Review

# Organometallic chemistry at the edge of polycyclic aromatic hydrocarbons

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## Abstract

Zirconocene and bisphosphine nickel chemistry developed in our labs and directed towards the derivatization and synthesis of polycyclic aromatic carbon compounds is reviewed. Complexes with the formula $Cp_2ZrMe(\eta^1\text{-PAC})$ (PAC = anionic polycyclic aromatic carbon ligand) eliminate methane to produce zirconacycles and yne complexes. Treatment of the zirconacycles with $L_2NiX_2$ (L = phosphine, X = Cl, Br) in the presence of alkynes results in metallacycle transfer to nickel and cycloaddition of the alkyne. The resulting polycyclic aromatic carbon compounds contain an additional ring. The nickelacycles may also be accessed by oxidative addition of Ni(0) to polycyclic aromatic dihalides followed by reduction. The application of this chemistry to the step-growth synthesis of single-walled carbon nanotubes is proposed.
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## 1. Introduction

Polycyclic aromatic carbon compounds constitute a large and important class of compounds [1]. Recent additions to this class include fullerenes and carbon nanotubes [2]. An intriguing result in this area appeared in a 1997 publication by Vollhardt and co-workers [3]. The formation of 'fullerene-type' materials (nested fullerenes and short multi-walled nanotubes) from the explosive decomposition of solid dehydroannulene **1** (Eq. (1)) was reported. Although more controlled non-explosive decomposition would be desirable, the observation of ordered carbon materials from a solid acetylenic precursor suggests that order (molecular and/or solid state) in the precursor may translate into order in the carbon product. Such a prospect has important implications as even now routes to fullerenes and single-walled carbon nanotubes involve relatively high temperature reactions with limited control over product formation [2,4].



$$\text{(1)}$$
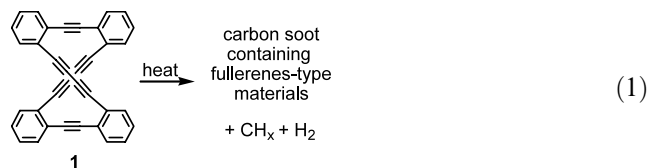
The synthesis of **1** is lengthy and it occurred to us that much simpler materials that decompose into carbon might give similar results. Group 11 metal acetylides $M_2C_2$ (M = Cu, Ag, Au) fit this description very well. These materials are easily prepared from $[M^+]$ salts and acetylene and are known to decompose to the metal and carbon (Scheme 1) [5].

This chemistry predates the introduction of current characterization techniques, in particular, transmission electron microscopy (TEM). We therefore prepared these compounds and examined their decomposition products under various conditions [6]. While we did observe many interesting features by TEM, including nested fullerenes, graphite coated metal particles, and possibly nanotubes, a deficiency of characterization facilities and funding forced us to abandon this work. Still, there seems to be much potential in this area with the availability of a variety of polyacetylenes [7] that would allow alteration of the carbon-to-metal ratio and structural changes and with the increasing knowledge of

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Scheme 1.



Fig. 1. Example Edge Complexe
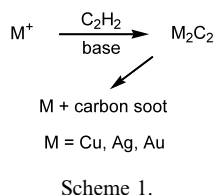
crystal engineering, solid state reaction chemistry [8], and Group 11 acetylide structures [9].

However, the main focus of this review is a project that grew out of the acetylide work and an interest in the metal catalyzed growth of carbon nanotubes. Various proposals for how the metal interacts with the tube and mediates its growth have been advanced [10–21]. Of interest here are those that involve metal atoms bonded to the edge of the growing end of the tube [11,13,14,22,23]. In several of these proposals the metal atoms bond to form either a five-membered metallacycle or an yne complex at the end of an armchair nanotube [21]. (The yne complex can also be considered a three-membered metallacycle.) In Scheme 2, this concept has been extended to complete metal atom coverage of the tube end for both the five-membered metallacycle **2** and the yne interaction **3**. This eliminates all dangling bonds and could be the situation for a metal particle attached to the tube end. An interesting feature of these two systems is their inter-conversion by a concerted shift of the metal atoms around the tube edge. That is, **2** and **3** are isomers. These interactions are specific for an armchair type nanotube. A zig-zag nanotube edge requires a four-membered metallacycle interaction **4** (Scheme 2) with no isomerism possible.

Metallacycle and yne complexes are well known in organometallic chemistry. Fig. 1 shows complexes that are analogous to the metal-nanotube edges in Scheme 2. Complexes **5**–**7** and their analogs are referred to here as 'edge complexes'. Many examples of yne complexes (**5**) [24] and five-membered metallacycles (**7**) [25–36] are known although they contain at most two aromatic rings in the carbon ligand. The four-membered metalla-

cycle complexes (**6**) [37] are much more limited and prior to our work, to be described below, there was but a single publication on these complexes. In examining the literature for edge complexes and their chemistry it became clear that they could also be important in the more general area of polycyclic aromatic carbon compound synthesis and derivatization and perhaps also in a low temperature synthesis of single-walled carbon nanotubes. It is in this direction that our research has moved and it is our work in this area that is reviewed here.
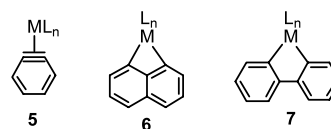
## 2. Edge complex synthesis

A particularly attractive potential route to edge complexes begins with the deprotonation of polycyclic aromatic hydrocarbon compounds (PAHs). Selective deprotonations from the bay region of triphenylene [38], phenanthrene [38], and biphenyl [39] by *n*-BuLi have been reported. The resulting dilithio reagents are suitable for reaction with transition metal halide complexes and we have found that treatment of $Cp_2TiCl_2$ with the triphenylene reagent **8** gives the structurally characterized five-membered metallacycle edge complex **9** (Scheme 3).

Attempts to extend the deprotonation chemistry to fluoranthene, which contains a five-membered ring, were unsuccessful. Unfortunately, instead of deprotonation addition is observed giving high yields of purple crystalline **10** (Eq (2)). The high stability of the fluorene anion fragment present in **10** is probably partly responsible for this different outcome. Analogous alkyl lithium additions were recently reported for bowl-shaped corannulene [40] and earlier for other PAHs [41–45]. This attractive route to edge complexes is therefore limited by the selectivity to deprotonation as opposed to addition.
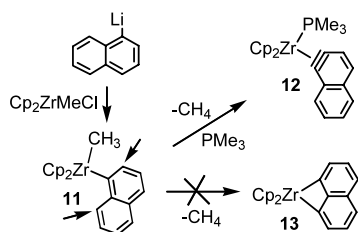


Scheme 2.



Scheme 3.

(2)
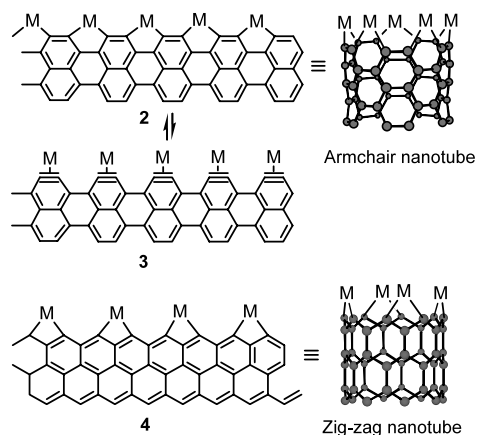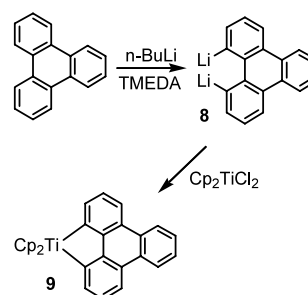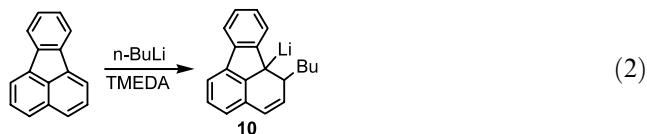
With the limitations of the deprotonation route we became interested in the hydrogen atom abstraction capabilities of the Cp$_2$ZrMe fragment. This fragment has been used extensively for the formation of benzyne and cyclic alkyne complexes [46,47]. To test the selectivity of the abstraction process we prepared Cp$_2$ZrMe(1-naphthanyl) 11 as outlined in Scheme 4. Abstraction in this system could occur from either the 2-position or the 8-position (see arrows) generating either the yne complex 12 or the four-membered metallacycle complex 13. Heating solutions of 11 to 70 °C results in exclusive abstraction from the 2-position to give yne complex 12. In situ generation of 12 has been previously reported [48].

Abstraction is directed to the 8-position by blocking the 2-position with a methyl group and formation of the four-membered metallacycle 16 by gentle heating of 14 is observed (Scheme 5). This synthesis of 14 represents a new entry into four-membered metallacycle edge complexes. This approach fails with a methoxy group and 15 does not eliminate methane up to 110 °C. An X-ray crystal structure determination of 15 and NMR nOe experiments show that coordination of the oxygen atom of the methoxy group adjacent to the Zr-bonded methyl group prevents access of the 8-hydrogen to the methyl group abstractor.

Even more effective than blocking with a methyl group is to add another six-membered ring. Anthracenyl complex 17 eliminates methane at room temperature giving the four-membered metallacycle complex 18 (Scheme 6) [49].

Expansion to the polycyclic systems coronene and corannulene has been unsuccessful. Both bromocorannulene and dibromocoronene are reduced to the parent PAH on reaction with n-BuLi, n-BuLi/tmeda, Li metal, or EtMgBr. Without the Li or Mg reagents the Cp$_2$ZrMeR complexes needed for the elimination reaction cannot be obtained. The facile reduction of the bromides can be attributed to the low-lying π*-orbitals in these large polycyclic aromatics. Other approaches to edge complexes of these two systems are being explored.
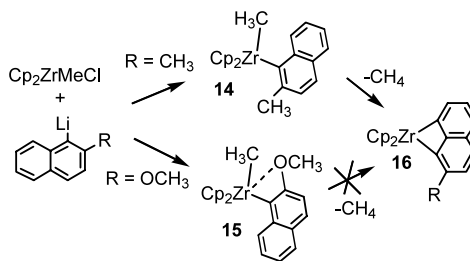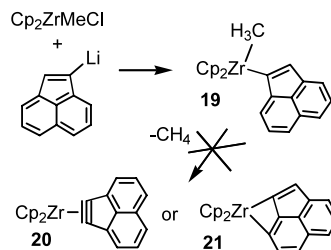


Scheme 5.
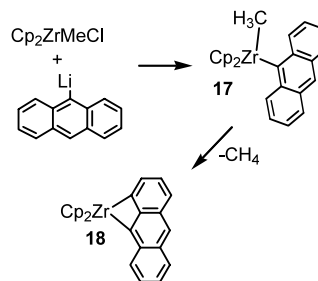


Scheme 6.

Two other polycyclic systems have attracted our attention. The acenaphthalenyl complex 19 is readily prepared and has, like the naphthalenyl complex 11, two possible hydrogen atom abstraction sites (Scheme 7). Since abstraction from the 2-position would generate a highly strained yne complex abstraction from the 8-position might be preferred. However, neither occurs and the complex is stable to at least 110 °C. This is perhaps not surprising, as the changes in angles imposed by the five-membered ring increases the distances between the Zr-bonded methyl group and the ring hydrogen atoms. A similar loss of hydrogen abstraction activity was observed in the non-aromatic five-membered ring complex Cp$_2$Zr(Me)(1-cyclopentenyl) [50].

The second system contains a four-membered ring and is prepared from commercially available 1-bromobenzocyclobutene (Scheme 8). Again, there are two possible abstraction sites for the methyl complex 22. The usually preferred β-hydrogen abstraction would yield anti-aromatic benzocyclobutadiene complex 23 and it was anticipated that abstraction might be more favorable from the 3-position to give the four-membered metallacycle 24. Methane evolution from 22 occurs on



Scheme 4.



Scheme 7.

Scheme 8.
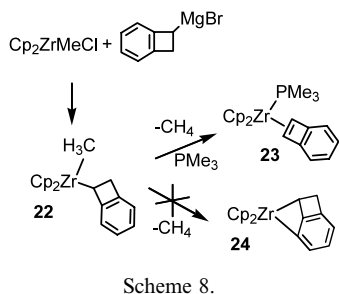
thermolysis at 70 °C and, in the presence of PMe$_3$, the benzocyclobutadiene complex **23** is isolated indicating that β-hydrogen abstraction remains more favorable. The structure of **23** reveals a strong contribution from a metallacyclopropane resonance form negating the *anti*-aromatic character of the benzocyclobutadiene ligand [51]. While not an edge complex, **23** is useful in the synthesis of polycyclic aromatics [52].

Dihaloaromatics provide another entry into edge complexes. Bennett and co-workers have used 1,2-dihalobenzenes and 2,3-dihalonaphthalenes in the synthesis of Ni aryne complexes [53–55]. We have applied an analogous approach to the synthesis of a four-membered nickelacycle from 1,8-dihalonaphthalene (Scheme 9). The resulting nickelacycle **25** is apparently unstable but may be trapped as discussed in Section 3.

Another interesting dihalide to which we have applied this approach is 1,2-dibromoacenaphthalene (Scheme 10). This was expected to give an yne complex but a highly strained yne incorporated into a five-membered polycyclic aromatic ring. Treatment of the 1,2-dibromide with Ni(COD)$_2$ and PEt$_3$ yields the oxidative addition product **26**. With PMe$_3$, the π-complex **27** is initially formed and converts rapidly at room temperature to the oxidative addition product **26**. Reduction of **26** with Na/Hg yields a solution containing a single product by $^{31}$P-NMR spectroscopy. This product, formulated as the acenaphthalyne complex **28**, is isolated when the reaction solution is separated from the NaBr and amalgam prior to solvent removal in vacuo. However, the mixed Ni–Hg complex **29**, a bimetallic edge complex, is isolated when the reaction solvent is removed in vacuo prior to separation from the NaBr and remaining amalgam. Complex **29** is also formed in
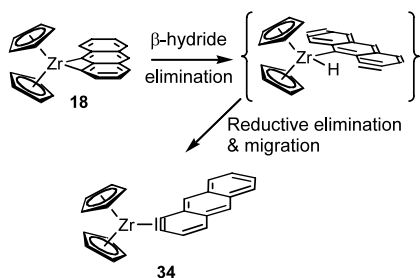


Scheme 10.
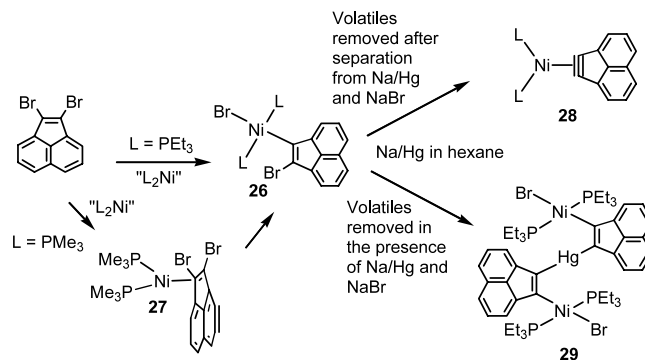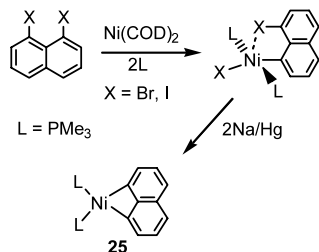
the reaction of **28** with HgBr$_2$ suggesting that it forms in the work-up from the reaction **28** with HgBr$_2$ at the amalgam surface. Although spectroscopic data are consistent with the formulation of **28**, efforts to isolate pure **28** or to grow crystals have not yet been successful and its unambiguous characterization has not yet been achieved.

## 3. Reaction chemistry

Although four-membered metallacycles of aromatic systems analogous to **16**, **18** and **25** had been reported [37] their reaction chemistry had never been explored and we were keen to investigate their reactions with unsaturated species. This type of metallacycle is particularly interesting since cycloaddition of a two-atom species such as an alkyne would yield a five-membered ring, important in the curvature of polycyclic aromatic molecules. Edge complexes can be considered to constitute a series of metallacycles: **5** (three-membered), **6** (four-membered), and **7** (five-membered). As such, the reaction chemistry of four-membered **16** and **18** might be expected to lie between that of three- and five-membered analogs. The observed reactions of **18** are shown in Scheme 11 [49]. Similar to the reactivity of three-membered analogs (yne complexes) [46,47], *t*-BuNC and selected aldehydes and ketones insert into the least hindered Zr–C bond giving **30** and **31**. However, more like the five-membered analogs alkyne insertion is not observed [56]. Instead, on vigorous heating (130 °C), **18** rearranges to yne complex **34**
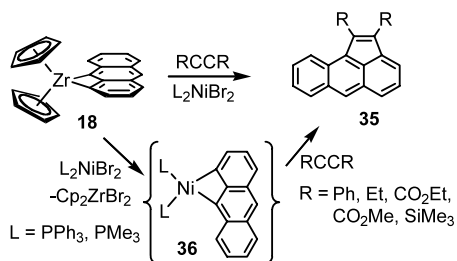


Scheme 9.
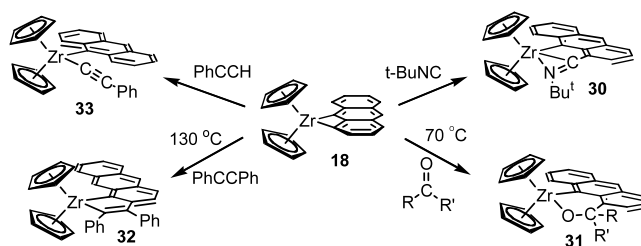


Scheme 11.

Scheme 12.



Scheme 14.

(Scheme 12), which is trapped by the added alkyne giving **32**. This rearrangement suggests that the three-membered metallacycle (yne complex) **34** is more stable than the four-membered metallacycle **18**. In contrast to PhCCPh, the terminal alkyne PhCCH behaves as an acid and adds across the Zr–C bond yielding the alkynyl–anthracenyl complex **33**.
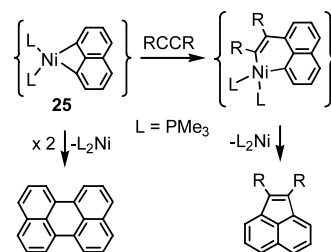
A clever way of getting around the low coupling reactivity of five-membered zirconacycles is to transfer the metallacycle to a more reactive (to alkyne coupling) metal center [57]. Application of this technique to the four-membered metallacycle **18** is successful. Transfer of the metallacycle to a $L_2Ni$ center (L = PPh$_3$, PMe$_3$) in the presence of an alkyne yields the cyclization products **35** with five-membered rings added to the original polycyclic aromatic system (Scheme 13).

We have investigated the transfer reaction by low temperature NMR spectroscopy for L = PPh$_3$ and find that transfer begins at ca. −20 °C as indicated by the disappearance of **18** and the appearance of Cp$_2$ZrBr$_2$. The stability of the resulting nickelacycle **36** is limited and if alkyne is not added before the solution reaches 0 °C the cyclization product **35** is not formed. Possible instability of the Ni metallacycle was expected as the five-membered nickelacycle **7** (ML$_n$ = Ni(PEt$_3$)$_2$) is unstable at room temperature [25].

A further indication of the possible instability of four-membered nickelacycles like **36** is found in our synthesis of Ni metallacycle **25** (Scheme 9). As described above, our approach follows that developed by Bennett and co-workers for the preparation of Ni benzyne complexes. However, instead of the expect nickelacycle, perylene, a dimer of naphthalene, is formed in close to quantitative yields (Scheme 14) [58]. Since the five-membered nick-
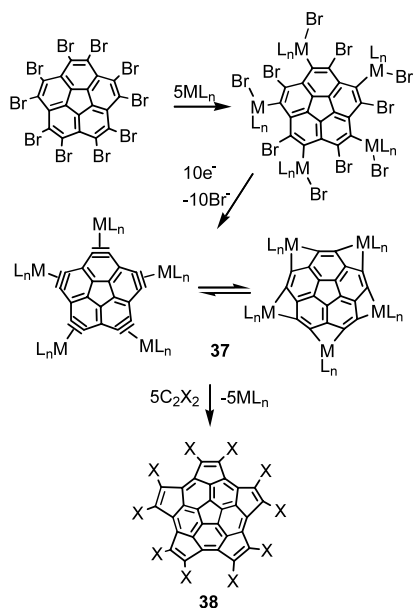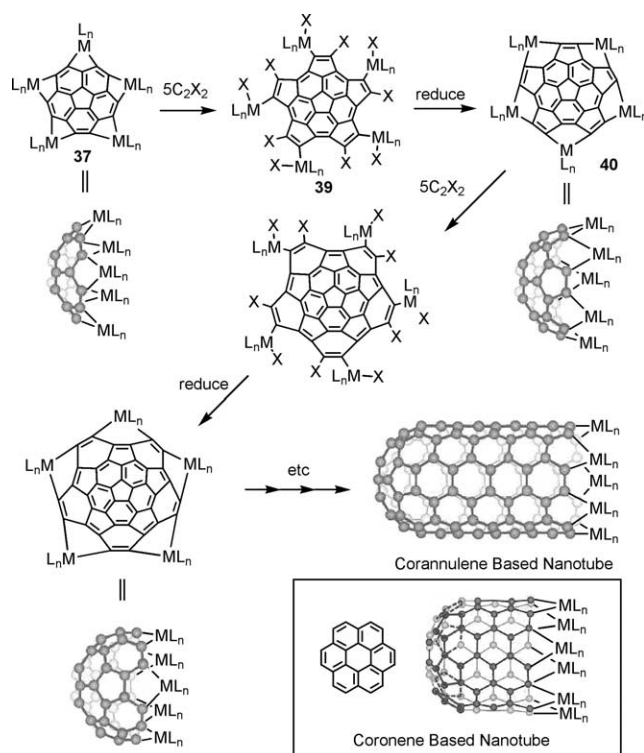
elacycle **7** (ML$_n$ = Ni(PEt$_3$)$_2$) decomposes to form tetraphenylene [25], a dimer of biphenyl, we thought that perylene might be forming by a similar decomposition of nickelacycle **25**. With this in mind, we repeated the reduction reaction in the presence of excess (six equivalents) diphenylacetylene and instead of perylene the coupled product acenaphthalene is isolated in high yield (Scheme 14). Perylene is found in only trace amounts but becomes a significant product when the amount of diphenylacetylene is reduced to two equivalents. Other acetylenes, RCCR (R = Et, SiMe$_3$) are less efficient at trapping **25** and even with six equivalents of alkyne perylene is the major product. These results suggest that **25** is less stable and/or slower reacting with alkynes than the analogous anthracenyl derivative **36**. Since slower reaction rates for a less hindered system are unlikely it is probably lower stability suggesting an increases in stability with greater numbers of six-membered rings in the polycyclic ligand. We are currently investigating other methods of generating four- and five-membered nickelacycles to better understand their stability and reactivity.

## 4. Conclusions and future outlook

Polycyclic aromatic carbon growth by the addition of alkynes and derivatization with nitrogen and oxygen containing unsaturated species is readily accomplished through organometallic reactions. Both five- and six-membered rings can be added to the polycyclic system. The addition of five-membered rings opens the possibility of using this chemistry to prepare curved polycyclic aromatics. Possible future applications include nanotube synthesis, growth, and derivatization. For example, a possible step-growth synthesis of an armchair carbon nanotube utilizing the chemistry demonstrated here is illustrated in Schemes 15 and 16. The synthesis begins with perbromocorannulene. Oxidative-addition of a low valent metal complex ML$_n$ at half of the sites followed by reduction gives the permetallated complex **37** (Scheme 15). Like the metallated edge of a nanotube, **37** can exist in either a metallacyclic form or an yne form. Coupling with alkyne C$_2$X$_2$ is expected to give



Scheme 13.

Scheme 15.



Scheme 16.

released Ni(0) has been demonstrated [59].) Resulting **39** is ready for reduction and formation of a new permetallated edge complex **40**. Repetition of this process results in the step-growth of a nanotube. An analogous process with perbromocoronene yields a larger diameter tube. Remarkably, the formation of the complete tube cap, with the required six 5-membered rings [60], occurs naturally in these reaction sequences for both coronene and corannulene. Current effort in our laboratory is directed towards delineating problem areas and establishing the viability of the reaction steps shown in Schemes 15 and 16.

### Acknowledgements

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cycloaddition product **38** with an additional layer of carbon on the edge.

Continued growth requires reattachment of $ML_n$ to the new edge of **38**. As shown in Scheme 16 this will occur automatically when X is a halide by oxidative-addition of $ML_n$ released in the cycloaddition reaction that gives **38**. (Cycloaddition of a bromoalkyne to a nickelacycle followed by oxidative-addition of the

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