from inorganic and materials chemists.

8. Acknowledgments

Financial support from the National Science Foundation (CHE 0715404) and Purdue University is gratefully acknowledged.

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CR8002592