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ortho-Arene Cyclynes, Related Heterocyclynes, and Their Metal Chemistry

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I. Introduction and Definition of Terms

A cyclyne is any ring of atoms having one or more alkyne units.[1] Dehydroannulenes are a subset of cyclynes schematically formed by dehydrogenating a ring of conjugated carbon−carbon double bonds (annulenes).[2] This review will discuss a subset of dehydroannulenes comprised of cyclooligomeric alkynes of the general formula $[RC{\equiv}C]_n$, where R is an *ortho*-substituted aryl group (benzene, thiophene, etc.) or a *cis*-alkene. Such systems are described by Sondheimer as benz-fused dehydroannulenes.[2b] Oligomeric cyclyne systems (Figure 1) include those with the following central pockets: a dimer of *cis*-substituted enyne units (cyclodienediyne) such as **1** (dibenzocyclyne); a trimer of enyne units (cyclotrienetriyne, abbreviated cyclotriynes) such as **2** (tribenzocyclyne or 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,-11-triyne);[3,4] a tetramer of enyne units (cyclotetraenetetraynes) such as **3** (tetrabenzocyclyne); a hexamer of enyne units (cyclohexaenehexaynes) such as **4** (hexabenzocyclyne). These cyclynes have ring sizes of 8−24 atoms.

Also addressed in this review are heterocyclic oligoynes (heterocyclynes) and the subgroup metallacyclic oligoynes (metallacyclynes) in which one or more linkages R of the general formula $[RC{\equiv}C]_n$ consists of a heteroatom or transition metal (Figure 2). Cyclynes with single carbon atom spacers are referred to as pericyclynes.[5] Pericyclynes are the subject of a recent review article and will not be discussed further here.[6] Also not discussed herein are small cyclynes which contain only one alkyne and their metal complexes. These have been the subject of two recent reviews.[1b,7] Alkynylated cyclobutadiene

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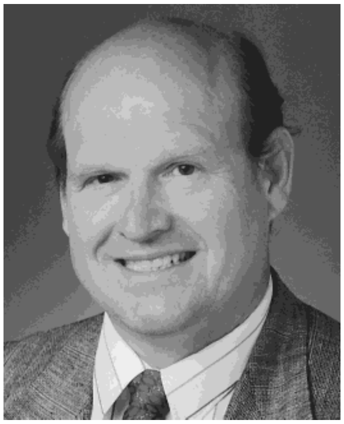

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Claire Tessier's involvement in chemistry began in 1970 when, as a high school student, she participated in ACS Project SEED at the University of Vermont under the direction of Klaus Wulff. She received a B.S. in chemistry in 1975 from the University of Vermont and a Ph.D. degree, under the direction of O. T. Beachley, Jr., in 1982 from the State University of New York at Buffalo. In 1981–2 she completed a postdoctoral position with D. F. Shriver at Northwestern University. She began her current position as a professor at the University of Akron in 1990. Her research interests include silicon, dendrimer, metal–alkyne, and metal–acetylide chemistries.

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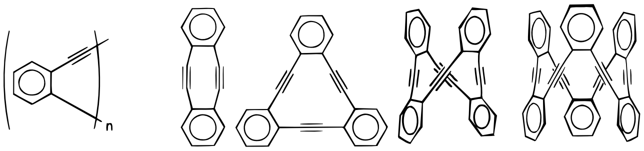


benz-fused cyclynes **1** **2** **3** **4**

Figure 1. Representative structures of benz-fused cyclynes including cyclic dimer **1**, trimer **2**, tetramer **3**, and hexamer **4**.

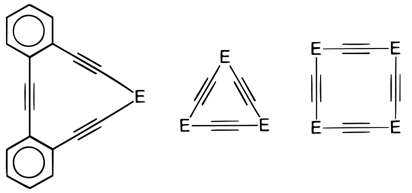


Figure 2. Examples of heterocyclynes E = CR_2, SiR_2, GeR_2, PR, PtL_2, and $TiCp_2$.

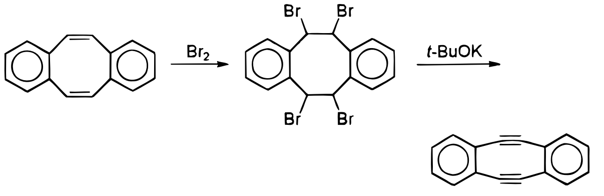
complexes have also been the subject of a recent review and will not be discussed further herein.[8] Cyclynes and heterocyclynes containing butadiynes will also not be discussed in this review.[9]

The ability of transition metals to bind to π-systems of alkynes[10] is well-known. In the transition metal complexes discussed herein, it is the alkyne functionality of the model system that dominates the chemistry. Cyclotriyne molecules such as **2** are conjugated, antiaromatic, planar molecules and have cavities large enough to encompass some low-oxidation-state first-row transition metals (distance from center of cavity to center of an alkyne is ca. 2.08 Å in **2**). The binding of metals within cavities solely by constituent alkynes is relatively new and has been observed with **2**, analogues of **2** and **3**, pericyclynes,[1a] and heterocyclynes. These metal complexes have been called metallocyclynes.

A large structural difference underlies the subtle spelling difference between prefixes "metallo" and "metalla". "Metallo" is traditionally applied to complexes that are defined to be π complexes, such as the *metallo*cenes, or inserted metal−atom complexes such as *metallo*porphyrins, whereas *metalla*cycles are defined to be carbocyclic rings with a metal atom(s) incorporated into the σ framework.[11,12] Distinction is often based upon metal−carbon distances and coordination geometry.[8a] A single carbon in a close interaction with a metal where electron pairs can be assigned as a σ bond[13] is termed a "metalla" complex, while multiple unsaturated carbons may occupy a coordination site on a metal to give a "metallo" complex.

II. Synthesis and Characterization of Cyclyne Ligands

Cyclooligomerization of *ortho*-ethynyliodoaryls is a proven synthetic route to cyclynes. A detailed procedure for the synthesis of **2** can be found in ref 14. Alternative syntheses of cyclynes include bromination/dehydrobromination[4c−g] and spontaneous rearrangements of proximal acetylenes in cyclicdiynes.[4h]



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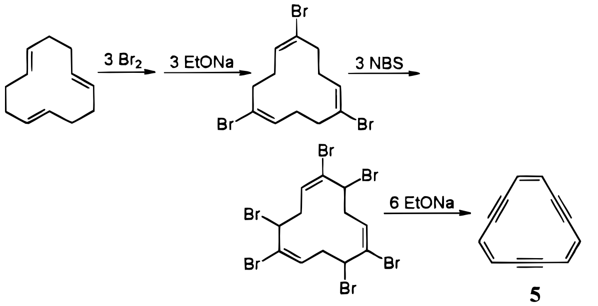


(2)

5

II.A. Bromination/Dehydrobromination

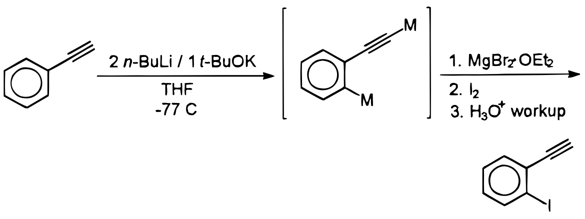
Bromination/dehydrobromination of annulene systems was one of the first methods employed in the synthesis of cyclynes and is the only known route to the dimeric **1**[15] and cyclo-1,5,9-triene-3,7,11-triyne, **5**,[4g] as outlined in eqs 1 and 2, respectively. Brominations are carried out at alkene carbons with bromine or at allylic carbons with *n*-bromosuccinimide. Bases are used for dehydrobromination. It is interesting to note that elimination of the bromine on the alkene in eq 2 can occur with either a hydrogen from the alkene to give an alkyne or a methylene hydrogen to give a cumulene resonance form (see section II.C.3).

II.B. Starting (*ortho*-Iodoaryl)acetylenes for Cyclooligomerization

Starting (*ortho*-iodoaryl)acetylenes for cyclooligomerization have been prepared in two ways. The first involves regioselective dimetalation of ethynyl-substituted aryls. The other involves less-selective coupling of an acetylene to an *ortho*-difunctional aryl or ethene moiety. The use of dialkyltriazenes as masking groups for aryl iodides, which was originally developed by Bario,[16] to form (*meta*-iodoaryl)acetylenes is well documented,[17] and their use to form (*ortho*-iodoaryl)acetylenes has been reported but not in detail.[18]

II.B.1. From Lochmann–Schlosser Super Base ortho-Dimetalation

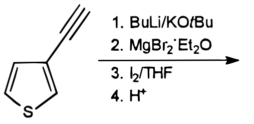
The Lochmann−Schlosser super bases, a 1:1 ratio of alkyllithium (LiC) to potassium alkoxide (KOR) denoted as "LICKOR" bases,[19] are known to deprotonate weakly acidic compounds without addition to C−C π systems.[20] THF will cleave in the presence of super bases, *n*-BuLi, and *n*-BuK; however, reasonable stability is attained at temperatures below ca. −50 °C.[21] Brandsma et al. developed the conditions for ortho-dimetalation of phenylacetylene using the Lochmann−Schlosser super base (eq 3).[22] Brandsma's modified base "cocktail" consisting of a 1:1:1 ternary mixture of *n*-BuLi, *t*-BuOK, and TMEDA in apolar solvents such as pentane or hexane is reported as being equally or even more effective in ortho-dimetalating phenylacetylene.[22b] A 1:2 ratio of *t*-BuOK to *n*-BuLi is sufficient for regiospecific ring metalation of phenylacetylene as well as ethynyl-2,5-methoxybenzene and 2-ethynylthiophene.[14,23,24] The exact mechanism for this metalation is still unclear; however, results are consistent with a chelating mechanism similar to that used to rationalize selective 2,2′-dimetalation of biphenyl with *n*-BuLi and TMEDA.[22b,25] A concise summary of super-base theory has been compiled by Mordini.[26] Disubstituted alkynes give substantial amounts of *meta*- and *para*-metalated products making *ortho* selectivity of metalations unique for terminal acetylides directly connected to an aryl ring.[26]



(3)

In the procedures of Brandsma phenylacetylene is treated first with 2 molar equiv of *n*-BuLi to give the acetylide and then with 1 molar equiv of *t*-BuOK to create the super base with the unreacted *n*-BuLi. Very good selectivity is observed in the dimetalation. The identity of the alkali metals as potassium or lithium in the dimetalated species is academic because they are both converted to the Grignard reagent by addition of $MgBr_2{\cdot}OEt_2$.[27] The di-Grignard reagent is a softer, kinetically less basic reagent, which avoids possible Wurtz coupling[28] side products and gives higher yields in reactions with I_2.[27] The synthetic sequence is completed with normal organic workup that consists of the following: neutralization with dilute acid, removal of excess I_2 with $Na_2S_2O_3$,[29] washing with brine, drying over $MgSO_4$, and flash-chromatographic purification.[30]

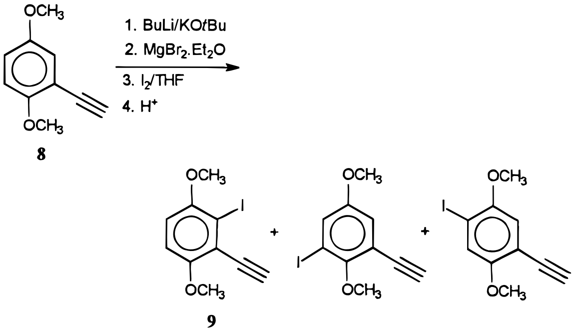
Complexation of metalating reagents by the substrate directs metalation to the immediate vicinity.[31] Metalation is efficiently directed to the position *alpha* to the sulfur and *ortho* to the ethynyl group in 3-ethynylthiophene, **6**, using 2:1 *n*-BuLi:*t*-BuOK. The yield of the derivative 2-iodo-3-ethynylthiophene, **7**, is 68% (eq 4).[23,32]



6 **7**

(4)

Although methoxy groups are *ortho*-directing in metalations[33] and super bases will metalate the position *ortho* to an acetylide, very little regioselectivity is observed in the dimetalation of ethynyl-2,5-dimethoxybenzene, **8** (eq 5).[24] Yields of 35% for ethynyl-2-iodo-3,6-dimethoxybenzene, **9**, and a combined yield of 39% for the other two isomers are obtained. Hence, the coordination-directing effect of the methoxy group reduces the directing effect of the alkali metal acetylide and *t*-BuOLi. The *ortho*-directing ability of the methoxy groups in metalations is thought to be a combination of coordination and

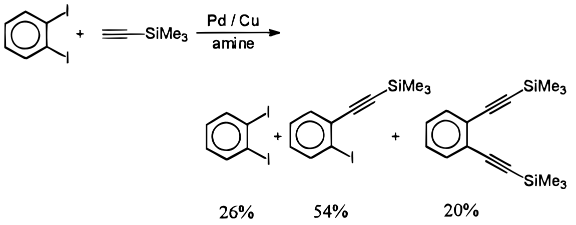


(5)

inductive effects of the methoxy groups. However, the *para*-positioning of the methoxy groups in **8** leads to a net cancellation of their resonance effects leaving only the chelating ability of the methoxy groups to direct metalation.

II.B.2. From ortho-Diiodoaryls

Palladium-catalyzed coupling[34] of (trimethylsilyl)acetylene with *ortho*-diiodoaryls provides another pathway to the starting monomers, *ortho*-ethynyliodoaryls (e.g. eq 6).[35] The efficiency of this method depends on the availability and nature of the starting *ortho*-diiodo moiety. Aryl bromides also undergo palladium-catalyzed coupling, but require more forcing conditions to react, and give lower yields of cross-coupled products.[36] The 2-position of 2,3-diiodothiophene is more reactive toward palladium-catalyzed coupling with (trimethylsilyl)acetylene as demonstrated by the 92% yield of 2-ethynyl-3-iodothiophene from this reaction.[23] This is in sharp contrast to systems without electronic resonance effects where the process is controlled by stoichiometry and dilution. *o*-Diiodoaryls with C_{2v} symmetry give product ratios of starting, to monosubstituted, to disubstituted compounds averaging 26:54:20 (eq 6).[35a,37]



(6)

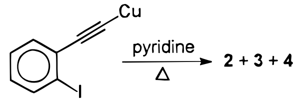
II.C. Cyclooligomerization

Control of cyclooligomerization and ring closure is most often achieved by high-dilution techniques or pseudo-high-dilution techniques such as use of suspensions of poorly soluble monomers and slow addition.[38]

II.C.1. Stephens–Castro Coupling

Copper acetylides can be prepared directly from CuCl and the terminal alkyne in aqueous ammonia.[4a,23,24,39] Alternatively, copper(I) acetylides can be made by reducing copper(II) with hydroxylamine (HCl salt) and aqueous ammonia in the presence of the acetylene.[40] In some cases the latter route gives better yields.

Copper (*o*-iodoaryl)acetylides will undergo cyclooligomerization using the method of Stephens and Castro[4a,14,41] by heating a roughly 0.1 M pyridine or dimethylformamide solution/suspension (eq 7). Yields of benzocyclynes are typically 47% **2**, 8% **3**, and traces of **4**. However, cyclooligomerization yields are dependent on the strain of the final product. In an analogous reaction, trithiophenecyclyne, **10**, is formed from 3-ethynyl-2-iodothiophene, **7**, in 21% yield (eq 8). The lower yield is presumably due to the strain produced by accommodating thiophene rings into the cyclyne.[37b]



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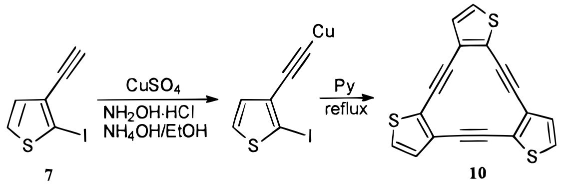
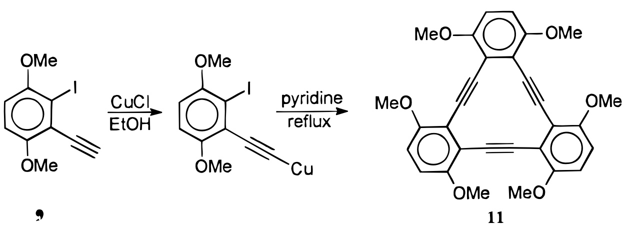


(8)

ortho-Coordinating substituents on the aromatic rings of the monomer can dramatically influence the success of the reaction.[41b] Cyclization of ethynyl-2-iodo-3,6-dimethoxybenzene, **9**, gives 1,2:5,6:9,10-tris-(2,5-dimethoxybenzo)cyclododeca-1,5,9-triene-3,7,11-triyne, **11**, in surprisingly high yield (80%) which corresponds to a 92% yield per bond formed (eq 9).[24]



(9)

This increased yield over that of **2** is attributed to the fact that methoxy groups are *ortho*-directing in Stephens–Castro coupling reactions. In contrast, the tetramer octamethyltetrathienylcyclyne, **13**, is formed preferentially over the trimer in the cyclization of the copper acetylide of 3-ethynyl-4-iodo-2,5-dimethylthiophene, **12** (eq 10 and Figure 3).[37b]

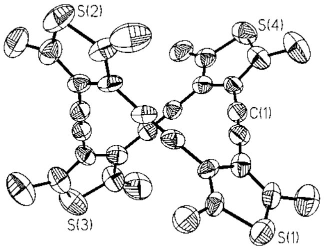
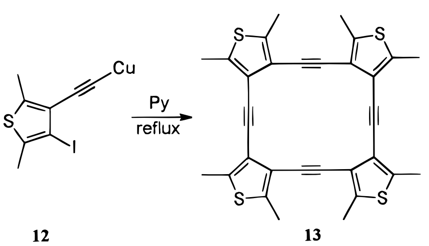
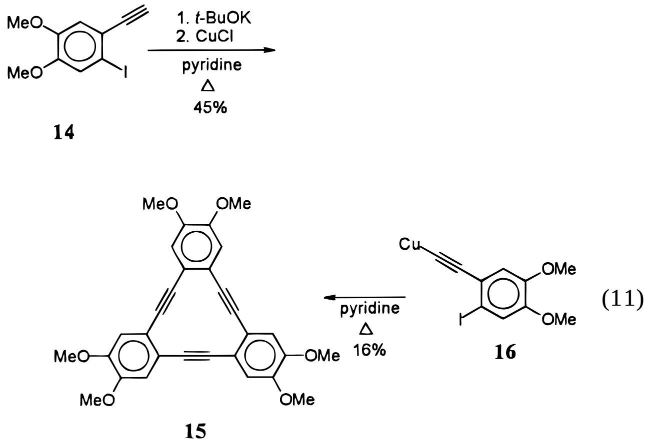


Figure 3. **13** drawn with 50% probability thermal ellipsoids.



(10)

When dry, copper acetylides are known to be shock and thermally sensitive.[42] Therefore, it would be advantageous to make them in-situ directly from reagents such as *t*-BuOCu[43] or via transmetalation with alkali acetylides.[44] Combining *t*-BuOK and ethynyl-2-iodo-4,5-dimethoxybenzene, **14**, stirring for 1 h, subsequently adding CuCl, and refluxing in pyridine gives a 45% yield of 1,2:5,6:9,10-tris(3,4-dimethoxybenzo)cyclododeca-1,5,9-triene-3,7,11-triyne, **15** (eq 11).[35a] The alkyne reagent was allowed to react with the base *t*-BuOK so that *t*-BuOCu was not preformed in this case. Use of small or catalytic amounts of Cu(I) salts and organolithium or Grignard reagents in place of preformed organocopper reagents has been reviewed.[45]

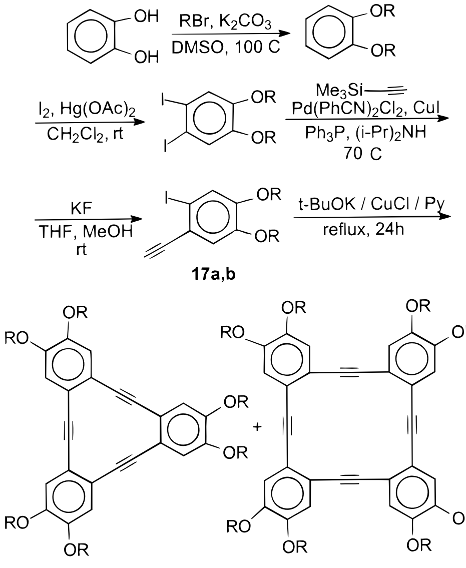


(11)

The carboxyl group of *p*-iodobenzoic acid makes the compound impervious to coupling with copper phenylacetylide.[43] Castro postulates that the "(copper) acetylide is held away from the substitution site."[41b] In the same study, methoxy groups were found to be *ortho*-coordinating and thereby *ortho*-directing. A similar argument can be made for the reduced yield of **15** from cyclooligomerization of the preformed copper (2-iodo-4,5-dimethoxyphenyl)acetylide, **16** (yield 16%[35a]). Here the copper acetylides might bind to the two methoxy groups at the 4,5-positions, away from the desired substitution site. Apparently, binding of the copper acetylide away from the substitution site is efficiently countered by either using the *t*-BuOK/CuI route or repositioning the methoxy substituents (see discussion of **9** above) with both methods giving higher yields.

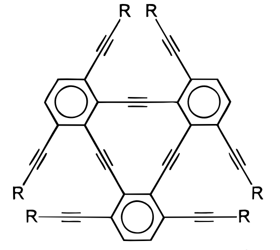
The cyclizations of **17a**,**b**, the syntheses of which are outlined in Scheme 1, were carried out by a modified Stephens–Castro coupling reaction.[46] The terminal alkyne reacted with *t*-BuOK and then CuCl in pyridine to form the copper(I) acetylide in situ. Refluxing the copper(I) acetylide in pyridine led to the formation of tris(4,5-didodecyloxyphenyl)cyclotriyne (**18a**, 17%) and tetrakis(4,5-didodecyloxyphenyl)cyclotetrayne (**18b**, 12%) from **17a** and tris(4,5-ditetradecyloxyphenyl)cyclotriyne (**18c**, 16%) and tetrakis(4,5-ditetradecyloxyphenyl)cyclotetrayne (**18d**, 16%) from **17b**.

Scheme 1



18a: R = $(CH_2)_9CH_3$
18c: R = $(CH_2)_{13}CH_3$
18b: R = $(CH_2)_9CH_3$
18d: R = $(CH_2)_{13}CH_3$

Similar modified Stephens–Castro procedures were used by Vollhardt to synthesize derivatives of hexaethynyltribenzocyclynes **19a**–**c**.[47]

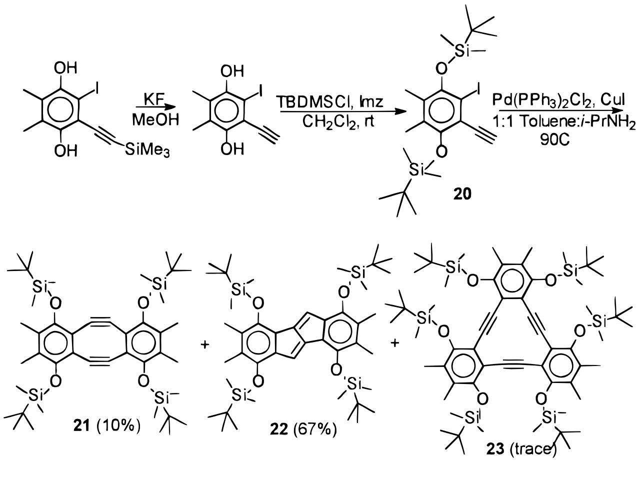


19a: R = $Si(CH_3)_2[C(CH_3)_2CH(CH_3)_2$
19b: R = Pr
19c: R = $CH_2C_6H_{11}$

II.C.2. Palladium-Catalyzed Couplings

Palladium/copper-catalyzed coupling of **20** in 1:1 *i*-Pr_2NH/toluene at 90 °C for 1 day gave dimer **21** in 10% and 2,3,7,8-tetramethyl-1,4,6,9-tetrakis[((1,1-dimethylethyl)dimethylsilyl)oxy]indeno[2,1-*a*]indene, **22**, in 67% yields (Scheme 2).[48] The mass spectrum also

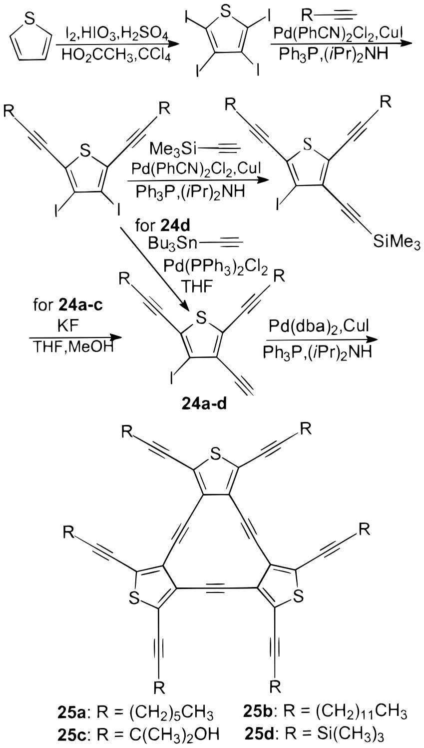
Scheme 2



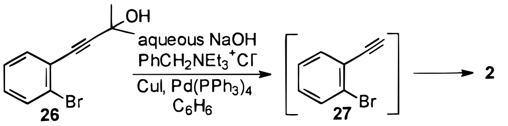
revealed the presence of traces of the trimer **23** and higher cyclics, e.g. the tetramer and the pentamer, and a series of linear oligomers. This is the only reported synthesis of a benzocyclyne dimer by the Sonogashira−Hagihara reaction.

Cyclization of **24a**−**d** in the presence of Pd−Cu catalyst in diisopropylamine led to the formation of final products tris(2,5-dialkynylthieno)cyclotriynes **25a**−**d** (Scheme 3).[46]

Scheme 3

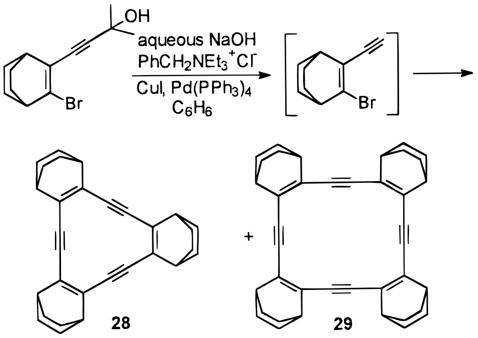


Linstrumelle reported deprotection of **26** in benzene with aqueous sodium hydroxide using benzyltriethylammonium chloride as the phase transfer catalyst followed by in situ palladium−copper-catalyzed coupling of intermediate **27** to give **2** (eq 12).[49]



(12)

Komatsu used the method of Linstrumelle[49] to form the trimer **28** (22%) and the tetramer **29** (9%) (eq 13).[50] Trimer **28** decomposes in deaerated solution after several days at room temperature. The X-ray structure of **29** has been reported (Figure 4). Compounds similar to **28** and **29** were reported by Tobe and Achiba.[51]



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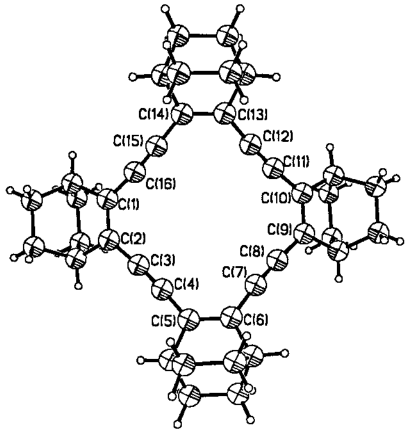
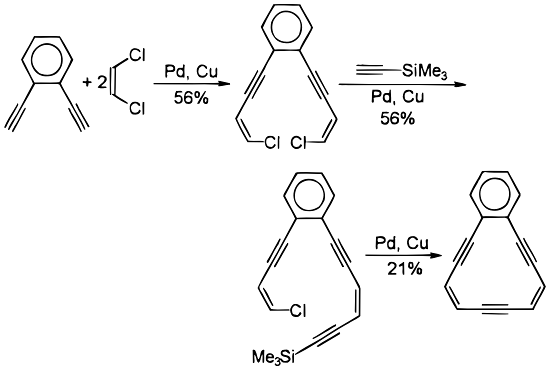


Figure 4. Thermal ellipsoid plot of **29**.

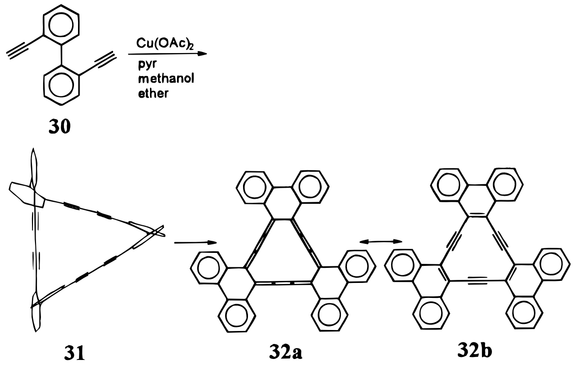
The palladium-catalyzed coupling route has greatly facilitated the synthesis of cyclotriynes not possessing 3-fold symmetry (eq 14),[49] higher cyclynes,[52] and polyynes.[53] However, ring closure of those smaller cyclotriynes having 3-fold symmetry is typically more effective using Stephens−Castro coupling of the copper acetylides.



(14)

II.C.3. Rearrangement of Proximal Ene–diynes

Cyclotriynes can also be formed from cyclooligomeric compounds with diyne units held close together by bridging groups. This reaction is similar to topochemical polymerization of polydiacetylenes.[54] Eglington coupling[55] of 2,2′-diethynylbiphenyl, **30**, presumably gives the strained intermediate **31**[56] (see eq 15) that rearranges to give cyclotriyne, **32**.[4h] The



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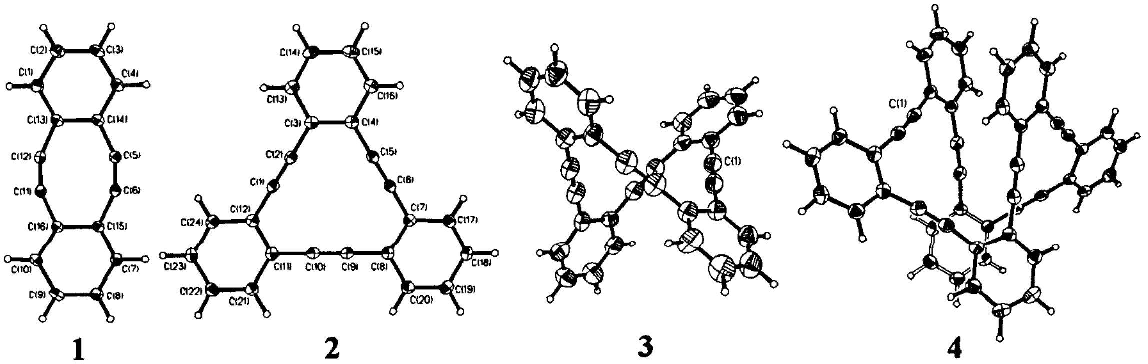
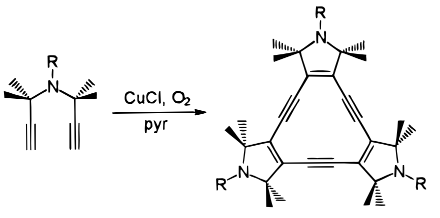


Figure 5. Structures of **1**−**4**. All thermal ellipsoids are drawn at the 50% probability level. Labeling sequences for **3** and **4** are consistent with that for **2**. Arbitrarily small hydrogen atoms and hollow bonds of one benzene ring of **4** are drawn for clarity.

cumulene resonance structure **32a** is considered to be the less stable than the cyclyne resonance structure **32b**.[57]

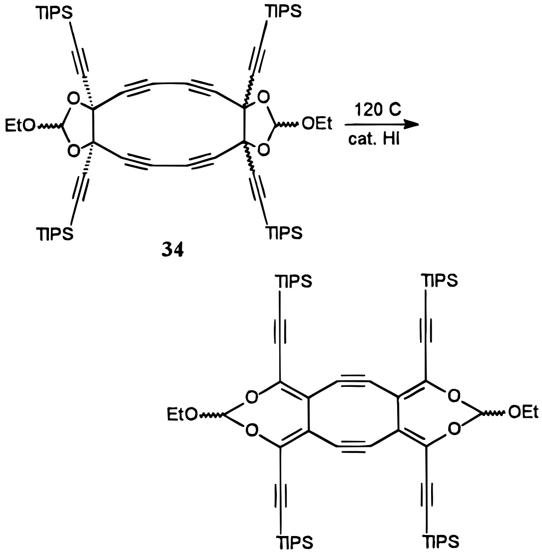
The Glaser coupling products of dipropargylamines $NR(CMe_2C{\equiv}CH)_2$ also undergo this rearrangement to form **33** (eq 16).[58]



33

(16)

Recently Diederich reported the rearrangement of **34** to produce the cycloocta-1,5-diyne **35**.[59] This compound has been characterized by X-ray crystallography.



35

(17)

II.C.4. Cyclooligomerization Products

From the Castro coupling of copper (*o*-iodophenyl)acetylide ligands **2**−**4** have been isolated and structurally characterized (Figure 5). The dimer **1** has not been isolated from cyclooligomerization reactions; however, its structure is shown for comparison. As noted above, derivative **21** of **1** has been isolated from cyclooligomerization reactions. Structures of the benzfused dehydroannulene series parallel those of the *ortho*-phenylene series[60] with the dimer **1**, trimer **2**, tetramer **3**, and hexamer **4** taking on planar (D_{2h}), planar (D_{3h}), saddle (D_{2d}), and twisted-boat (D_2) conformations, respectively. Macrocyclic oligomers with *ortho*-substituted benzodiyne repeat units mirror these geometries.[61]

i. A Cyclodienediyne. Compound **1** is surprisingly stable but is clearly more strained than the higher oligomers depicted in Figure 5. In **1** molecular strain is evidenced by lengthening of the inner $C(sp^2)-C(sp^2)$ bonds (1.431 Å) and a 24.3° deviation of the alkyne bond angles from linearity. The distance between the alkyne carbons to the centroid of the ring is approximatley 1.44 Å resulting in a very small pocket. This pocket is too small for a metal to bind within; however, several transition metal complexes of this ligand have been reported as discussed in section III.A.1.

ii. Trimeric Cyclooligomerization Products. The six sp- and six sp^2-hybridized carbons that comprise the cyclotriynes only have 180 and 120° angles. A planar geometric figure will necessarily have angles which sum to a multiple of 360°; hence, the trimeric cycles can deviate little from planarity if idealized hybridization is assumed for the carbon atoms. In general only slight ring tipping of the aryl rings contributes to deviations of atoms from the least-squares planes of cyclotriyne molecules. The crystal structure of **2** has been reported at room temperature[62] and in a low-temperature study.[63] The pocket of all trimeric cyclooligomerization products is large enough to accommodate at least the smaller transition metals (see below).

iii. Tetrameric Cyclooligomerization Products. Compound **3** exhibits polymorphic structures in the space groups monoclinic $P2_1/c$ (from methylene chloride) and tetragonal $P4_12_12$ (from acetone).[64] The particular polymorph exhibited depends on the solvent used in crystallization, although solvent molecules are not present in either structure. Packing forces and space-group-imposed symmetry lead to small differences in the two models. Solvation effects are more obvious in **13** which also exhibits polymorphism but with solvent inclusion in two monoclinic $C2/c$ unit cells differing in size and content.[37b] The pocket of **3** is

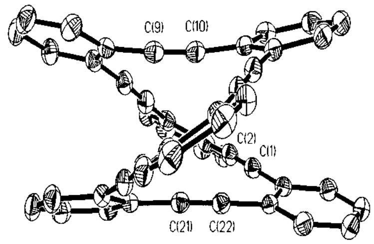


Figure 6. Plot of **4** viewed parallel to the principal chiral axis. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

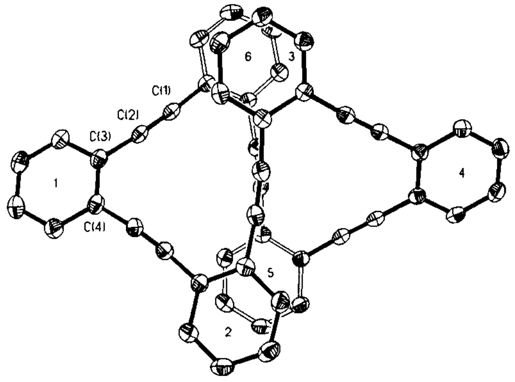


Figure 7. A shadowed Figure 8 and a similarly oriented view of **4**. Thermal ellipsoids drawn at the 50% probability level. Carbon−carbon bonds in the rear are drawn as hollow bonds and hydrogen atoms are omitted for clarity.

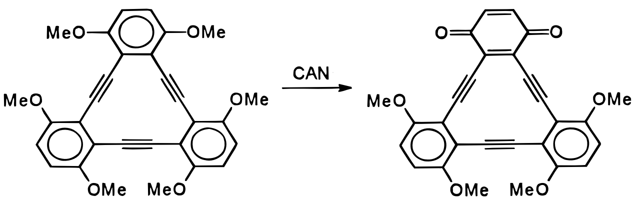
large enough to accommodate 2nd and 3rd row transition metals.

iv. Hexameric Cyclooligomerization Product. The helical atropisomer of **4** crystallizes in a centrosymmetric space group ($P2_1/c$) with both M and P enantiomers present. Assignment of the dissymmetric point group D_2 is idealized for these structures. The principle helical axis extends through the two peripheral rings and between the two eclipsed tolane moieties (see Figure 6). Two other helical axes parallel one another in the D_2 atropisomer passing perpendicular to the primary helical axis through the central cavity to the left and right of the eclipsed tolane moieties. The latter two helical axes are most evident when the molecule is viewed side-on as a shadowed figure eight (see Figure 7). The crown (D_{3d}) atropisomer of **4** depicted at the beginning of this review has not been isolated. Unlike *o*-hexaphenylene, the two atropisomers of **4** could possibly be interconverted by twisting a benzo ring through the large central pocket. It is also possible that in the chiral D_2 form the benzo rings can slide past one another to rapidly interconvert enantiomeric M and P helical structures as occurs in *o*-hexaphenylene at 125 °C.[65] Interconversion of M and P enantiomers, i.e., the D_2 drastically twisted-boat conformations, is possible by untwisting the boat and reversing direction of the original twist. The additional torsional operation of forming a new boat with new bow and stern benzo rings makes possible interconversion of all benzo rings in the chiral form. Both postulates are supported by a single set of AA′BB′ resonances observed for **4** indicative of a centrosymmetric structure or rapid interconverion of rings. The larger pocket of **4** makes a preponderance of the crown atropisomer in solution a possibility, while the chiral, solid-state structure of the crystalline sample used for solution NMR suggests rapid interconversion of rings.

II.D. Quinone Systems

Demethylation of aryloxyl methyl ethers to form quinones or hydroquinones can be accomplished by a variety of chemical[66] and electrochemical[67] methods. Quinones and hydroquinones are interrelated by interesting redox processes and form metal complexes with a variety of transition and main-group metals.[68] By incorporation of quinone or hydroquinone functionality in a cyclotriyne ligand, it may be possible to prepare mixed-metal systems in which a metal atom occupies the center of the cyclotriyne ring and a different metal binds to the quinone or hydroquinone moieties.

Combining **11** with ammonium cerium(IV) nitrate, CAN,[66c,d] in acetonitrile selectively converts one of the phenyl rings to a 1,4-benzoquinone giving the polar ligand quinone **36** (eq 18).[24] Compound **11** is only slightly soluble and quinone **36** is insoluble in acetonitrile. After one of the dimethoxyphenyl groups is converted to a *para*-quinone, the product precipitates before the remaining dimethoxyphenyl groups can be converted to quinones. This method is based on previously reported oxidations of methoxyphenyl alkynes to quinone alkynes.[69] Argentic oxide[70] and nitric acid[66b,71] have been unsuccessful in completing the oxidation.[72] Preliminary evidence suggests that an alternate synthetic route to cyclic quinone alkynes is possible.[73]



11 **36**

(18)

The presence of methoxy groups on an aromatic ring has the effect of decreasing the oxidation potential of the aromatic compound and stabilizing the radical cation generated by a one-electron anodic oxidation.[74] The radical cations are stabilized by electron delocalization resulting from interaction of the π-electron system of the aromatic ring with the electron pairs on the oxygen atom. The presence of methoxy groups also has the effect of shifting reduction potentials to more negative values than for the parent compound. Cyclic voltammagrams of **11** and **15** are quite similar with each showing one quasi-reversible oxidation wave in chloroform with (n-Bu)$_4$NPF$_6$ as the supporting electrolyte.

Controlled current electrolysis[75] of **15** in chloroform with (n-Bu$_4$)NPF$_6$ as the electrolyte under argon gave purple needles of the (PF$_6$)(n-Bu$_4$NPF$_6$) charge-transfer salt of **15**. X-ray diffraction shows the crystals to be disordered. Copper wires were attached

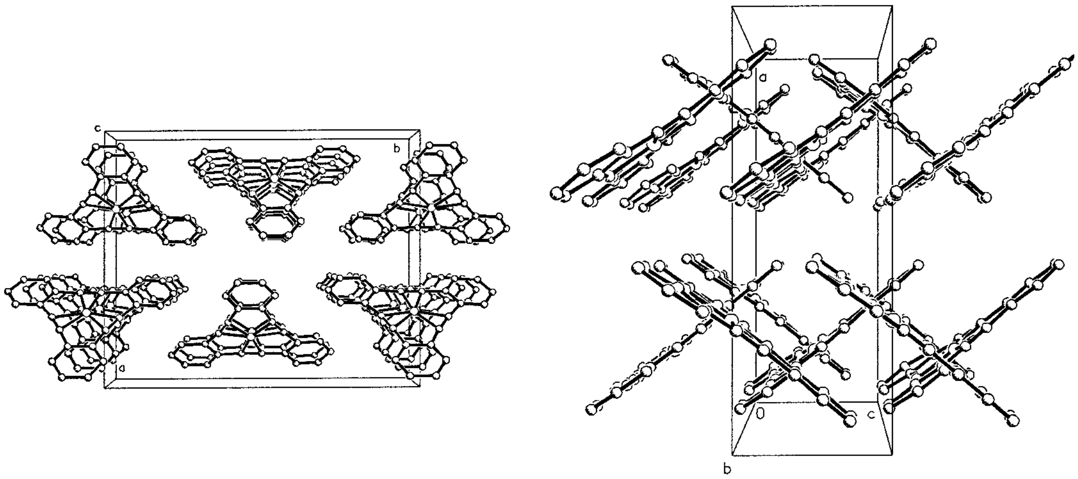


Figure 8. Views perpendicular to the *c* axis and *b* axis of **37**.

to either end of the long axis of the crystal with silver epoxy, and conductivity was determined by a two probe method to be 1.8 × 10^{-2} (Ω cm)$^{-1}$. Electrical conductivity measurements using a four-point probe AC technique performed on iodine exposed **15** gave a room-temperature conductivity of 1.65 × 10^{-4} (Ω cm)$^{-1}$.[35a]

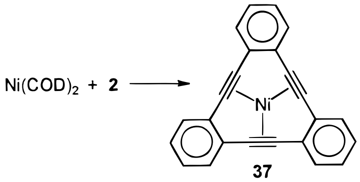
III. Metallocyclynes

The planarity of cyclotriynes such as **2**, **10**, **11**, **15**, and **18** invites comparison to planar systems based on porphyrin and phthalocyanine ligands.[76] A brief comparison of these two systems gives an appreciation for the unique nature of cyclotriyne metallomacrocycles. Ligands of the porphyrin and phthalocyanine metallomacrocycles are planar, have an extensive π-system, bind the metal through relatively hard nitrogen atoms, and have a formal negative charge(s). The resultant metallomacrocycle contains a metal in a positive oxidation state. Cyclotriyne systems are also planar and have an extended π-system; however, cyclotriynes are neutral and can bind a metal via three soft, polarizable alkyne donors. This allows formation of complexes with a formal zero oxidation state of the metal. Cyclotriyne ligands possess three alkynes with the ability to donate 2−4 electrons/alkyne depending on the electronic demands of the metal(s). Group theoretical analysis[77] shows that all 12e$^-$ of cyclotriynes alkyne pockets are available for bonding.[78] Whereas, porphyrins have neutral and negative nitrogen binding sites and depending on the ligand can lead to cases of bi-, tri-, and tetracoordination of metals.[79] These contrasts give metallocyclynes properties which differ significantly from those of nitrogen donor metallomacrocycles.

III.A. Nickel(0) Coordinated to Only Alkynes

III.A.1. Nickel Complex of Tribenzocyclyne ***2***

Interaction of **2** with metal moieties has resulted in the synthesis of a wide variety of novel metallic derivatives. Compound **37**, the nickel complex of **2**, was the first planar occupied-cavity metallocyclyne to be synthesized and structurally characterized.[80] This complex is synthesized by combining Ni(COD)$_2$ (COD = 1,5-cyclooctadiene) and **2** (eq 19). COD



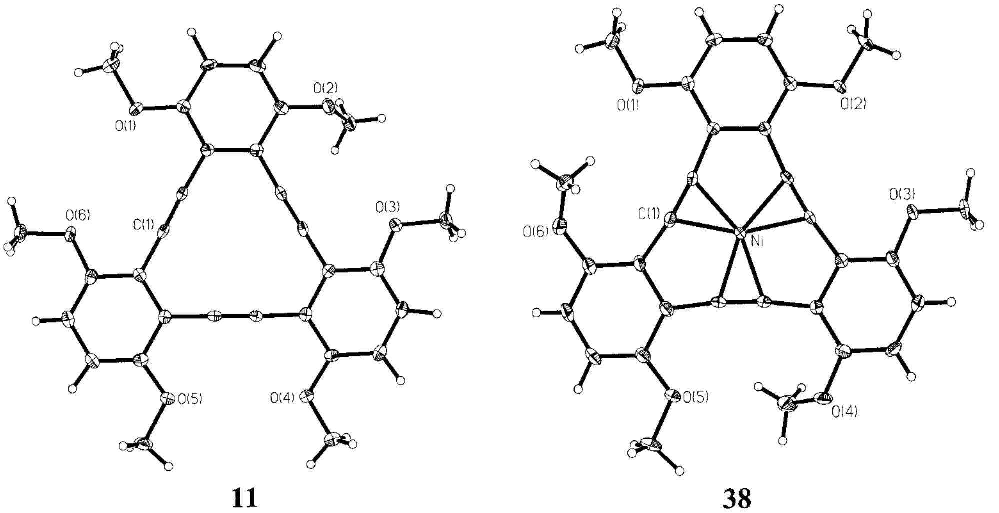
37

(19)

ligands are displaced by the ligand **2** to form a complex with the nickel atom coordinated to three alkynes in an η^2 fashion (average nickel to alkyne carbon distance of 1.958(5) Å) and located in the center of the planar cyclotriyne.

In **37** each alkyne is a 2e$^-$ donor and therefore **37** is a 16-electron complex. Evidence for this is provided by the small 6.2(9)° average distortions of the alkyne−carbon bonds from linearity, a small 16 ppm downfield shift of the alkyne ^{13}C NMR signal (93.6 to 109.6 ppm), and a shift to lower energy of the alkyne stretching frequency (2208 to 1955 cm^{-1} with weak stretches at 1963 and 1969 cm^{-1}).[80] Typical four electron donor alkynes exhibit $\nu_{C\equiv C}$ bond stretches from 1810 to 1772 cm^{-1} and greater distortion (32−61°) of the alkyne bonds from linearity.[81] Sometimes larger ^{13}C NMR chemical shifts are observed for 4e$^-$ donor alkynes;[82] however, a classic 4e$^-$ donor alkyne complex, [(COD)Ni]$_2$(μ-$C_6H_5C\equiv CC_6H_5$) also shows a relatively small (106.9 − 89.3 = 17.6 ppm) ^{13}C NMR chemical shift difference from the free alkyne resonance.[83] These data are consistent with limited back-donation of nickel electron density into the π* orbitals of the alkynes.[84]

Metallocyclyne **37** fits planarity and stacking requirements for a molecular metal.[85] Packing diagrams (Figure 8) show a slipped stack arrangement of molecules. Other compounds useful in the preparation of one-dimensional conductors show similar packing patterns: tetrathiolfulvalene (TTF), tetracyanoquinone (TCNQ), and unoxidized nickel phthalocyanine.[76,86] A view along the *b*-axis of **37** shows a herringbone pattern of molecules with an interplanar distance of 3.37 Å (Figure 8). These packing diagrams display the inherent stacking tendencies of complexes which contain planar **2**.



11 **38**

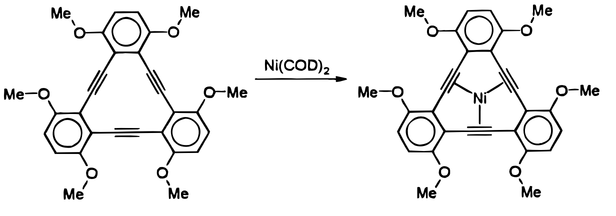
Figure 9. Thermal ellipsoid diagrams of **11** and **38** drawn at 50% probability.

The unsaturated and nonionic nature of **2** provides **37** sufficient redox activity to make reduction or oxidation possible. Oxidation with I_2 or using electrochemistry results in decomplexation after which free **2** is recovered. Cyclic voltammetry of **37** in THF shows two consecutive quasi-reversible waves at strongly reducing potentials which suggests consecutive formation of a monoanion and dianion.[87] The monoanion $\mathbf{37}^-$ and dianion $\mathbf{37}^{2-}$ are formed sequentially when **37** is reduced with lithium, sodium, or potassium. As with stoichiometric reductions of transition-metal alkene and alkyne complexes,[88,89] solvated complexes are produced in these solution phase reductions. Of the various combinations of alkali metals and sequestering agents examined, cryptand-(2.2.2) (C222) with potassium in THF gives the best yields of the dianion. As will be discussed later (section V), reaction of **2** with excess lithium gives cyclization. Sequential formation of the red-brown dianion from blue **37** occurs via formation of an intermediate purple monoanion. The uncomplicated EPR spectrum for the monoanion is consistent with a planar radical species.[90] The dianion is diamagnetic. EPR spectra of sodium doped **2** in dimethoxyethane show coupling of the lone electron spin with that of the benzo hydrogens as do spectra of the potassium-doped parent compound tribenzo[*a*,*e*,*i*]cyclododecene.[91]

By combination of **37** and $\mathbf{37}^{2-}$ in various ratios, an n-doped material has been obtained.[92] A two probe powder conductivity study of the resultant powders gave a conductivity of 2×10^{-3} $(\Omega\ \mathrm{cm})^{-1}$ at 0.5 e^-/**37** (1:3 ratio of $\mathbf{37}^{2-}$ to **37**). The insulator **37** becomes conducting upon partial reduction. Upon further reduction, conductivity again decreases. Similar reduction of transition metal-free **2** gives a conductivity of 8×10^{-5} $(\Omega\ \mathrm{cm})^{-1}$.

*III.A.2. Nickel Complexes of (Alkoxyphenyl)cyclynes **11** and **18A***

In a manner similar to that used for the synthesis of **37**, complex **38** was prepared from the reaction of **11** with $Ni(COD)_2$ (eq 20). Ligand **11** and its nickel complex **38** have been characterized by X-ray crystallography (Figure 9).[93] The alkyne carbons of **11** show a 20.06 ppm ^{13}C NMR downfield shift (93.73 to 113.79 ppm) and a bathochromic shift in the IR spectrum for the carbon−carbon triple bond stretch from 2211 to 1968 cm^{-1} on complexation with nickel. These shifts are comparable with those observed in going from **2** to **37**.



11 **38**

(20)

Complex **38** stacks in layers similar to graphite[94] with an interplanar distance of 3.4513 Å (Figure 10).

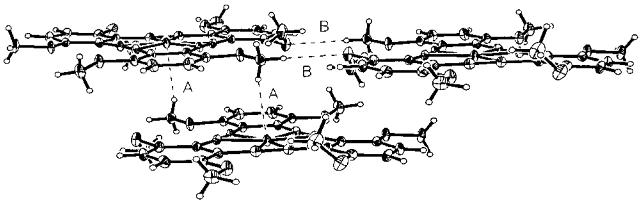
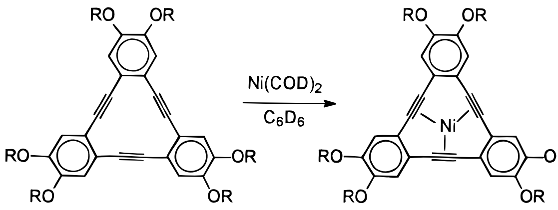


Figure 10. (A) Agostic and (B) hydrogen-bonding interactions of **38**.

This contrasts with the slipped stacked herringbone pattern of **37**. The structure of **37** has an intermolecular hydrogen-bonding interaction (C−H--O) and the first reported *inter*molecular agostic C−H--Ni interaction. M−H−C *inter*molecular agostic interactions have been suggested as intermediates in chemical reactions.[95] These interactions appear to be responsible for differences between the packing of **37** and **38**. All hydrogen atoms of the low-temperature structure of **38** were located in the electron density map and were refined isotropically.

Similarly to the Ni(0) complexes discussed above, complexation of **18a** results in the formation of **39** (eq 21).[46] This compound was synthesized as part of a project to make materials designed to be discotic metallomesogens based on a cyclotriyne core with



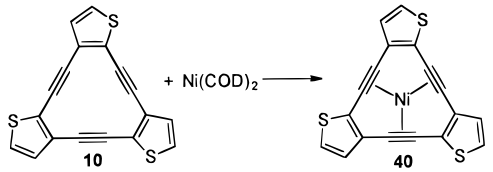
18a: R = $(CH_2)_9CH_3$ **39**: R = $(CH_2)_9CH_3$

(21)

alkyl side chain substituents. Compounds **18** and **39** did not show liquid crystal behavior.

III.A.3. Nickel Complex of Trithiophenecyclyne **10**

Substituting for benzo rings of **2** with 2,3-thiophene rings results in **10**. X-ray crystallography of **10** shows that the alkynes are more strained and that the cavity is slightly larger than those of **2**.[32] The nickel complex of **10**, **40**, has been synthesized (eq 22) and it is thermally less stable than **37**.[96]



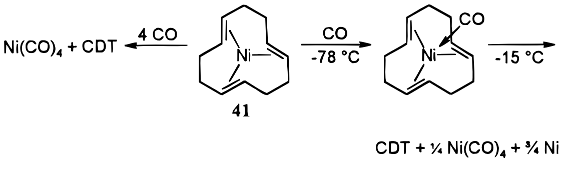
10 **40**

(22)

III.A.4. Reactivity of Ni(0) Metallocyclynes with Small Molecules

The reactivity of nickel cyclotriyne complexes with small molecules has been examined to see if there is a reactivity difference based on different substituents around the cyclotriyne pocket. Nickel metal on exposure to CO forms $Ni(CO)_4$[97] and is the only metal to react appreciably with CO at standard temperature and pressure.[98] In fact, exposure to CO is one way nickel catalysts are removed from reaction mixtures,[99] and nickel metal is purified.[100] Exposure of allyl and 1,3-butadiene complexes of Ni(0) to CO gives $Ni(CO)_4$ and dimerized and trimerized ligand coupling products.[101]

The reactivity of 16-electron tris(olefin) complexes such as Ni[η^6-(*E*,*E*,*E*)-CDT] (**41**) is associated with the vacant fourth coordination site, and therefore, similar behavior might be expected for **37**, **38**, and **40**.[99] Compound **41** reacts readily with CR_2N_2, CO,[102] CNR, PR_3,[103,104] and hydride sources. With PR_3 at room temperature and CO at low temperatures the reaction gives 1:1 addition products without decomplexing the three olefin moieties of the CDT ligand. However, in the case of the CO adduct, disproportionation and degradation of the complex occur at higher temperatures (eq 23).



41

(23)

The reactivity of **37** and **38** with small molecules has been examined.[92,93] A range of reactivities is observed with CO, O_2, $CDCl_3$, CH_3CN, H_2O, and CO_2. As with $Ni(COD)_2$, catalytic decomposition ensues on exposure of these complexes to $CDCl_3$.[105,106] However, **37** is unreactive with water as is **41**. Adduct formation is indicated with **37** and CH_3CN, while CO_2 effects no change on the complex. Preliminary evidence suggests **40** is more reactive toward O_2 than is **37** or **38**.[37b] In solution **37** and **38** react rapidly with O_2 and CO. In the solid state, **38** reacts very slowly with O_2, whereas it reacts very rapidly with CO. This suggests the possibility of using **38** or a derivative as a CO sensor based on the dramatic color change.[107] The chief drawback to such a venture is the notoriously poisonous reaction product $Ni(CO)_4$.[108] If a larger metal was inserted into the cyclotriyne cavity or if a cyclotriyne with a smaller cavity was combined with $Ni(COD)_2$, a more stable M(cyclotriynes) complex might be expected. Such experiments have shown that altering substituents on the periphery of the ring system greatly alters reaction chemistry at the central metal in the solid state. Reactivity differences between **37** and **38** toward small molecules in the solid state probably stem from differences in their solid-state packing arrangements.

III.A.5. Comparison with Other Ni(0) Alkyne Complexes

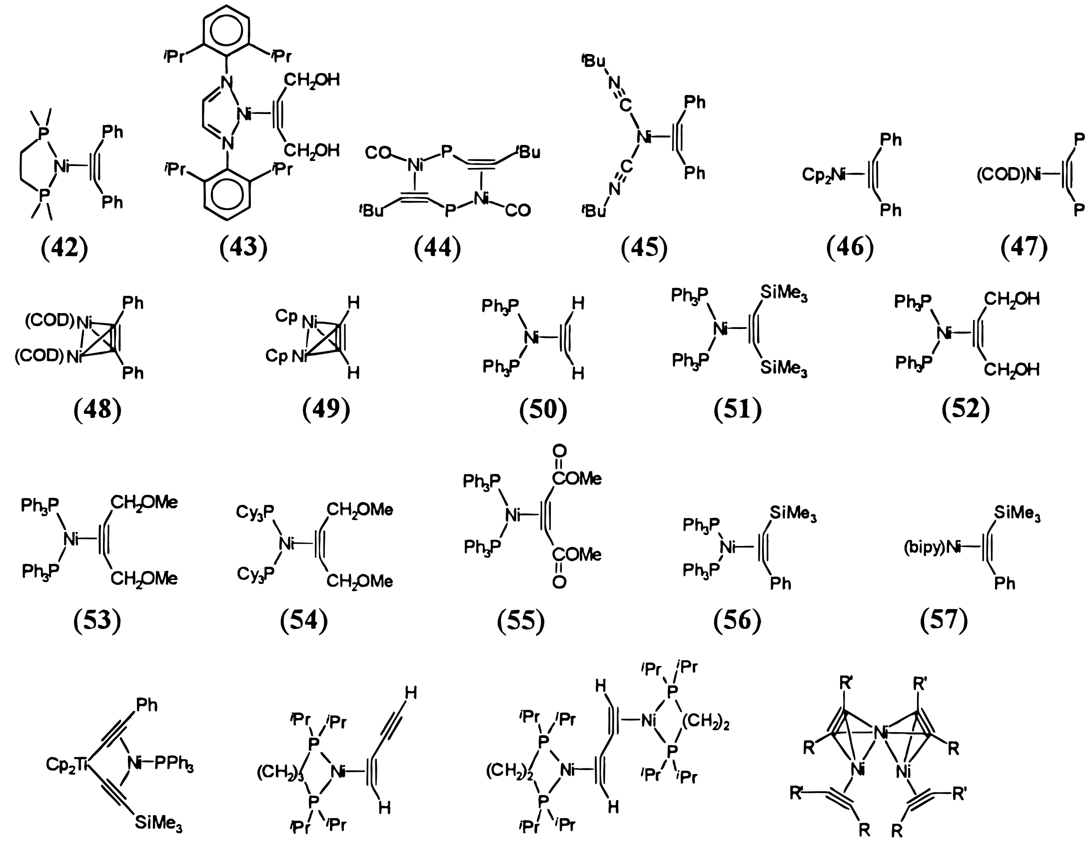
The bonding geometry displayed in **37**−**40** is unique when compared to other nickel alkyne complexes (**42**−**61**; see Chart 1). A comparison is given in Table 1 of the Ni−C(alkyne) and C≡C distances of **37**, **38**, and several representative nickel(0) alkyne complexes. Inspection of Table 1 reveals that **37** and **38** have comparatively long nickel alkyne bond distances and show far less distortion of the C≡C−C angles from linearity with respect to other Ni(0) alkyne complexes. This may be explained by the relatively rigid nature of the framework of **2**. Short C≡C bonds, slightly distorted C≡C−C angles, and

Table 1. Bond Lengths and Angles for Selected Nickel−Alkyne Complexes

compd[a]	Ni−C (Å)	C≡C (Å)	C≡C−C (deg)
37[80,92]	1.958(5)	1.240(10)	173.8(9)
38[93]	1.953(5)	1.242(5)	173.6(4)
42[109]	av 1.878(2)	1.290(3)	av 146.0(6)
43[110]	1.840(3)	1.273(7)	152.4(3)
44[111]	av 1.914(10)	1.280(14)	*b*
45[112]	av 1.899(19)	av 1.284(16)	148.6(14)
46[113]	av 1.89(1)	1.35(3)	av 140(3)
47[114]	av 1.880(2)	1.284(5)	av 149.4(13)
48[115]	av 1.927	1.386(11)	140.6(4)
49[116]	1.884(4)	1.341(6)	148.1(5)
50[117]	av 1.878(6)	1.239(4)	148(2)
51[118]	1.927(2)	1.256(2)	143.3(1)[c]
52[119]	1.834(7)	1.273(7)	141.4(12)
53[120]	av 1.897(1)	1.261(4)	av 148.1(15)
54[120,121]	av 1.903(6)	1.271(7)	av 136.9(28)
55[120,122]	av 1.863(21)	1.279(8)	144.7(7), 137.9(6)
56[123]	1.884(6), 1.926(6)	1.273(8)	138.7(5), 148.2(5)
57[124]	1.850(3), 1.890(3)	1.282(4)	145.1(3), 149.4(2)
58[125]	av 2.00(1), av 2.05(2)	av 1.253(4)	148.4(4), 134.1(3), 160.4(3), 165.2(3)
59[126]	1.876(6), 1.887(6)	1.279(9)	146.2(6), 177.9(7)
60[126]	av 1.881(35)	1.272(4)	149.4(3)
61[127] 2e donor	av 1.886(6)	av 1.255(6)	av 153.6(11)
4e donor	av 1.932(33)	av 1.322(2)	av 146.6(5)

[a] Structures shown in Chart 1. [b] Not reported. [c] C≡C−Si.

Chart 1. Compounds for Table 1



(42) (43) (44) (45) (46) (47)

(48) (49) (50) (51) (52)

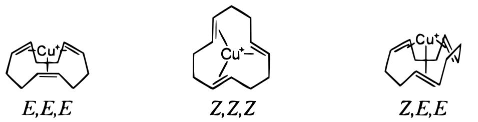
(53) (54) (55) (56) (57)

(58) (59) (60) (61)

comparatively long M−C(alkyne) distances of **37** and **38** are consistent with limited back-donation of nickel electron density into the π^* orbitals of the alkynes. The chelating effect of the three alkyne groups may compensate for any destabilization in the metal cyclotriyne complexes.

III.B. Copper(I) Complexes of Tribenzocyclyne 2

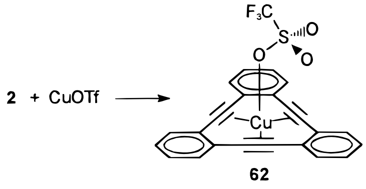
Copper(I) cationic complexes of cyclododeca-1,5,9-triene (CDT) ligands are isoelectronic with their nickel(0) counterparts.[128] In these complexes the triflate anion has been considered to be noncoordinating. Trifluoromethansulfonic acid (CF_3SO_3H) has been reported to be the strongest monobasic acid known.[129] Hence, copper(I) triflate has a better chance of forming isostructural counterparts of the nickel(0) complexes than copper(I) halides in which the halides are strongly coordinating and compete with carbon π systems for coordination sites.[128,130] Equivalent ^1H NMR chemical shifts of the vinyl hydrogens and a single stretching band in the IR suggest symmetrical structures for the *E*,*E*,*E* and *Z*,*Z*,*Z* complexes (Figure 11). A very small shift in the ^{13}C NMR resonances ($\Delta\delta = -5.1$ ppm) is observed for the vinyl carbons of the CDT ligands on formation of the complex $Cu^I[\eta^6$-(*E*,*E*,*E*)-CDT](OTf).



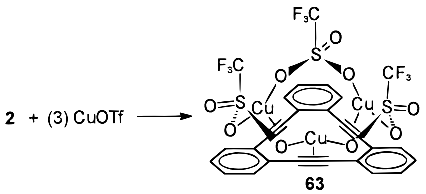
E,*E*,*E* *Z*,*Z*,*Z* *Z*,*E*,*E*

Figure 11. Copper(I) complexes of three configurations of cyclododeca-1,5,9-triene.

Depending on stoichiometry and reaction conditions, as shown in eqs 24 and 25, two different Cu(I) complexes have been obtained from reaction of $Cu_2(C_6H_6)(OTf)_2$ (OTf = OSO_2CF_3) with **2**. Complex **62** is synthesized by mixing saturated benzene solutions of $Cu_2(C_6H_6)(OTf)_2$ and **2** (molar ratio = 1:2).[131] Complex **63**, on the other hand, was initially obtained by a solution diffusion method.[132] Separate benzene solutions of $Cu(OTf)_2(C_6H_6)$ and **2** (molar ratio = 1:1) were placed in an H-tube and allowed to diffuse into each other over a 3-week period. Crystals were formed at the copper-rich end of the H-tube. Complex **63** can also be synthesized by heating benzene solutions of stoichiometric quantities of **62** with Cu_2-



(24)

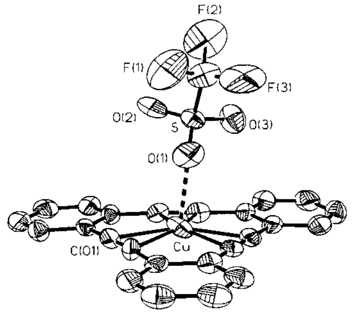


(25)

Table 2. Comparison of the Structures of Metallocyclyne Systems

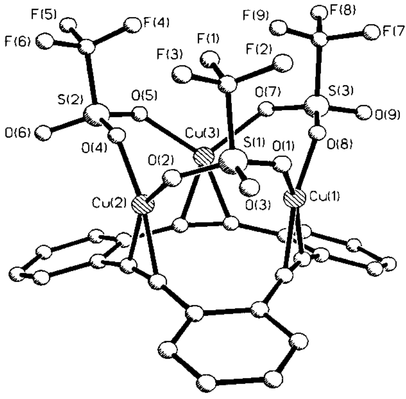
compd	M−C (Å)	C≡C (Å)	C≡C−C (deg)	M−plane (Å)[a]	$\nu_{C\equiv C}$ (cm^{-1})
37, Ni(**2**)	1.958(5)	1.240(10)	173.8(9)	0.0338(8)	1983, 1963
38, Ni(**10**)	1.953(5)	1.242(5)	173.6(4)	0.011(1)	1968
62, Cu(**2**)(OTf)	2.060(4)	1.222(10)	177.8(6)	0.1809(9)	2085
63, Cu_3(**2**)$(OTf)_3$	1.996(3)	1.237(8)	163.0(8)−166.0(8)	1.88(2)	2065
64, Co_4(**2**)$(CO)_9$	2.059(9), 1.965(9)	1.306(14)	144.9(5)−152.7(6)	0.6993, 1.737(13)	1865
66, Co_4(**3**)$(CO)_{12}$	1.976(11)	1.332(10), 1.194(7)	149.8(5), 171.3(17)[d]		2105, 1855
67, Co_4(**10**)$(CO)_{12}$	1.975(33)	1.333(10), 1.203(7)[d]	132.0(4), 145(2), 173(2)[d]		2096, 1856
68,$[Ag($**2**$)_2]^+$ staggered	2.74(4)	1.19(3)	177(2)	1.8071, 1.7650	2208, 2180
68, $[Ag($**2**$)_2]^+$ eclipsed,	2.47(2)−2.94(2)	1.17(3)	176(2)	1.7756, 1.7667	2208, 2180
Ag(**2**)BF_4					2208, 2180
69a, Ag(**29**)OTf	2.714(7)−2.863(7)		170.0(8)−174.1(8)		2155
69b, Ag(**29**)SbF_6	2.52(1)−3.05(2)		164(1)−170(1)		weak
70, Pt(**1**)$(PPh_3)_2$	2.02(4)−2.14(3)	1.35(5)	141(3)−147(3)		1771, 1744
1	1.44	1.200	155.8		
2	2.09[b]	1.202(3)	177.9(11)		2208
3	2.53[c]	1.197(4)	177.2(14)		2214
9	2.15[b]	1.194(6)[c]	175.9(3)		2203
10	2.07[b]	1.194(7)	177.8(8)		2211
29		1.203(4)			2251, 2173

[a] Rms deviation of metal from least-squares plane of ligand defined by the 6 alkyne carbons. [b] Average distance from the alkyne carbons to the centroid of the alkyne carbons. [c] Average distance from symmetry-related alkyne carbons. [d] Alkyne not coordinated to metal.



62

Figure 12. Crystal structure of **62** with thermal ellipsoids drawn at 50%. Hydrogen atoms are omitted for clarity.



63

Figure 13. Crystal structure of **63** with thermal ellipsoids isotropic. Hydrogen atoms are omitted for clarity.

(OTf)(C_6H_6) or by mixing $Cu_2(OTf)(C_6H_6)$ and **2** in methyl ethyl ketone followed by precipitation with benzene. The overall geometry of the copper(I) cavity complex **62** can be described as trigonal pyramidal with the Cu(I) ion coordinated to the three alkynes of **2** (average copper to alkyne carbon distance of 2.060(4) Å) and semicoordinated to the oxygen of the triflate anion (Cu(I)−O = 2.549(5) Å) (Figure 12). The trinuclear complex Cu_3(**2**)$(OTf)_3$ (**63**) can be described as a cofacial bimacrocycle. Three copper atoms and bidentate bridging triflates form a 12-membered macrocycle with "CuOSO" as the repeat unit. This copper macrocycle is bound to the alkynes of the ligand **2** via the copper atoms. The C≡C stretching frequencies for **62** and **63** are within 20 cm^{-1} of one another indicating the number of electrons donated by each alkyne in both complexes is very similar (see Table 2).[133] On this basis and from the distortions of the alkynes, each alkyne in both complexes acts as a $2e^-$ donor. The simplified bonding scheme for Cu_3(**2**)$(OTf)_3$, **63**, shown in eq 25 does not show the distortion of the ligand **2** from planarity found in the crystal structure (Figure 13). The benzo groups are bent an average of 19(3)° from the plane of the alkynes. Trifluoromethyl and benzo groups point away from their respective macrocycles. The "CuOSO" metallamacrocycle is distorted from 3-fold symmetry; however, Cu−C distances do not vary significantly from the mean 1.996(3) Å (range 1.991(8)−2.001(7) Å). The ^{1}H NMR spectrum of a mixture of **62** and **63** shows broad peaks between the chemical shifts for those species indicating an exchange process between the two.[39] This exchange process and the formation of **63** from polymeric $Cu_2(C_6H_6)(OTf)_2$ (solid-state structure[134]) suggests that the cyclyne **2** is acting as a template for three Cu(OTf) units.

III.C. Cobalt Complexes of Cyclynes

III.C.1. Cobalt Complexation of Tribenzocyclynes

On the basis of the hypothesis that **2** is acting as the template for the formation of the tricopper aggregate **63**, the use of this template effect to form clusters was investigated. When dicobalt octacarbonyl is combined with **2**, the cluster Co_4(**2**)$(CO)_9$ (**64**, Figure 14) is formed in high yield (eq 26).[135] Complex **64** contains a combination of the previously mentioned modes of coordination in that one of the cobalt atoms is in the cavity of **2**, coordinated to the three

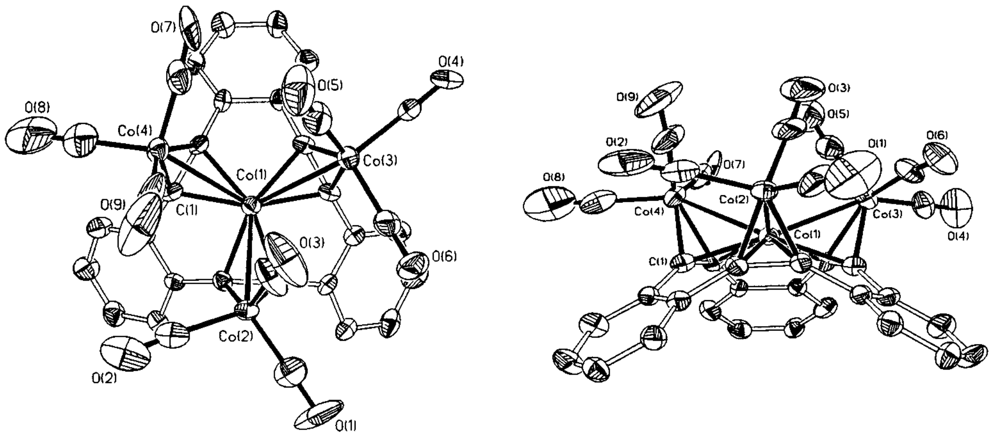
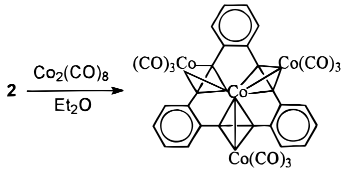


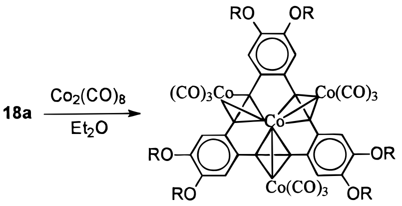
Figure 14. Two views of $Co_4(TBC)(CO)_9$, **64**, with thermal ellipsoids drawn at 30%. Hydrogen atoms are omitted for clarity.

alkynes as in **37**, and the other three cobalt atoms are each bound above an alkyne similar to **63**. In addition three Co−Co bonds exist in this unique cluster with the central cobalt bound to all three of the other cobalt atoms (Co−Co = 2.67−2.71 Å). These Co−Co bonds are slightly longer than those of dicobalt coordinated alkynes (2.46−2.52 Å).[136] In **64** each alkyne acts as a 4e$^-$ donor as evidenced by 144.9(5)−152.7(6)° acetylenic C≡C−C bond angles which are typical for dicobalt coordinated alkynes[137] and by the shift of the $\nu_{C\equiv C}$ stretch from 2217 to 1865 cm^{-1}.[37b] This is the only isolated tetranuclear transition-metal cluster with a 66 electron count. Reaction of $Co_2(CO)_8$ with **2** occurs at milder conditions than those required to convert $Co_2(CO)_8$ to $Co_4(CO)_{12}$. The cluster $Co_4(CO)_{12}$ is known to complex acetylene with loss of 2 CO ligands so that all four cobalt atoms are coordinated to the alkyne.[10b] Reaction of $Co_4(CO)_{12}$ with **2** gives a complex which is spectroscopically different by IR spectroscopy from **64**, although full characterization was not possible. These observations suggest **2** is indeed acting as a template for cluster formation. When **18a** is combined with dicobalt octacarbonyl, tetracobalt complex **65**, similar to **64**, is formed (eq 27).



64

(26)



65: R = $(CH_2)_9CH_3$

(27)

III.C.2. Cobalt Complexation of a Trithiophenecyclyne 10

Combination of **10** with dicobalt octacarbonyl results in the complexation of two of the three alkyne groups in a standard manner with dicobalt hexacarbonyl moieties to form complex **66**, even when dicobalt octacarbonyl is used in large excess (eq 28).[32] The X-ray structure of this complex (Figure 15) indicates that carbonyl ligands shield the remaining alkyne from complexation by additional dicobalt octacarbonyl. The IR spectrum of **66** shows a reduction in the C≡C stretch of both the complexed and uncomplexed alkynes (Table 2). We postulate that the resistance of **66** to lose carbon monoxide and rearrange to a structure with bonding similar to that of **64** stems from a net reduction in strain placed on the alkynes of free **10**. Complexation of two of the alkynes in **10** relieves the strain as has been observed in other strained alkyne complexes[138] but places the third alkyne out of effective range for intramolecular complexation by cobalt because of the larger pocket in **10** relative to **2**. There are indications that a complex of **2** similar to **66** is initially formed when **2** is combined with dicobalt octacarbonyl, but this compound readily converts to **64**. This may be due in part to the strain-free conformation of the alkynes in **2** which gives rise to closer proximity of the third alkyne relative to **10**. Attempts to trap such an

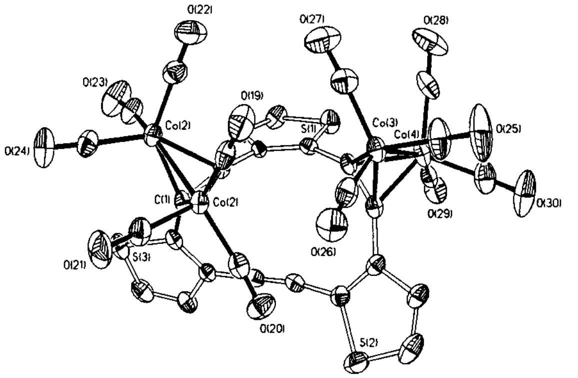
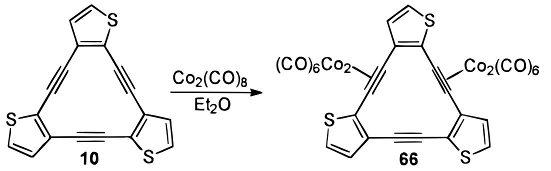


Figure 15. $Co_4(TTC)(CO)_{12}$, **66**, thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.



(28)

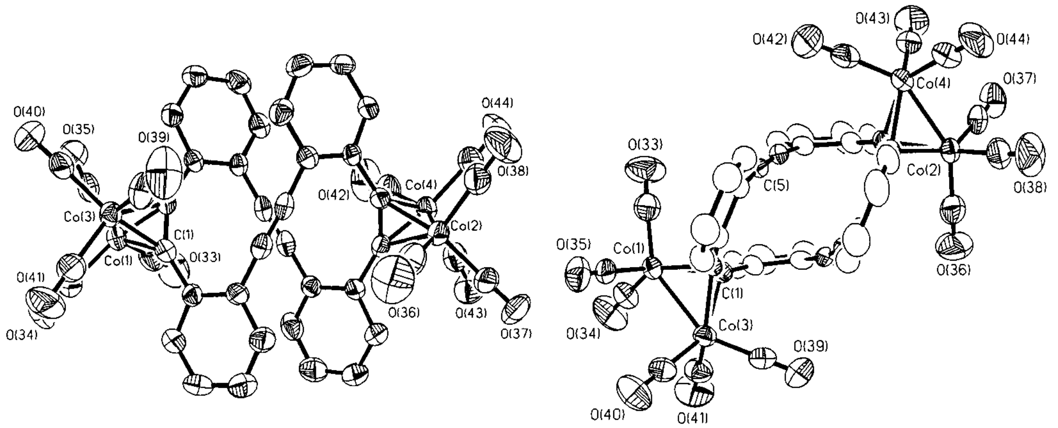
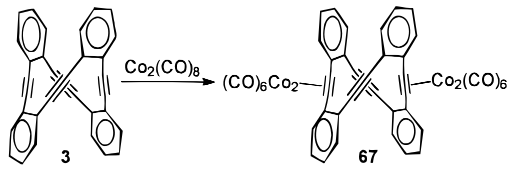


Figure 16. Thermal ellipsoid plots of **67** with thermal ellipsoids drawn at 50% probability. Hydrogens omitted for clarity.

intermediate with only two metal-complexed alkynes in the formation of **64** have thus far not been successful. Use of Me_3NO to decarbonylate **66** may lead to products similar to **64**.[139]

III.C.3. Cobalt Complexation of Tetrabenzocyclyne 3

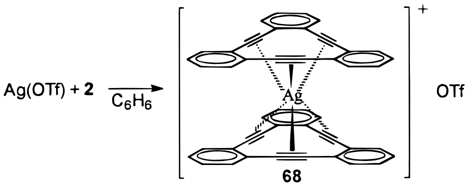
Reaction of **3** with dicobalt octacarbonyl produces **67**[64] (eq 29) in which two of the four alkynes are bound to $Co_2(CO)_6$ moieties in a normal fashion (Figure 16).[136,140] The other two alkynes of **3** cannot be coordinated to metals even when 4 equiv of $Co_2(CO)_8$ is used nor is any rearrangement observed. Shielding of unbound alkynes by $Co_2(CO)_6$ moieties and hindered rotation of these moieties into the pocket of **3** are possible explanations. Not only is there a reduction in strength of the coordinated alkyne but also of the uncoordinated alkyne shown by the 109 cm^{-1} shift of its stretching frequency (Table 2). Complexation of alternate alkynes reduces the volume of the central pocket and draws the two uncomplexed alkynes toward one another.



(29)

III.D. Silver(I) Complexes of 2 and 29

Known silver(I) to π-alkyne carbon bond lengths (2.27(1)−3.10(3) Å)[141] are too long to allow coordination of silver(I) within the cavity of **2** (2.08 Å). Consistent with this expectation, the unprecedented silver sandwich complex **68** is formed when **2** and Ag(OTf) are combined in benzene (eq 30). The isolated crystals of **68** also contain the free ligand **2** and hexane. Solution NMR of the crystals in toluene-d_8 shows no shift of the ^{1}H resonances from those of **2**, indicating either dissociation or rapid exchange processes are taking place. The IR spectrum shows two $\nu_{C\equiv C}$ bands at 2208 and 2180 cm^{-1} corresponding to free and complexed **2**. The band at 2180 cm^{-1} is higher in energy than is found for most 2e$^-$ donor alkyne complexes and is consistent with a very weak interaction.



(30)

The crystal structure of **68** shows segregated chains of stacked sandwiches parallel to the 2_1 axis. In contrast to the copper(I) complexes **62** and **63**, the triflate anions of **68** are noncoordinating and are found in the channels separating the stacks of sandwiches.[142] Free ligand **2** and hexane are also present in channels so that they and the triflate anions, in effect, segregate the stacked chains of sandwiches. Both staggered and eclipsed conformations of the sandwich are present in the asymmetric unit and they show significant distortions from ideal D_{3d} and D_{3h} symmetries (Figure 17). Each silver cation is weakly coordinated to all six alkynes; however, the eclipsed $[Ag(\mathbf{2})_2{}^+]$ sandwich of **68** has a broader range of Ag−C distances (2.47(2)−2.94(2) Å) than does the staggered sandwich (2.67(2)−2.81(2) Å). In the eclipsed sandwich the silver is bound more tightly to four of the six alkynes. This suggests a bonding scheme in which each of four alkynes contributes two electrons and two alkynes remain largely noninteracting to give an 18e$^-$ complex. The more symmetric structure of the staggered sandwich suggests an alternative bonding scheme in which all alkynes contribute equally. To obtain an 18 electron count, a net 1.333 electrons is donated by each alkyne.[143] Precedence for nonintegral electron donation by alkyne ligands can be found in the group theoretical analysis of the complex $(OC)W(R{-}C{\equiv}C{-}R)_3$.[144] Alternatively, both eclipsed and staggered conformations can be viewed as electrostatic interactions of the silver cation with two molecules of **2**.

In the crystal structure of **68**, sandwiches are stacked metal over metal with alternating eclipsed and staggered forms. Each of the ligands **2** of the staggered sandwiches is eclipsed with but translated away from the neighboring eclipsed sandwich (Figure 18). This gives an alternating step function (2_1 axis) having a periodicity of two sets of four approximately eclipsed ligands **2** with nodes at the staggered sandwich's silver atoms. It should be made clear that the silver atoms do not reside on the 2_1 axis; however,

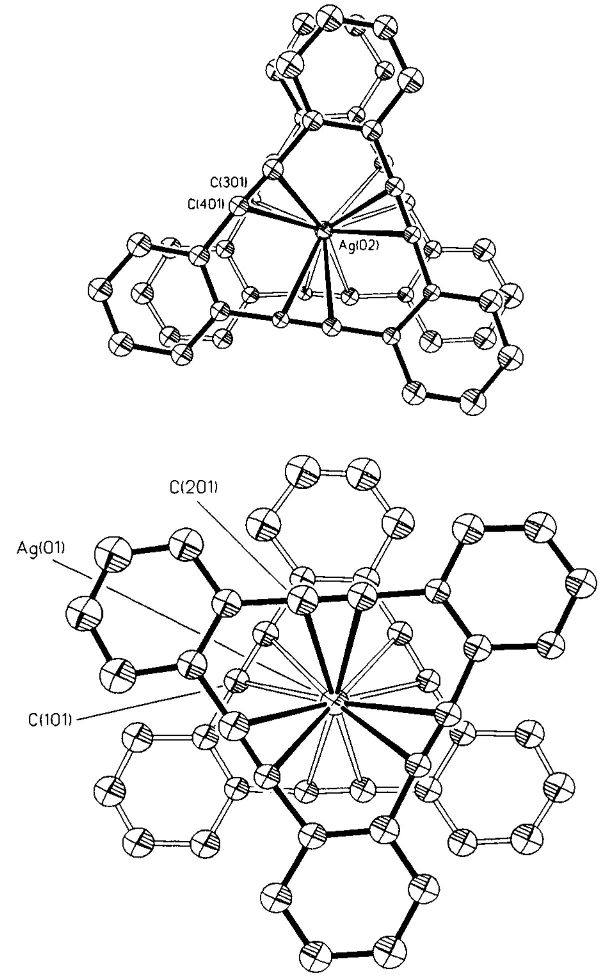


Figure 17. Eclipsed and staggered Ag$^+$(**2**)$_2$ cations of **68**. Thermal ellipsoids are drawn at 20% probability.

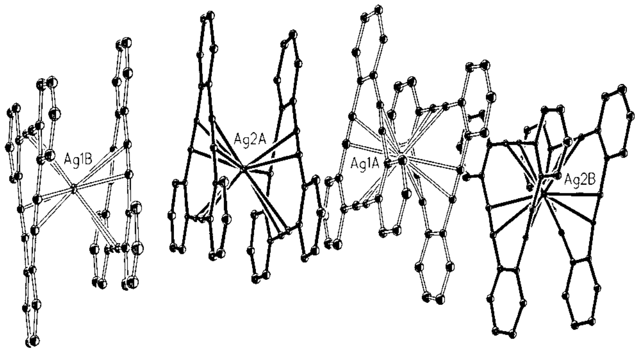


Figure 18. Stacking arrangement of the Ag$^+$(**2**)$_2$ moieties in **68**. Staggered configurations are drawn with hollow bonds.

the 2_1 symmetry operator generates the outermost molecules of Figure 18. The four unique interligand spacings range from 3.45(1) to 3.58(1) Å.

The reaction of AgBF$_4$ with **2** has been examined.[145] Due to low solubility ^{1}H NMR of the crystalline product was not possible in toluene-d_8, and in acetone-d_6 the silver ion was coordinated to acetone. The IR spectrum of the AgBF$_4$ complex again shows stretches for complexed alkyne (2180 cm^{-1}) and free **2** (2208 cm^{-1}). Crystals of this compound were grown; however, solution of the X-ray diffraction data was not possible.

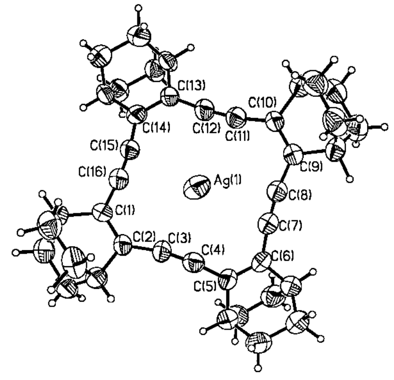
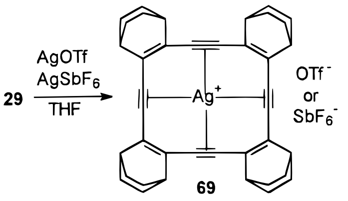


Figure 19. Ag$^+$(**29**) cation of **69**.

Komatsu has reported the reaction of **29** with Ag(OTf) and Ag(SbF$_6$) in THF to form the silver cyclyne complexes **69a**,**b**, respectively (eq 31).[146] This clearly

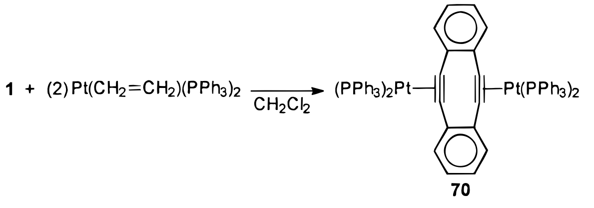


(31)

demonstrates that tetradehydro[16]annulene ligands have a suitable cavity size for the incorporation of second and third row metals. The Ag–C(alkyne) bond distances in **69a**, 2.714(7)–2.863(7) Å, and **69b**, 2.52(1)–3.05(2) Å, are comparable to those observed in **68**, 2.47(2)–2.94(2) Å, indicating very weak Ag–C(alkyne) bonding interactions (Figure 19). Both the IR and ^{13}C NMR spectra are also indicative of weak Ag–C(alkyne) interactions. In the IR the C≡C stretching band was observed at 2155 cm^{-1} for **69a**, relative to 2251 and 2173 cm^{-1}for **29**. The alkyne carbons of **69a** show very small shifts in the ^{13}C NMR from that of the free ligand **29**. In **69a**,**b** the counteranions have short distances to the silver cation (2.31(1) and 2.67(1) Å), relative to **68** in which the counteranion is not coordinated.

III.E. Platinum Complexes

As noted above, the pocket of **1** is much too small to accommodate a transition metal in the plane of the ring. Metal complexation to the alkynes with the metal exterior to the pocket has been reported.[147] Reaction of **1** with Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$ or Pt(PPh$_3$)$_4$ gives **70** (eq 32). This complex has been crystallallographically characterized (see Table 2).



(32)

III.F. Conclusions Drawn from Solution Complexation

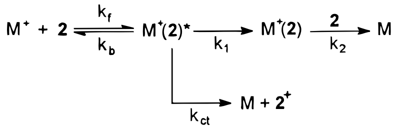
Interaction of **2** with three or more metal moieties as in complexes Cu$_3$(**2**)(OTf)$_3$, **63**, and Co$_4$(**2**)(CO)$_9$, **64**, results in far more severe distortions of the bond angles at the alkyne carbons than in the cavity complexes Ni(**2**), **37**, Ni(**11**), **38**, and Cu(**2**)(OTf), **62**, or in the sandwich complex **68**. Of the latter four complexes, statistically significant distortions of C≡C−C angles from the mean value in free **2** (177(1)°) occur only in **37** (173.8(9)°). Bond angles with alkyne carbon vertexes in Co_4(**2**)$(CO)_9$, **64**, range from 144.9(5) to 152.7(6)° and in Cu_3(**2**)$(OTf)_3$, **63**, from 163.0(8) to 166.0(8)° demonstrating the difference between $4e^-$ and $2e^-$ donor alkynes, respectively. Distortions from linearity of the C≡C−C angles in **37**, **38**, **62**, and **68** are smaller than those observed in most other metal alkyne complexes.[10] A higher IR stretching frequency of the C≡C correlates well with a greater C≡C−C bond angle.

A comparison is presented in Table 2 of C≡C stretching frequencies and bond distances and C≡C−C bond angles for transition metal complexes of cyclynes. Bonding geometry of the nickel atom and alkyne carbons in **38** is virtually identical to that of **37**.[80,92,93] Average Ni−C(alkyne) distances are 1.955(3) Å for **38** and 1.958(5) Å for **37**, which are considerably shorter than the Cu−C distance of 2.060 Å for **62**. The average C≡C−C angles are 173.6(4)° for **38** and 173.8(9)° for **37**, which are significantly greater than the distortion of 177.8(6)° observed for **62**. Nickel atoms are essentially in the planes described by the six alkyne carbons of both **37** and **38**, while the copper atom is slightly above the plane of the alkyne carbons in **62**.

IV. Gas-Phase Complexation of Tribenzocyclyne 2

Studies of gas-phase complexation of cyclynes with transition-metal and main-group ions have provided chemical bonding information free from solvent and packing force effects and serve as a valuable guide to possible synthetic targets. Using laser desorption ionization, an ion cyclotron resonance (ICR) spectrometer's ion trap is filled with metal ions M^+, while simultaneously a background pressure of neutral **2** is maintained in the cell using thermal desorption from a solid probe.[143,148] This technique allows for the formation of exclusively monometallic complexes due to high repulsive energies involved in bringing two or more M^+ into close vicinity. A mechanism for the radiative association consists of two steps with rates k_1 and k_2 (Scheme 4). The ICR technique does not provide structural information; however, on the basis of solution and solid-state results, M^+(**2**) for larger metals would have an open-face sandwich structure while smaller metal ions would fit within the alkyne pocket. Presumably the M^+(**2**)$_2$ ion is a sandwich compound with the metal ion sandwiched between two **2** ligands as in **68**. For those metal ions small enough to fit within the cavity of **2**, the rate of complexation of another neutral **2** (k_2) should be reduced, as has been observed by Dearden's group in studies of alkali metal ions with crown ether molecules.[149] Charge transfer from M^+ to **2** in the unstabilized collision complex M^+(**2**)* competes with formation of M^+(**2**) (Scheme 4). It is expected that the sum of $k_1 + k_{ct} + k_b$ equals the orbiting collision rate in the ICR spectrometer. However, reaction efficiency ($k_1 + k_{ct}$) is usually much less than unity indicating the rate of unproductive, orbiting collisions (k_b) is significant. A conceptual argument for surprisingly slow or nonexistent charge-transfer reactions in cases of exothermic charge transfers is given by Dunbar.[150]

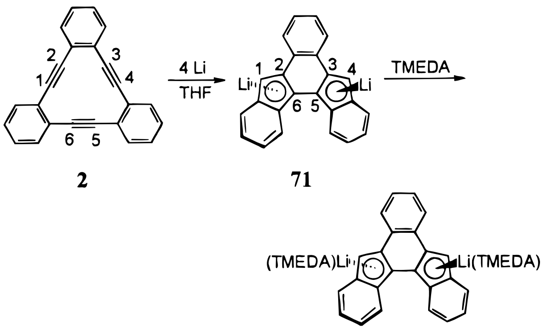
Scheme 4



The reaction chemistry depicted in Scheme 4 is unusual with respect to other gas-phase organometallic chemistry[148b] because **2** remains intact in the complex without loss of neutrals.[143] This result indicates considerable stability of the ligand **2**. M^+(**2**) is formed for most of the 22 ions surveyed[151] with the exceptions of Cs^+, which is unreactive, and Au^+ and Zn^+, for which exothermic charge-transfer reactions dominated. The M^+(**2**)$_2$ complex is formed readily with similar rates for all first-row transition metals through Mn^+, which is the 18-electron system (assuming each alkyne of **2** donates two electrons). For Fe^+, which gives the 19-electron system, the rate of formation is lower. While for Co^+, Ni^+ and Cu^+, only the M^+(**2**) complex is formed having 16, 17, and 18 electron counts, respectively. This is consistent with these metals being within the pocket of **2**. Both M^+(**2**) and M^+(**2**)$_2$ complexes are readily formed for most ions with the exceptions of those late transition metals able to fit within the pocket of **2** and some ions which have poor affinity for **2**: K^+, Al^+, and Pb^+. These gas-phase results are consistent with compounds synthesized and characterized in solution and the solid state (vide infra). The gas-phase chemistry of cyclynes with different pocket sizes should be examined. Larger pockets may be able to form stable monomeric complexes with larger transition metals than those found with **2**.

V. Lithium-Induced Cyclization of Cyclynes

The investigation of the interaction of alkali metals with cyclyne ligands has resulted in an unprecedented lithium-induced cyclization reaction of **2** to form a novel helicene dianion **71**. A 95% yield of the TMEDA solvate of the dianion **71** is obtained from the four-electron reduction of **2** (eq 33).



(33)

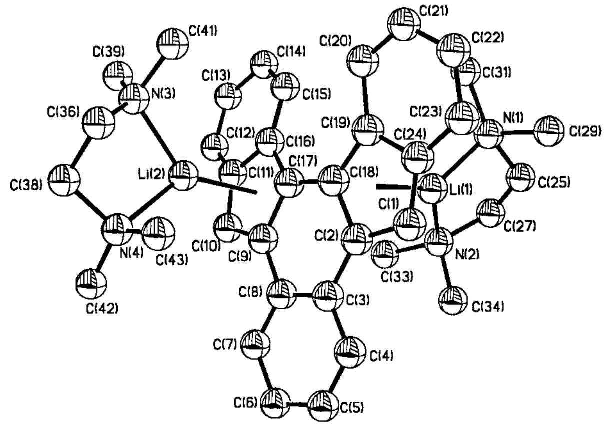


Figure 20. Thermal ellipsoid plot of the TMEDA adduct of **71** with isotropic thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity.

The X-ray crystal structure[152] of the tetramethylethylenediamine (TMEDA) solvate of **71** shows the two helical enantiomorphs cocrystallize (Figure 20). The helical axis passes through the center of the cleft created by the *ortho*-annulated series of 6-, 5-, 6-, 5-, and 6-membered rings. The cyclopentadienyl rings are each π-bound to a lithium cation which is in turn chelated by TMEDA. The two lithium atoms are on opposite sides of the molecule. Deuterium incorporation at carbons 1 and 4 when lithium-induced cyclization is run in THF-d_8 indicates that THF is the proton source for the reaction.

Tetramer **3** and hexamer **4** also undergo lithium-induced cyclization, although only the products of the former have been fully characterized.[153,154] The mechanism for lithium-induced cyclization of cyclynes given in Scheme 5 is consistent with dimerization of lithium-generated radical anions.[155] Propagation to form intermediates **b** and **c** in Scheme 5 is similar to thermally induced "diagonal" Bergman reactions.[156] It is uncertain when protonation takes place. Reaction products of the cyclization of **3** consist of a *d*,*l*-pair of diastereomers, **72a**+**b**, and a meso compound, **72c** (Figure 21). Solid-state structures of these reaction products suggest a correlation between the stereogenic centers and the adjacent helical axis: *S* centers are associated with *P* helical axes and *R* with *M*.

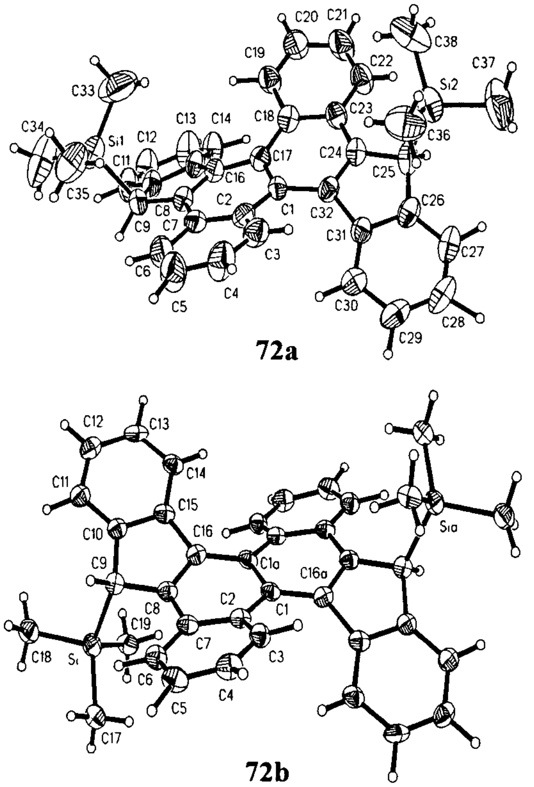


Figure 21. Thermal ellipsoid plots of one of the *d*,*l*-pair **72a** (*S*,*P*,*S*,*P* shown and *R*,*M*,*R*,*M*) and the meso compound **72b** (*R*,*M*,*S*,*P*) drawn at 50% probability.

VI. Heterocyclynes

Cyclynes with different pocket sizes can be constructed with main-group or transition-metal atoms replacing the benzo rings. In this section the heterocyclynes of silicon, germanium, phosphorus, titanium, and platinum are described. Of these, the chemistry of the silicon and platinum heterocyclynes is best developed. Crystallographic data for heterocyclynes are listed in Table 3.

VI.A. Main-Group Heterocyclynes

VI.A.1. Group 14

Cyclosilethynes have been reviewed recently[157] but, because of the importance of this chemistry to the developing chemistry of the heterocyclynes described below, several examples (**73**–**76**) are included here. Particular emphasis is placed on cyclosilethynes that

Scheme 5

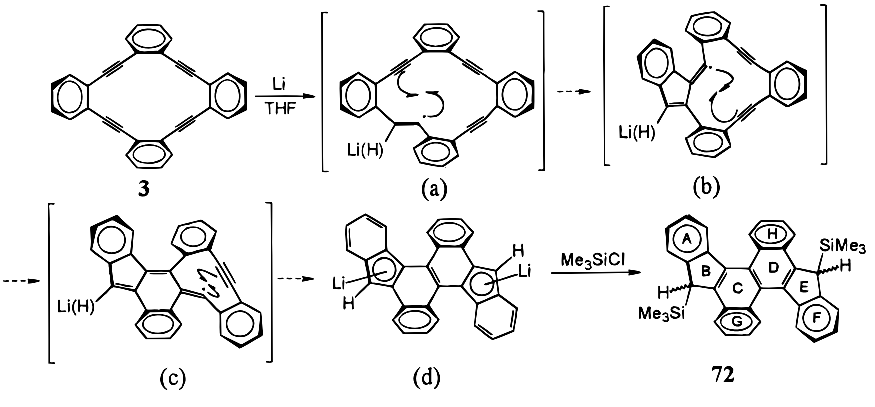


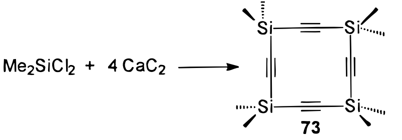
Table 3. Comparison of the Structures of Selected Heterocyclynes (E = Hetereoatom, M = Centroid of Ring or Metal Complexed to Alkyne)

compd	E−M (Å)	E−C (Å)	M−C (Å)	C≡C (Å)	C≡C−C (deg)	C≡C−E (deg)	ring C−E−C (deg)
79a	2.655[a]	1.823(5)	2.067[a]	1.211(7)	175.3(5)	163.2(4)	100.1(2)
79b	2.615[a]	1.822(3)	2.068[a]	1.207(4)	174.6(3)	163.0(3)	101.6(1)
79c	2.684[a]	1.899(3)	2.090[a]	1.205(4)	175.6(3)	162.1(3)	100.6(1)
80a	2.548(1)	1.847(3)	2.017(3)	1.254(5)	169.5(3)	151.3(3)	105.4(1)
80b	2.509(2)	1.840(5)	2.014(5)	1.252(6)	169.1(5)	149.9(4)	107.0(2)
80c	2.592(1)	1.931(4)	2.032(4)	1.245(6)	167.4(5)	148.6(4)	105.1(2)
81		1.865(8)	1.993(8)	1.34(1)	147.0(7)	152.4(6)	114.9(3)
82		1.887(6)		1.199(7)	177.4(6)	160.0(5)	100.8(2)
83		1.92(3)	1.97(2)	1.37(2)	143(2)	145(2)	
84		1.828(6)		1.204(7)	178.2(6)	174.5(5)	
89a	2.774(1)	2.075(3)	2.020(2)	1.251(4)	172.0(3)	159.1(2)	92.4(1)
90a		1.977(8)		1.20(1)	171.9(9)	172.9(7)	84.4(3)
90b		1.992(9)		1.20(1)	176.2(9)	172.3(8)	82.9(3)
90c		2.01(2)		1.20(2)	175(2)	172(2)	82.8(2)
90d		1.994(3)		1.197(4)	175.8(3)	170.6(3)	82.8(2)

[a] Average distance from the alkyne carbons to the centroid of the alkyne carbons.

might be expected to form coordination compounds with transition metals.

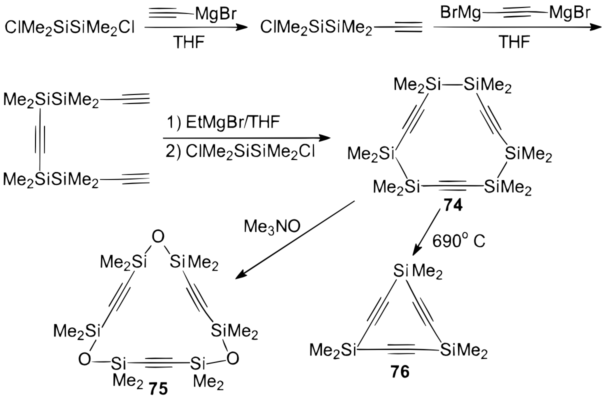
Octamethylcyclotetrasilethyne, **73**, was synthesized by Voronkov and Pavlov[158] by the reaction of dichlorodimethylsilane with calcium carbide (eq 34). The homologous series $(Me_2SiC{\equiv}C)_n$, $n = 4-10$, has been reported.[159,160]



(34)

Compound **74** was synthesized by the use of Grignard reagents as outlined in Scheme 6.[161] Treatment of **74** with NMe_3O gave **75**. Thermolysis of **74** gave **76** in relatively high yield.

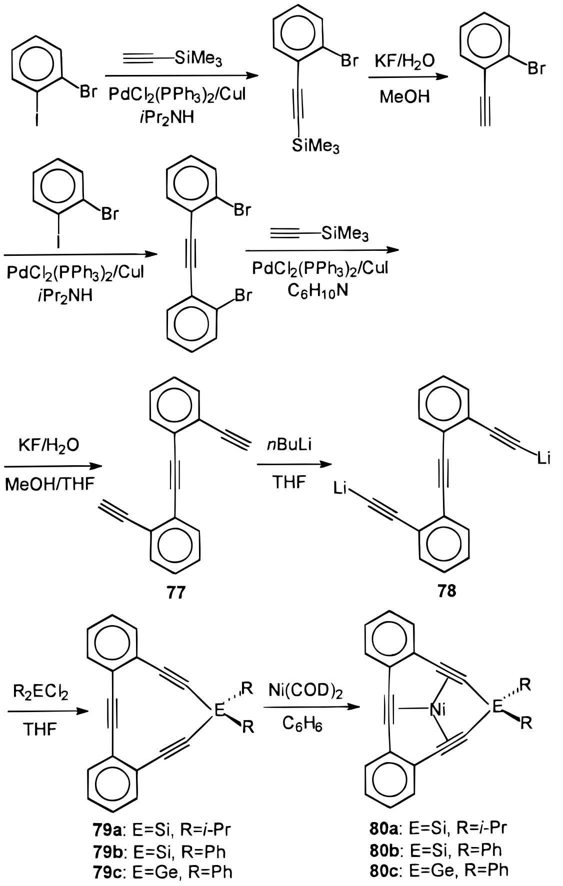
Scheme 6



Simple coordination chemistry of **73**−**76** has not been described. The pocket of **73**−**75** should be large enough to encapsulate a variety of transition metal moieties. The pocket of **76** is smaller, and therefore, it might form half-sandwich or sandwich complexes with metals. Treatment of metal carbonyls with **74**−**76** or related compounds results in cyclization reactions and, in some cases, complexation of metal carbonyl moieties to the resultant alkenes or arenes. This chemistry has also been reviewed.[157,162] Hyperconjugation between silicon and adjacent π-systems is a common phenomenon,[163] and this factor is probably responsible for the rearrangement, rather than coordination, chemistry observed with metal carbonyls. Silicon−silicon bonds can also interact with π-systems. Photoelectron spectroscopy and molecular orbital studies indicate that such an interaction in **74** destabilizes the π-system.[164] Such a destabilization would clearly affect the coordination chemistry. Also, the complexation of Si−Si bonds to metal centers has been proposed.[165] These various factors suggest a very rich coordination chemistry of **73**−**76** is possible.

The formation of a series of silicon and germanium heterocyclynes has been reported (Scheme 7).[166]

Scheme 7



Reaction of 2,2′-diethynyltolane, **77**, with *n*-butyllithium in THF at room-temperature resulted in immediate formation of the deep red dilithium dianion **78**. As will be shown, compounds **77** and **78** are the precursors to many of the heterocyclynes described herein. To avoid the formation of oligomers and polymers, the colorless heterocyclynes **79a**−**c** were prepared by adding very dilute solutions (0.002 M) of the ER_2Cl_2 (E = Si, Ge) reagent to **78**. Higher yields and milder reaction conditions were noted in the synthesis of the germaniun cyclyne **79c** relative to the silicon cyclynes. Reactions of **79a**−**c** with $Ni(COD)_2$ gave deep red complexes **80a**−**c** in very high yields.

Signals in the ^1H NMR spectra of complex **80a**,**b** are shifted downfield from the resonances in the spectra of the free ligands. Similar results were observed for **37** relative to **2**.[7] Except for the signal for the alkyne carbons α to the silicon atom, the ^{13}C NMR signals of **80a**−**c** are shifted downfield relative to those of **79a**−**c**. The α-carbon resonance shifts upfield from 96.9 ppm in the free ligand **79b** to 73.8 ppm in **80b** indicating the coordination of Ni(0) strongly shields the alkyne carbons adjacent to the silicon. These resonances could only be assigned by using ^1H-coupled ^{13}C NMR experiments. A $^1H\{^{29}Si\}$-HMBC NMR experiment[167] showed an upfield shift when **79b** (−45.0 ppm) was complexed to nickel(0) to give **80b** (−52.4 ppm). The IR spectra of the ligand **79b** exhibits one strong band at 2153 cm^{-1} for the acetylenic stretch whereas the nickel complex **80b** shows strong and weak bands at 1996 and 1922 cm^{-1}, respectively.

The free ligands **79a**−**c** are air and thermally stable. A THF solution of **80b** reacts with air to form the free ligand within 5 min. Decomposition to the free ligand is also observed within 2 min when CO is bubbled into an air-free THF solution of **80b**. These reactions are more rapid than those of **37**. However, solid **80b** does not react with CO or air even after being exposed to either for 1 year.

The X-ray structures of compounds **79a**,**b** and **80a**,**b** have been obtained, and the structures of **79c** and **80c** are shown in Figure 22 with relevant bond distances and angles presented in Table 3. An interesting feature of these crystal structures is that the ligands **79a**−**c** and their respective nickel complexes **80a**−**c** possess isomorphous structures. Also, the four diphenyl-substituted compounds **79b**,**c** and **80b**,**c** are isomorphous. This is not the case with the ligands **2** and **10** and their respective nickel complexes **37** and **38** where the packing of **2**, **10**, **37**, and **38** is probably largely controlled by $\pi-\pi$ interactions. Though **79a**−**c** and **80a**−**c** also possess a planar pocket and π-system (the group 14 atom and C1−C10), $\pi-\pi$ interactions would be disrupted by the isopropyl or phenyl substituents on the group 14 atom.

The data in Table 3 show that the sizes of the cavities of the ligands **79a**−**c** are comparable to those of **2** and **10**. The cavities of the nickel complexes **80a**−**c** are smaller than those of the ligands **79a**−**c**. Free ligands **79a**−**c** appear to have pockets slightly smaller than **2**, whereas their corresponding complexes, **80a**−**c**, have significantly larger pockets than **37**. In the free ligands **79a**−**c** the substituents on the alkynes adjacent to the group 14 atom are held in a "cis" configuration whereas in **80a**−**c** they are held in a "trans" configuration. Like the alkynes between the benzo rings of **80a**−**c**, "cis" configurations are observed for all the alkynes in the nickel complexes **37** and **38**. The coordination of a nickel atom into the trialkyne pockets of **79a**−**c** enlarges the ring C1−E−C10 (E = Si or Ge) angles by about 5°. Significantly longer silicon and germanium alkyne carbon bond lengths are found in **80a**−**c** relative to those in **79a**−**c**. However in both the complexes and in the free ligands, E−C distances show the shortening expected for E−C(sp) as compared to E−C(sp^3).[168] In **80a**−**c** relatively short Ni−E separations were observed; however, definitive evidence for a dative Ni→E interaction was not obtained.

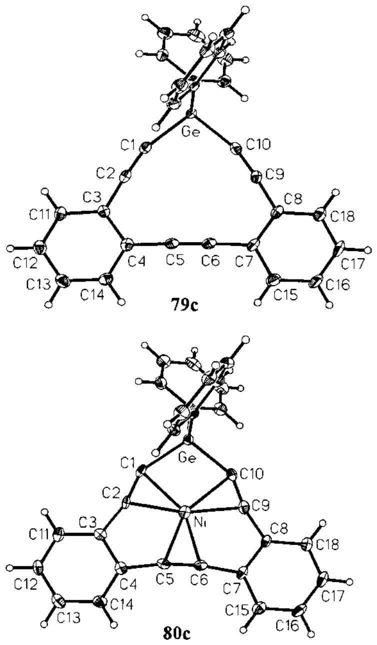
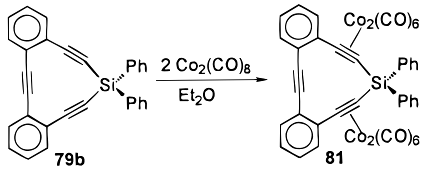


Figure 22. Thermal ellipsoid plots of **79c** and **80c** with thermal ellipsoids drawn at the 50% probability level.

The reaction of 2 molar equiv of $Co_2(CO)_8$ with **79b** in diethyl ether proceeds cleanly and completely to give the deep red complex **81** (eq 35).[169] No complexation of the third alkyne of **79b** is observed when excess $Co_2(CO)_8$ is used.



(35)

As shown by its crystal structure (Figure 23 and Table 3), **81** is an analogue of **66** and not **64**. The cobalt carbonyl moieties selectively coordinate to the alkynes adjacent to the silicon heteroatom, even though there are two bulky phenyl groups on this atom. The fact that the alkynes adjacent to the silicon atom in **79b** are bent and thereby strained may be responsible for the selectivity. The inner C1−Si−C10 bond angles expands from 101.6(1)° in **79b** to 114.9(3)° in **81**. The lengthening observed upon complexation of the C≡C alkyne bonds in **81** is comparable to the lengthening observed in **66**, and Co−Co bond

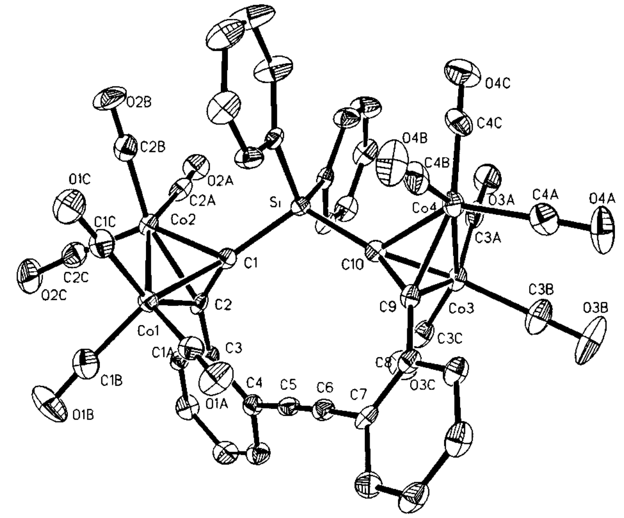
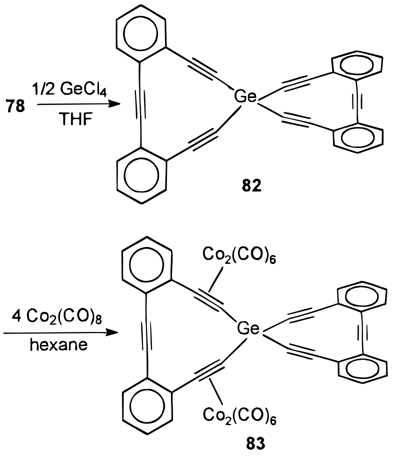


Figure 23. Molecular structure of **81** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

lengths are similar in the two complexes.[32] The ligand **79b** is severely distorted in the complex **81**.

Addition of germanium tetrachloride to **78** in a 1:2 molar ratio resulted in the formation of the spiro compound **82** in 64% yield (Scheme 8).[169] The structure of **82** (Figure 24) shows that the tetrahedral germanium atom forces the two rings to be roughly perpendicular to one another with a skew angle of 98.6°. The distances and angles for the rings of **82** are very similar to those of **79a**−**c**.

Scheme 8



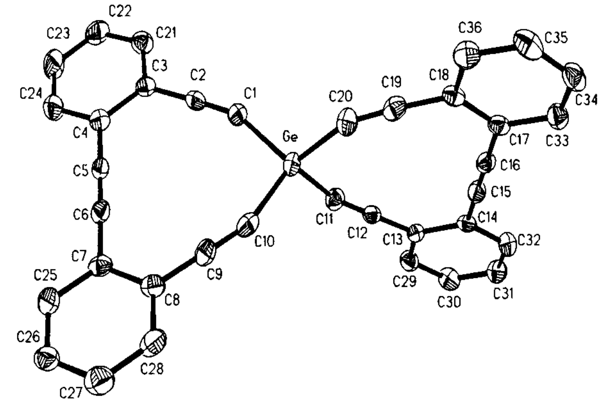


Figure 24. Molecular structure of **82** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

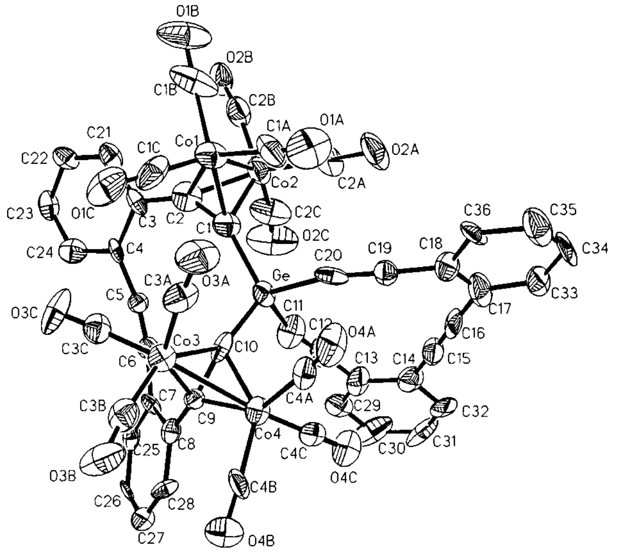


Figure 25. Molecular structure of **83** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

The reaction of **82** with $Co_2(CO)_8$ in a 1:4 ratio gave the single product **83** in 80% yield (Scheme 8). Even under more forcing conditions the other alkynes of **82** did not react. Complex **83** shows appreciable solubility in hexane whereas **82** is virtually insoluble. A similar increase in the solubility of the cobalt complexes **66**, **67**, and **81** with respect to their free ligands was also observed.[32,64,169] The crystal structure of **83** (Figure 25) showed that only two alkynes adjacent to the germanium atom and within the same ring were complexed to dicobalt hexacarbonyl moieties. The two alkynes adjacent to germanium in the other pocket ($C11{\equiv}C12$ and $C19{\equiv}C20$) apparently do not react with $Co_2(CO)_8$ because of the steric hindrance from the two $Co_2(CO)_6$ moieties complexed to $C1{\equiv}C2$ and $C9{\equiv}C10$. As in **81**, the ring of ligand **82** to which the cobalt moieties are bound is severely distorted in the complex **83**.

The selectivities observed in the synthesis of **81** and **83** has led to the hypothesis that $Co_2(CO)_8$ selectively reacts with bent alkynes over linear alkynes in the same molecule. A bent alkyne would be of higher energy due to strain and would be more sterically accessible than a linear alkyne because the substituents are bent away from the metal. Therefore, a bent alkyne would be more reactive. Complexation would give a decrease in strain in the bent alkyne because alkynes bound to $Co_2(CO)_6$ moieties (or other metal moieties) are typically bent. It is probable that other metals and reagents will exhibit similar selectivity with bent versus linear alkynes. Selective complexation of a strained alkyne over an unstrained alkyne also implies that the bonding of $Co_2(CO)_6$ to a strained alkyne moiety would be stronger than $Co_2(CO)_6$ bonding to an unstrained alkyne.

The heterocyclyne **84**, which contains a silicon−silicon bond within the ring, has been prepared by the reaction of **78** and $ClMe_2SiSiMe_2Cl$ (Scheme 9).[170] The X-ray structure (Figure 26) shows that the ring

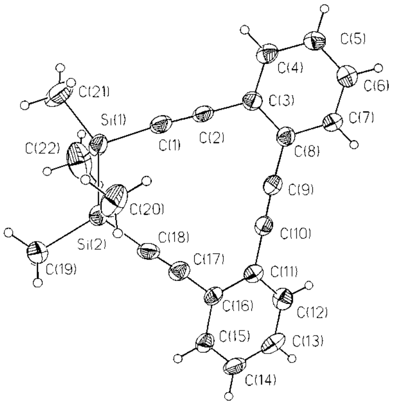
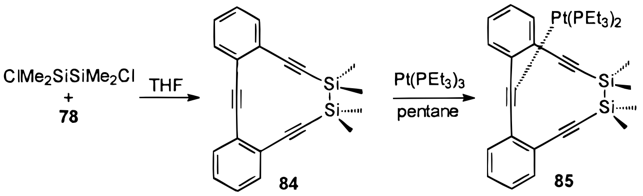


Figure 26. Molecular structure of **85** with thermal ellipsoids drawn at 50% probability.

Scheme 9



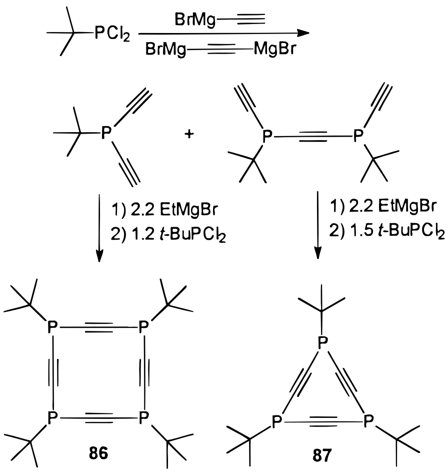
is nonplanar and that the alkynes are all equally unstrained as indicated by the nearly linear Si−C≡C and C−C≡C angles. The Si−Si bond length of 2.330(2) Å is close to the average value in a cyclic disilane (2.372 Å)[168e] and is another indication of the lack of strain in **84**. In contrast to **79a**−**c**, the benzo rings of **84** are no longer in the same plane. The cavity of **84** is larger than those of **79a**−**c**.

The reaction of **84** with Pt(PEt$_3$)$_3$ gives **85** (Scheme 9). The location of the Pt(PEt$_3$)$_2$ moiety was determined by 2D NMR. Unlike the cobalt complexes derived from **79** and **82**, the platinum selectively binds the alkyne between the benzo rings. Because of the lack of strain in the alkynes adjacent to the silicon atoms of **84**, other factors must govern the selectivity of the platinum in **85**.

VI.A.2. Group 15

Scott and Unno communicated the synthesis of phosphinocyclynes **86** and **87** by a procedure analogous to the synthesis of **74** (Scheme 10).[171] Compound **86** is a mixture of all four possible isomers whereas **87** exists as the cis,trans-isomer, and in both cases interconversions between isomers was not observed. Interesting UV−vis properties were described for **86** and **87**, but the origin of these properties was not explained. These heterocyclynes have been mentioned in two reviews,[172] but their coordination chemistry has not been reported.

Scheme 10

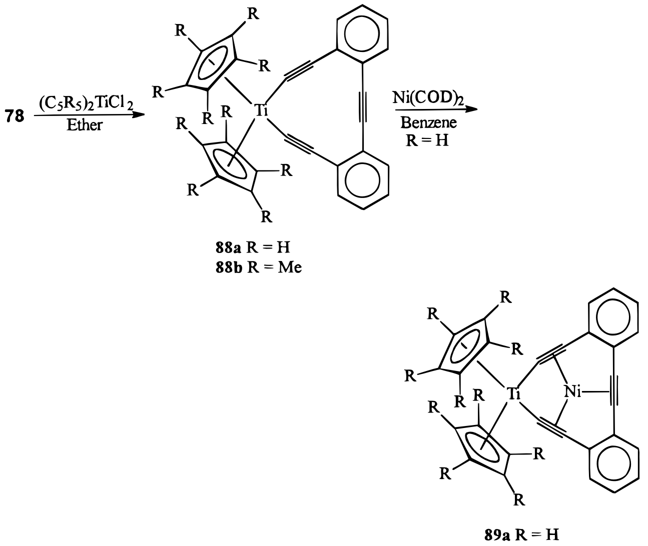


VI.B. Transition Metal Heterocyclynes

VI.B.1. Group 4

The red complexes **88a**,**b** are formed from **78** and the respective titanocene dichloride in 24% and 39% yield (Scheme 11). The reaction of **88a** with Ni(COD)$_2$ in benzene results in the formation of **89a** (Scheme 11, crystal structure Figure 27).[173] The complex **89** has a red color, which is very similar to the color of the starting compound **88a**. This is very different than the reactions of **2** and **79a**−**c** with Ni(COD)$_2$, which show dramatic color changes from colorless to deep blue and deep red, respectively.

Scheme 11



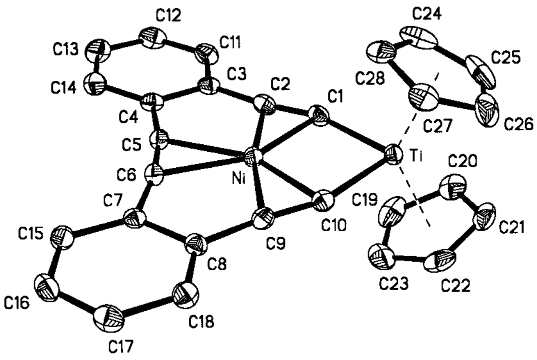


Figure 27. Molecular structure of **89a** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

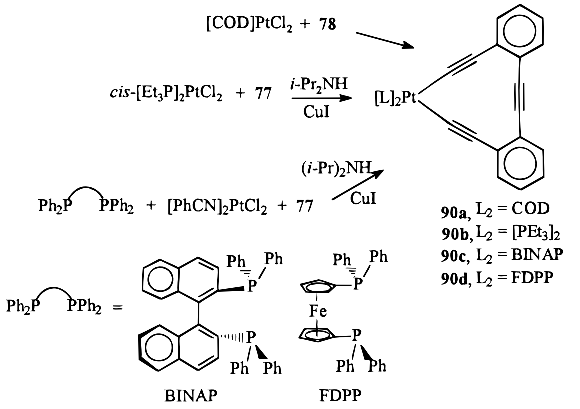
Complexes **88a**,**b** can survive in air for a few hours in the solid state and a short period in solution. They are light sensitive even in an inert atmosphere and especially in solution. Complex **89a** appears to be completely stable to carbon monoxide, and no rapid reaction was observed when oxygen, or water and air, were allowed to react with a benzene solution of **89a**. This behavior contrasts that of the nickel complexes **37** and **80b** which react rapidly with these reagents to give the free the ligands **2** and **79b**. The stability of **89a** appears to involve an indirect stabilization of the Ni−alkyne bonds via donation of electron density of the type Ni → π^* → Ti. The upfield shifts for the protons and the carbons of the cyclopentadienyl ligands in **89a** relative to those in **88a** are consistent with this stabilization mechanism. Another indicator of the stabilization may be the shift of the acetylide−carbon atom adjacent to the heteroatom. These carbons atoms show downfield shifts in **89a** relative to **88a** whereas the highly air-sensitive nickel complexes **80a**−**c** show upfield shifts relative to the air-stable **79a**−**c**. This stabilization process may also apply to the titanium acetylide tweezer complexes in general, though **89a** appears to be less reactive than the similar $(C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2Ni(CO)$.[173,174] The cyclic nature of the ligand in **89a** may also impart stability relative to other titanium acetylide tweezer complexes. We note that an alternative or supplemental stabilization mechanism may involve titanium−nickel bonding, which is suggested by the relatively short Ti− Ni distance in the crystal structure of **89a**.

VI.B.2. Group 10

The heterocyclynes of platinum show the greatest variety, and examples of neutral, dianionic, single pocket, or double pocket heterocyclynes have been prepared.[175]

A series of neutral single pocket heterocyclynes **90a**−**d** have been synthesized (Scheme 12). The combination of lithium acetylide **78** with $[COD]PtCl_2$ gave **90a** in 35% yield. Heterocyclynes **90b**−**d** were prepared in 61−88% yield by employing the method of Hagihara,[176,177] which involved the neutral bis(acetylene) ligand **77**. For **90b** the bis(phosphine)platinum dichloride was used as a reagent, whereas for **90c**,**d** the chelating phosphine and $Pt(Cl)_2(N{\equiv}CPh)_2$ were used. Syntheses of **90a**−**d** were conducted under high-dilution conditions.

Scheme 12



Crystal structures of **90a**−**d** were obtained, and the structure of **90d** is shown in Figure 28. All four compounds have a planar ring consisting of the platinum and C1−C9 atoms. Attempts to make the nickel complexes of **90a**−**d** have met with limited success. In the case of **90b** a nickel complex was formed at 0 °C but it decomposed at room temperature.

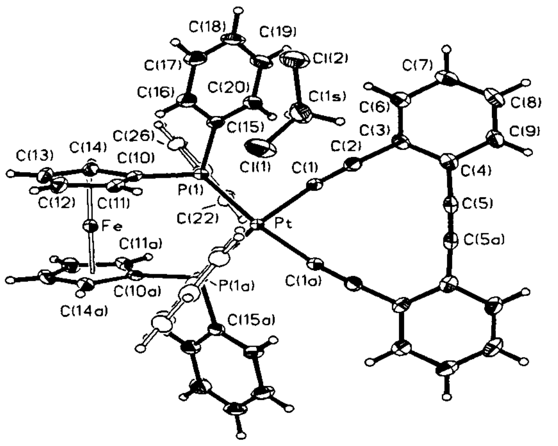
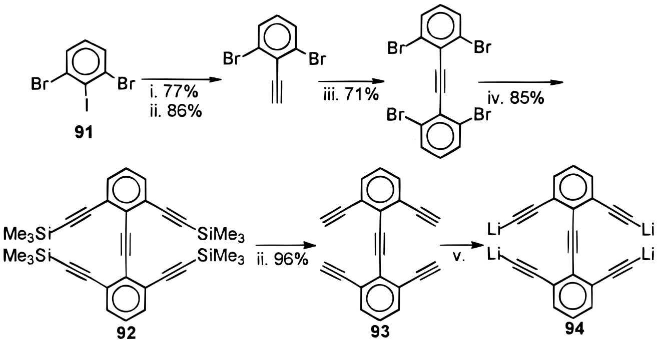


Figure 28. Thermal ellipsoid plots of **90d**. Thermal ellipsoids are drawn at the 50% probability level. Hollow bonds are used for clarity.

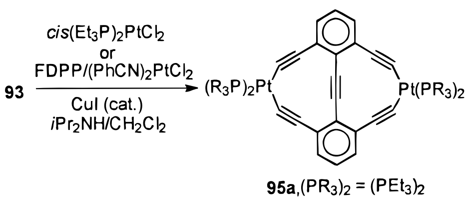
The ligand **93** has been used to prepare platinum heterocyclynes with two pockets. The synthesis of **93** beginning from **91** is outlined in Scheme 13. The strategy of the synthesis was similar to that employed for **77**, and all steps proceed in better than 70% yield. The intermediate compound **92** was characterized by X-ray crystallography. Compound **93** can be converted to the tetralithium compound **94** by reaction with *n*-BuLi. The three compounds **92**−**94** should be useful for the synthesis of two-pocket heterocyclynes of elements other than platinum.

Scheme 13



Reagents and conditions:
i. Me_3SiCCH, $(PhCN)_2PdCl_2$, PPh_3, CuI, $(i\text{-}Pr)_2NH$, 7h, 75°C
ii. KF, H_2O, MeOH-THF (1:1), 10h
iii. **91**, $(PhCN)_2PdCl_2$, PPh_3, CuI, Et_3N-THF (1:1), 90°C, 3 d
iv. Me_3SiCCH, $(PhCN)_2PdCl_2$, PPh_3, CuI, Et_3N-benzene (1:1), 50°C, 1 d
v. 4 *n*-BuLi, THF

The first two-pocket platinum heterocyclynes **95a**,**b** have been prepared in yields of 66% and 57%, respectively, from **93** (eq 36) by using a strategy



(36)

95a,$(PR_3)_2 = (PEt_3)_2$
95b,$(PR_3)_2$ = FDPP

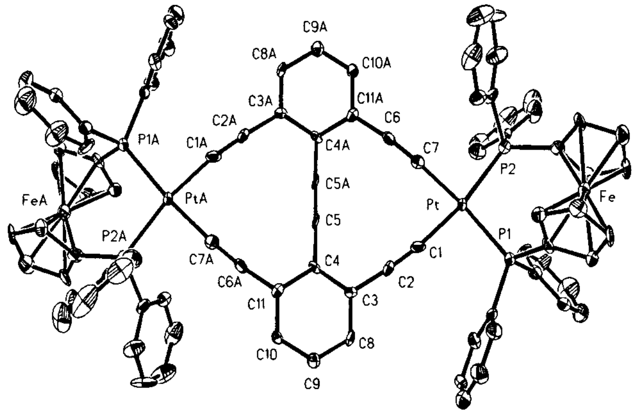


Figure 29. Thermal ellipsoid drawing of **95b** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

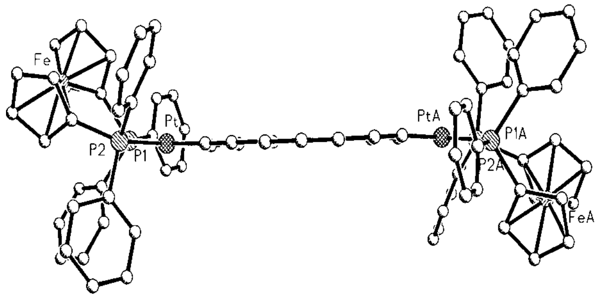


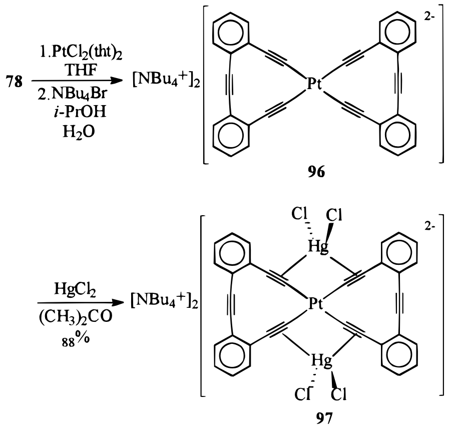
Figure 30. Side view of **95b**.

similar to that utilized to make the corresponding single-pocket heterocyclynes **90b**,**d**. Compound **95b** has very low solubility in organic solvents. The crystal structures of both **95a**,**b** have been obtained, and two views of the structure of **95b** are shown (Figures 29 and 30). The latter view emphasizes the fact that the two pockets (platinum atoms and C1–C11) of **95b** lie in a single plane. The cis-configuration of the platinum atoms is reflected in the positive ^{31}P NMR chemical shifts and the magnitudes of the ^{195}Pt–^{31}P coupling constants for **95a** ($J_{\mathrm{Pt-P}} = 2407$ Hz) and **95b** ($J_{\mathrm{Pt-P}} = 2276$ Hz).[178]

Like that of **90a**–**d**, the coordination chemistry of **95a**,**b** has not yet yielded stable complexes. Attempts to form complexes of **95a**,**b** with Ni(0) and Co(0) appear to cause decomplexation of the Pt from the alkynes.[179] The starting platinum heterocyclynes were not recovered. This is consistent with the metal depolymerization of extended platinum alkyne systems with added metals.[165]

Compound **96** is a dianionic platinum heterocyclyne with two different binding areas for coordination chemistry.[175b] The syntheses of **96** and its mercury complex **97** are shown in Scheme 14. In the latter complex the dianion functions as a double tweezer[174,180] toward the two $HgCl_2$ moieties while the two pockets (defined by C1–C10 in Figure 31) remain vacant. Compounds **96** and **97** are among the first tetraalkynylplatinum complexes to have been crystallographically characterized, and **97** is one of the first mercury alkyne complexes to have been so characterized (Figure 31).[181] The coordination chemistry of the pockets of **96** has not yet been reported.

Scheme 14



VII. Conclusion

In summary, studies of metallocyclotriynes indicate that the size of the metal with respect to the size of the cyclotriyne cavity and the metal to cyclotriyne stoichiometry are important factors in determining the mode of metal to cyclotriyne bonding that will be observed in the product. Only Co, Ni, and Cu are small enough to bind within the cavity of a tribenzocyclyne derivative. The size of the pocket and its electronic properties can be controlled by modifying substituents on the periphery of the cyclyne ligands. These structural modifications affect initial yields of the cyclyne ligands as well as the reactivity of the ligand toward transition metals, reactivity of the metallocyclotriyne with small molecules, and conductivity of the doped metallocyclotriynes. With larger metals, sandwich systems are formed. Compound **3** and derivatives have pockets of sufficient

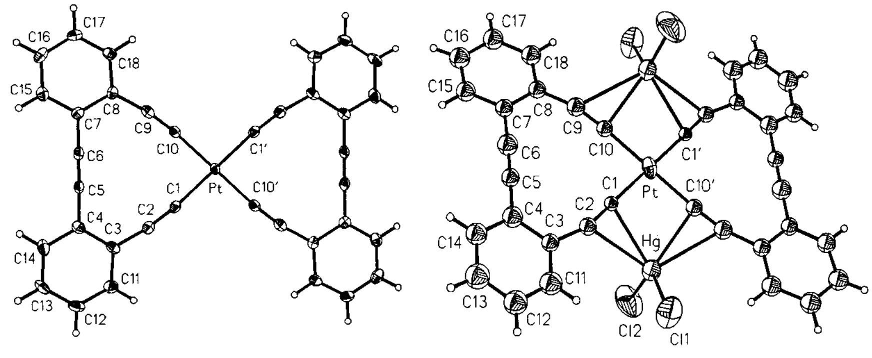


Figure 31. Thermal ellipsoid plots of the dianions of **96** and **97**.

size to allow the coordination of 2nd and 3rd row transition metals within the pocket. To date, the binding of metal moieties to cyclynes or heterocyclynes via the aromatic rings has not observed. Selective coordination of metals to strained alkynes in heterocyclynes has been observed. With titanium heterocyclynes, nickel(0) complexes are formed that are stable to carbon monoxide and oxygen, whereas nickel(0) complexes of cyclotriynes and silicon heterocyclynes are very sensitive to carbon monoxide and oxygen. Nickel(0) complexes of platinum heterocyclynes are not stable above 0 °C. Metallocyclyne chemistry will continue to have significant and surprising advances particularly in the area of heterocyclyne chemistry.

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(3) Also given two other names: tribenzo[*a,e,i*]-5,6,11,12,17,18-hexadehydrocyclododecene and *sym*-tribenzotridehydro[12]annulene.

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