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Carbocyclic Ring Expansions with Alkyne and Carbene Sources Mediated by Nickel(0) Complexes: Structure of the Critical Organonickel Intermediates[1]

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Abstract: Experimental evidence is assessed concerning the nature of organonickel intermediates involved in the cyclotrimerization and the cyclotetramerization of alkynes, as well as the *cross*-oligomerization of alkynes with carbene sources, as mediated by nickel(0) complexes. In the former processes a sequential series of nickelacycloalkapolyenes are the productive intermediates and in the latter *cross*-oligomerizations nickel(0)-carbene complexes themselves are critical precursors to the ultimately generated carbocycles.

The formation of carbocyclic rings by agency of nickel reagents is a versatile and valuable technique in modern organic synthesis, as evidenced by many of the present contributions to this Symposium-in-Print. However, the seminal discoveries responsible for the current prominence of organonickel chemistry were announced a scant 50 years ago.[2] In the period of 1938-1945 Walter Reppe's group at the I G Farbenindustrie AG first observed the facile cyclotrimerization of acetylene to benzene by nickel carbonyl phosphine complexes and the even more astonishing cyclotetramerization of acetylene into cyclooctatetraene by nickel(II) cyanide. These spectacular empirical discoveries attracted the attention of industrial chemists worldwide and led to burgeoning interest in the possible reactions of unsaturated hydrocarbons and transition metal salts or carbonyl complexes.[3] But it was the fundamental studies of Günther Wilke and his group at the Max-Planck-Institut für Kohlenforschung, principally during the period of 1955-1970, that transformed such nickel catalysis, as applied to the oligomerization of olefins and dienes, from an empirical art to the science of homogeneous catalysis by structurally defined transition metal complexes. By choice of the ligands available to the coordinating nickel(0) center, Wilke's group found that the degree of oligomerization could often be controlled (dimer vs trimer), as well as the regioselectivity in olefin dimerization and the asymmetric induction in the stereoselectivity for the *cross*-coupling of olefins.[4-6]

Over the last 20 years our group has attempted to elucidate the nature of the important organonickel intermediates involved in the cyclotrimerizations and cyclotetramerizations of alkynes originally reported by Reppe.[7] In addition to such *homo*-oligomerizations of alkynes themselves, we have been interested in nickel-promoted *cross*-oligomerizations of alkynes with carbene sources such as $Me_3Si–N=C$[8] and $R_2C:Ni$[9] and the nature of the organonickel intermediates likely involved in these cyclizations.

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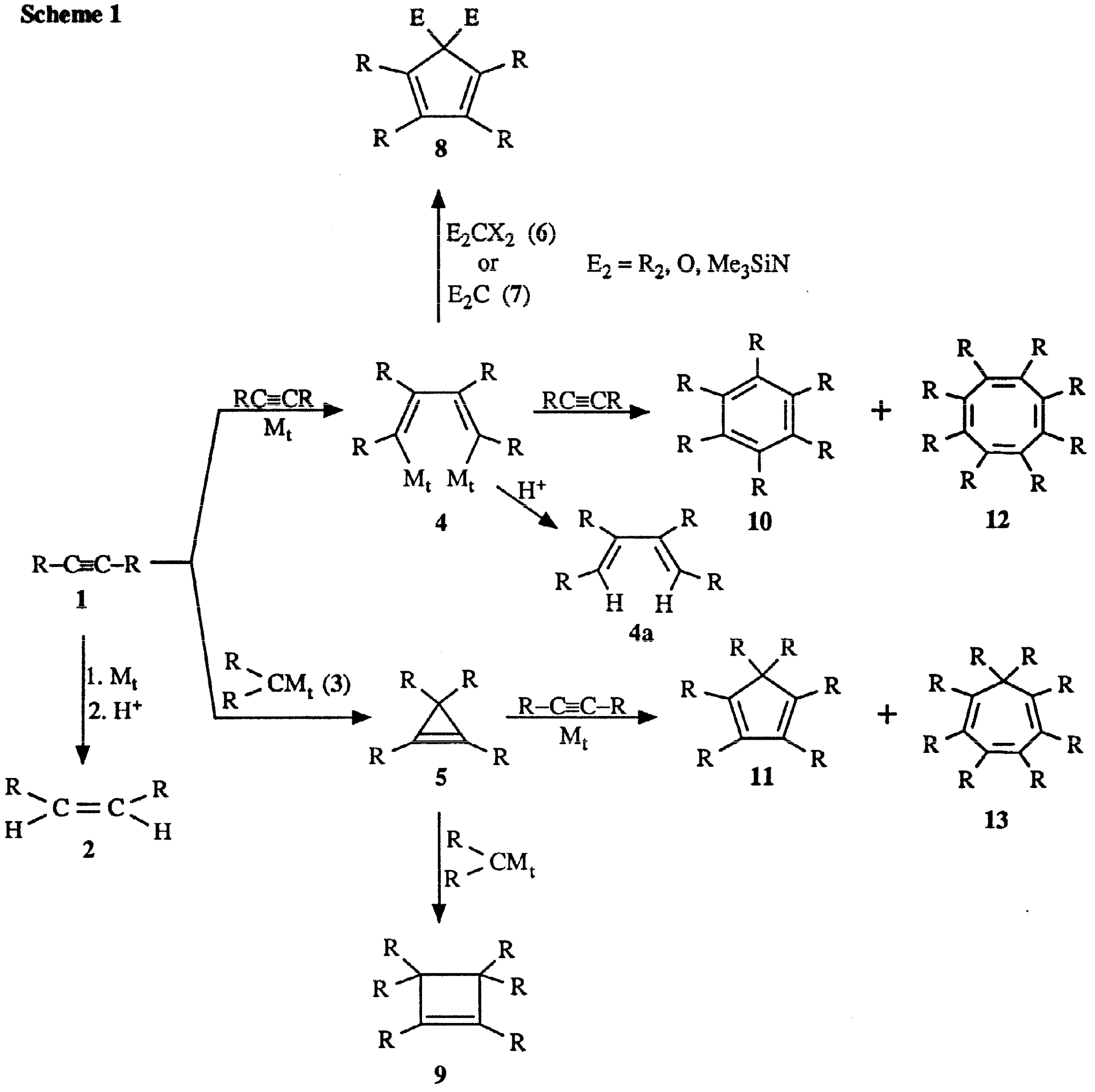
The purpose of this report is to present and analyze both existing and newly obtained data published here concerning the detailed structure of these nickel intermediates. Of pertinence to organic synthesis is that *homo*-oligomerization of alkynes leads to even-membered carbocycles while *cross*-oligomerization of alkynes and carbene sources could generate odd-membered carbocycles. Motivating this research is the hope that identifying the organonickel intermediates crucial to these diverse carbocyclizations may permit us to control the particular carbocyclization obtained by choice of reaction conditions. Illustrative of this expectation is Wilke's finding that the formation of benzene or cyclooctatetraene from acetylene does not depend on the use of $Ni(CN)_2$ or $(CO)_2(Ph_3P)_2Ni$ as the catalyst. The nickel(0) complex, $(Cod)_2Ni$, can be substituted for $Ni(CN)_2$ and cyclotetramerization proceeds normally. Thus it is clear that nickel(0) can produce either the trimer or the tetramer but the precise ligands on nickel determine the principal pathway of reaction.[10]

Overview of the Observed and Possible Transformations of Alkynes and Carbene Sources by Subvalent Transition Metal Reagents (M_t) such as Nickel(0).

Observed or potential products obtainable from the *homo*-oligomerizations of alkynes themselves (**2**, **4**, **10** and **12**) or from the *cross*-oligomerizations of alkynes and carbene sources (**5**, **8**, **9**, **11** and **13**) are summarized in Scheme 1. Up to the present, all the carbocycles with exception of structure **13** have been isolated, where R in alkyne **1** is H, alkyl or aryl and R_2 in **3** is O, Me_3SiN or Ph and H. However, in accounting for the formation of the observed metal-free hydrocarbon products, **2**, **4a**, **5**, **8**, **9**, **11** and **12**, from potential organonickel precursors, one must take into consideration the isomeric pairs of nickel complexes depicted in Scheme 2. Thus, for example, (Z)-olefin **2** might arise from the protodenickelation of either nickelacyclopropene **14a** or the alkyne-nickel(0) complex **14b**. Likewise, the (E,E)-alkadiene **4a** might stem from the protodenickelation of **15a** or **15b**. Further, the interaction of **14a** or **14b** with a carbene may produce nickelacyclobutene **16a** or the nickel(0)-vinylcarbene complex **16b**. By an additional insertion of an alkyne into **16a** or **16b** either the nickelacyclohexadiene **18a** or the nickel(0)-butadienylcarbene complex **18b** could result, whose nickel(0)-elimination could generate cyclopentadiene **11**. Finally, an alkyne insertion into **15a** or **15b** could lead either to a 7-nickelabicyclo[2.2.1]heptadiene **17a** or to nickelacycloheptadiene **17b**, whose nickel(0)-elimination could generate cyclotrimer **10**. As will be seen, the alternative cyclotetramerization of alkyne **1** to yield **12** is thought to proceed via the dimerization of either **15a** or **15b** and subsequent loss of nickel(0).

In reaching a decision on which isomer of the foregoing pairs of potential organonickel intermediates is the most likely productive precursor in these *homo*-oligomerizations of alkynes and *cross*-oligomerizations of alkynes and carbene sources, we have relied on three kinds of evidence: 1) isolation of the organonickel intermediate from the reacting catalytic system and its structure determination; 2) synthesis of putative intermediates by an alternative, unambiguous route and learning whether such an intermediate can act as a catalyst in the oligomerization; and 3) chemical trapping of the intermediate from the reacting catalytic system and its isolation as a stable derivative. Assigning a definite structure to such organonickel intermediates on the basis of these lines of evidence is not always straightforward but requires a judicious weighing of available evidence. The

Scheme 1



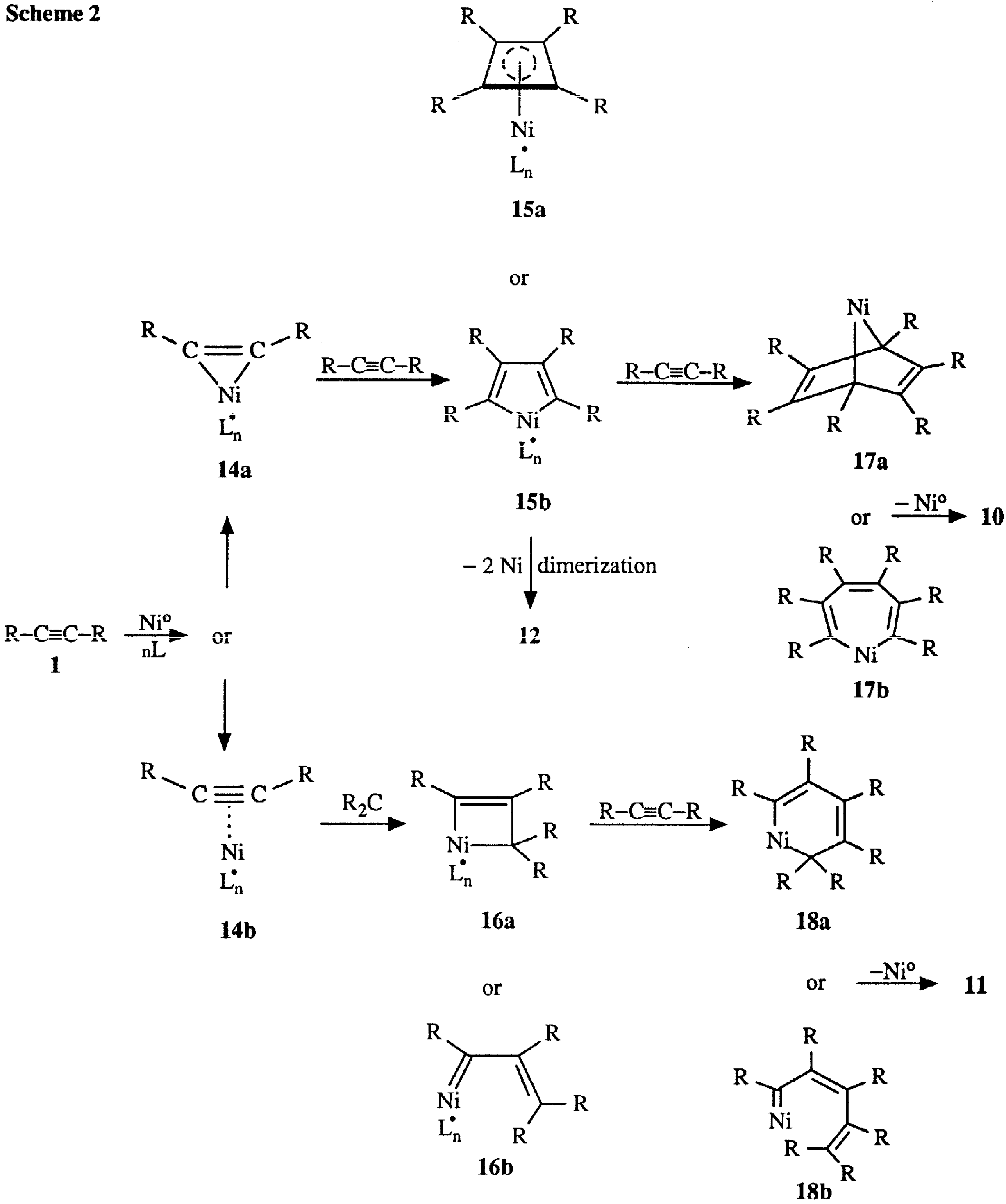
scope and limitations of such structural arguments are possibly best conveyed by beginning with a consideration of the isomeric pair, **14a** and **14b**, and inquiring whether such a complex is a nickel(II) structure of a nickelacyclopropene type (**14a**) or rather a simple nickel(0) pi-complex (**14b**).

HOMO-CYCLOOLIGOMERIZATIONS OF ALKYNES

Nickel-Alkyne Complexes of Type 14 Have the Structural and Chemical Properties of a Nickelacyclopropene (14a).

The (1:1:1) complex of nickel(0), diphenylacetylene (**19**) and 2,2′–bipyridyl (**20**) (Scheme 3) was readily obtained as a black solid from the interaction of the acetylene **19** with (Bpy)(Cod)Ni. Its

Scheme 2

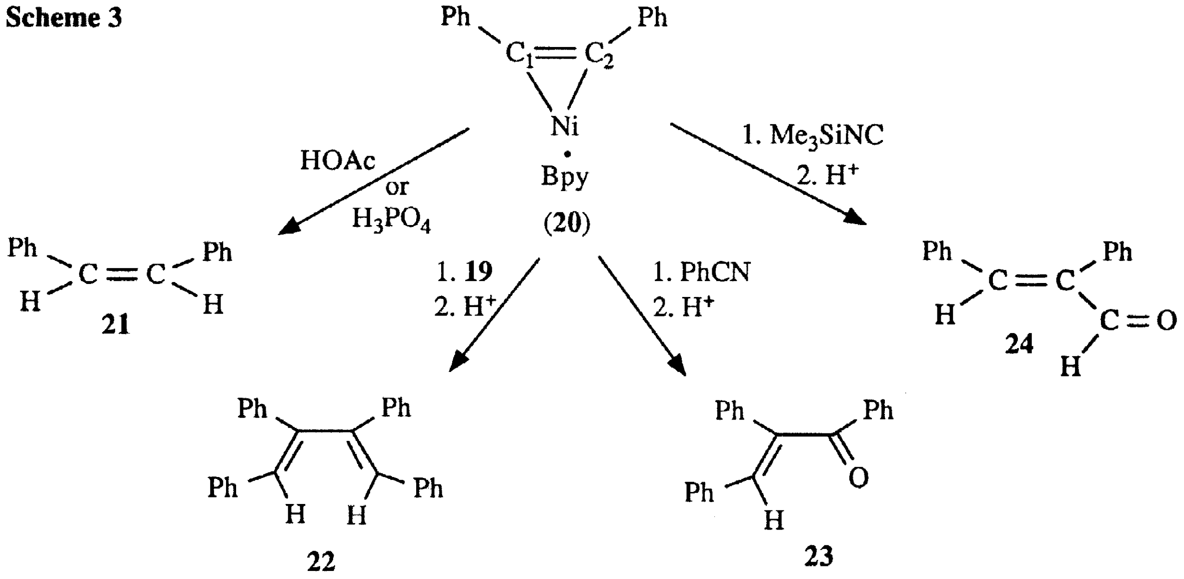


infrared absorption at 1770 cm^{-1} was lowered by 500 cm^{-1} from the expected C≡C stretch. Its single crystal XRD showed a C_1–C_2 separation of 1.30Å and C_1–Ni or C_2–Ni separations of 1.86-1.87Å.[11]

Since unambiguous <u>sigma</u> C–Ni bonds show separations of 1.94-1.95Å[12] and since the C=C bond length in cyclopropene is 1.304Å,[13] we can conclude that the bonding in **20** more closely resembles a nickelacyclopropene complex **14a** with a nickel(II) oxidation state. Its somewhat shorter C–Ni bonds would suggest d_π–p_π back-bonding and both its infrared C–C absorption and the C_1–C_2 separation would accord better with a C=C bond in **20**.

The chemical properties of **20** also correspond better with those expected of a nickelacyclopropene like **14a**. Protodenickelation to give exclusively the (Z)-olefin (**21**)[15] and the various insertions of an alkyne (**22**),[14] a nitrile (**23**)[15] or trimethylsilyl(iso)cyanide (**24**)[16] are accounted for in a straightforward fashion (Scheme 3). Even if we view **14a** and **14b** as alternative resonance structures of the 1:1 complex of **19** with nickel(0), such evidence would compel us to conclude that **14a** more closely corresponds to the real structure of **20**.

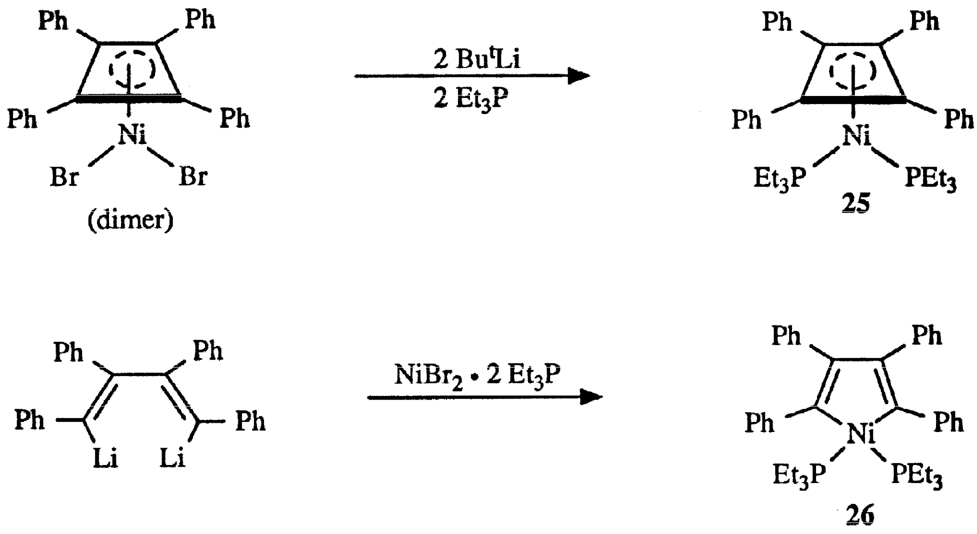
Scheme 3



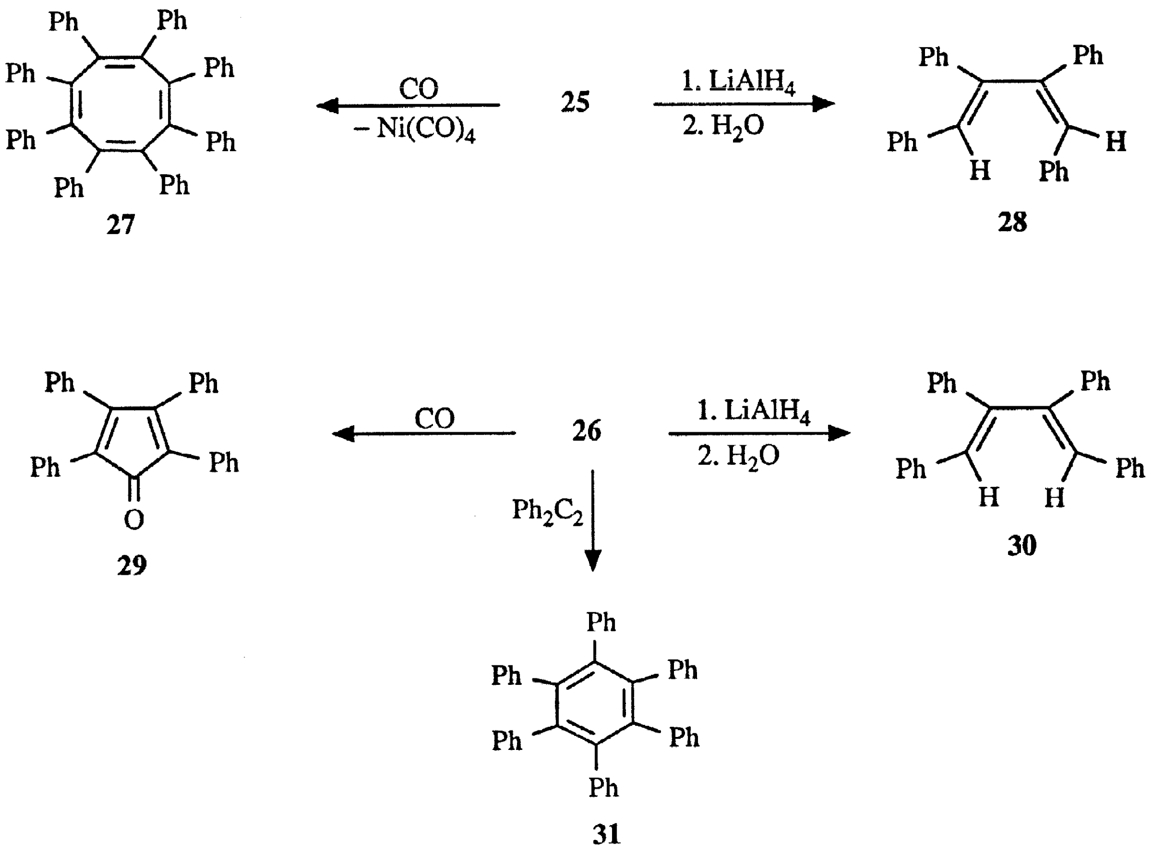
The Interaction of Nickel(0) with Two Alkynes Leads to Nickelacyclopentadienes (15b), Rather than to Cyclobutadiene-Nickel(0) Complexes.

Deciding on the next productive intermediate in the cyclooligomerization of alkynes can be made by the unambiguous synthesis of types **15a** and **15b** and the ascertainment of their individuating chemical properties. The syntheses of the cyclobutadiene-nickel(0) complex **25** and the nickelole complex **26** are given in Scheme 4. The structure of **25** was established by XRD[17] and that of **26** by characteristic chemical reactions.[18] Particularly useful were the individual reactions of **25** and **26** with CO and with $LiAlH_4$ and subsequent hydrolysis (Scheme 5). Complex **25** yielded, upon such treatment, octaphenylcyclooctatetraene (**27**) and (E,Z)-1,2,3,4-tetraphenyl-1,3-butadiene (**28**), respectively. On the other hand, nickelole **26** produced only the tetracyclone **29** with CO and only the (E,E)-tetraphenylbutadiene isomer (**30**) with $LiAlH_4$.

Scheme 4



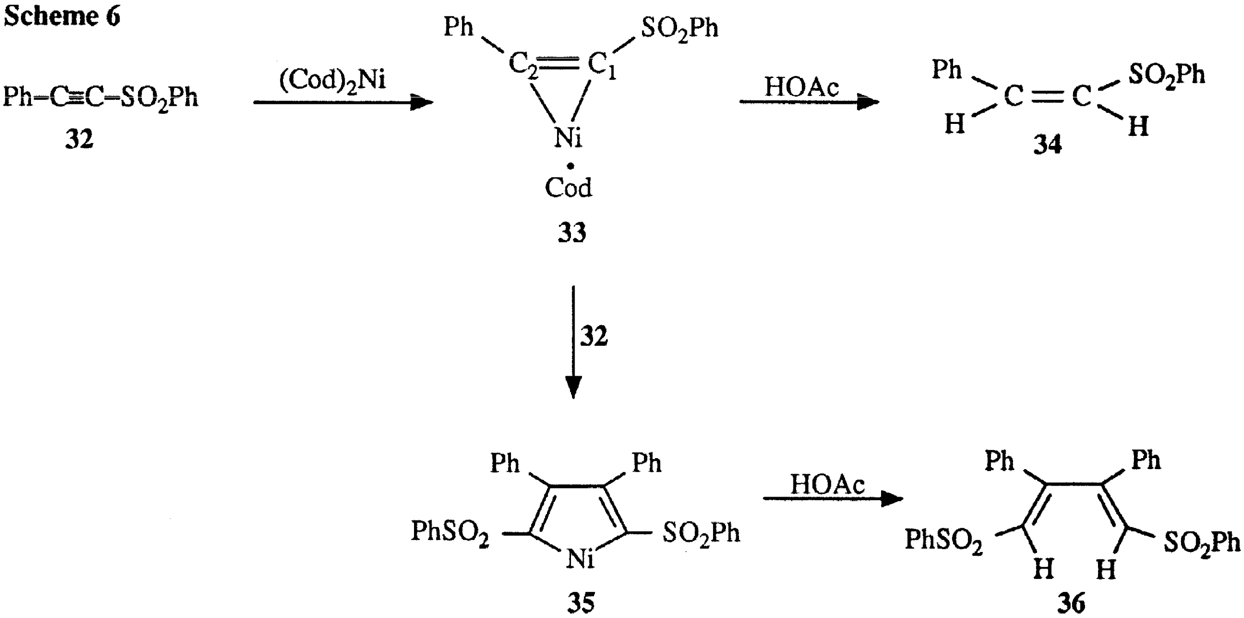
Scheme 5



These criteria in hand, we then allowed two equivalents of diphenylacetylene to react with (Bpy)(Cod)Ni (a moderate oligomerization catalyst) in the presence of CO or its equivalent, Me_3SiNC. Hydrolytic workup led to the isolation of hexaphenylbenzene (**31**) and **29**, but none of **27**. Similarly, such an oligomerization in the presence of $LiAlH_4$ and subsequent hydrolysis yielded **31** and some of diene **30** but no **28**. Based upon these observations, we conclude that no cyclobutadiene-nickel(0) complex of type **15a** is a productive intermediate in such oligomerizations.[19]

Insight into the polar factors operative in the formation of intermediates **14a** and **15b** can be gleaned from the behavior of phenyl phenylethynyl sulfone (**32**) towards $(Cod)_2Ni$. Reaction in a 1:1 ratio in THF led to a quantitative yield of the (Z)-olefin **34** upon protolysis of the precursor **33**;[20] but a similar reaction of a 2:1 ratio of **32** and $(Cod)_2Ni$ gave, among other products (cf. infra), as the only diene, compound **36** (Scheme 6).[15] Exclusive formation of this diene indicates that **32** inserts exclusively and regioselectively into the C_2–Ni bond of **33** to give **35**.

Scheme 6



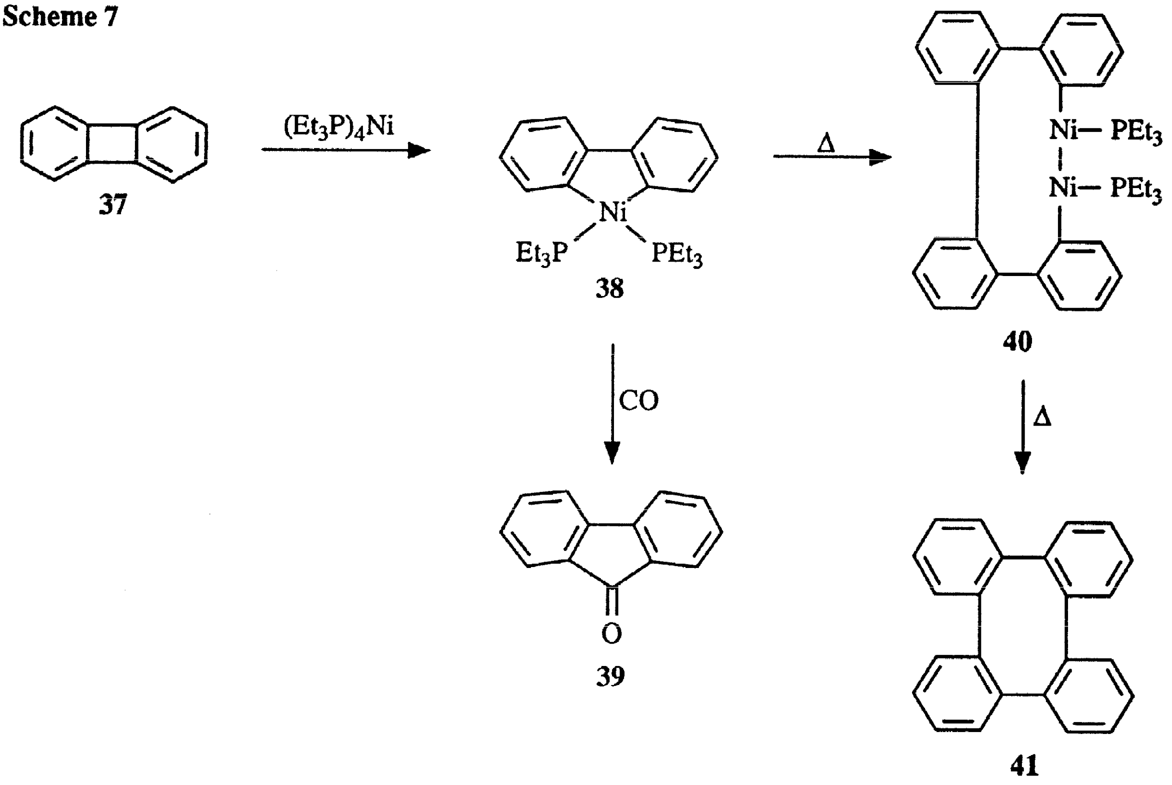
This selective insertion seems not likely due to steric effects but rather to the polar character of the C_2–Ni and the C≡C bonds, respectively. The strongly electronegative $PhSO_2$ group attached to C_1 should exert a great stabilizing effect on the C_1–Ni bond and thus retard insertion of **32** at this site.

It will next be shown that nickeloles of type **15b** are productive intermediates either for cyclotetramerization of alkynes or for cyclotrimerization of alkynes.

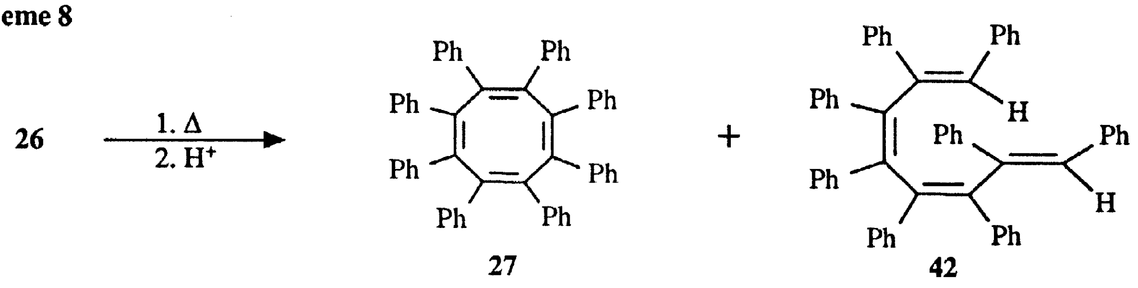
The Thermal Decomposition of Nickelole 15b Leads to the Ultimate Cyclotetramerization of Alkynes.

Our first insight into the mechanism of cyclotetramerization was achieved from our studies of the synthesis and chemical characterization of dibenzonickeloles (**38**)[21] (Scheme 7). The finding that **38** is converted above 25°C into **40** (characterized by XRD) and that **40** upon stronger heating produces **41** suggested to us that simple nickeloles like **26** might behave similarly. Indeed, when **26** was heated in refluxing toluene and then hydrolyzed, chiefly **27** and a small amount of **42** were isolated.[18] The latter compound undoubtedly stemmed from the analog of **40** (Scheme 8).

Scheme 7



Scheme 8

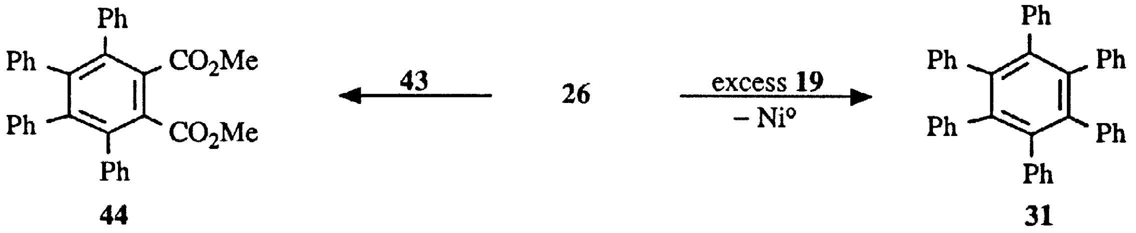


Generated in the Presence of an Alkyne and a Suitably Coordinated Nickel Center, Nickelole 15b Can Preferentially Effect the Cyclotrimerization of the Alkyne via 7-Nickelabicyclo[2.2.1]-heptadiene 17a.

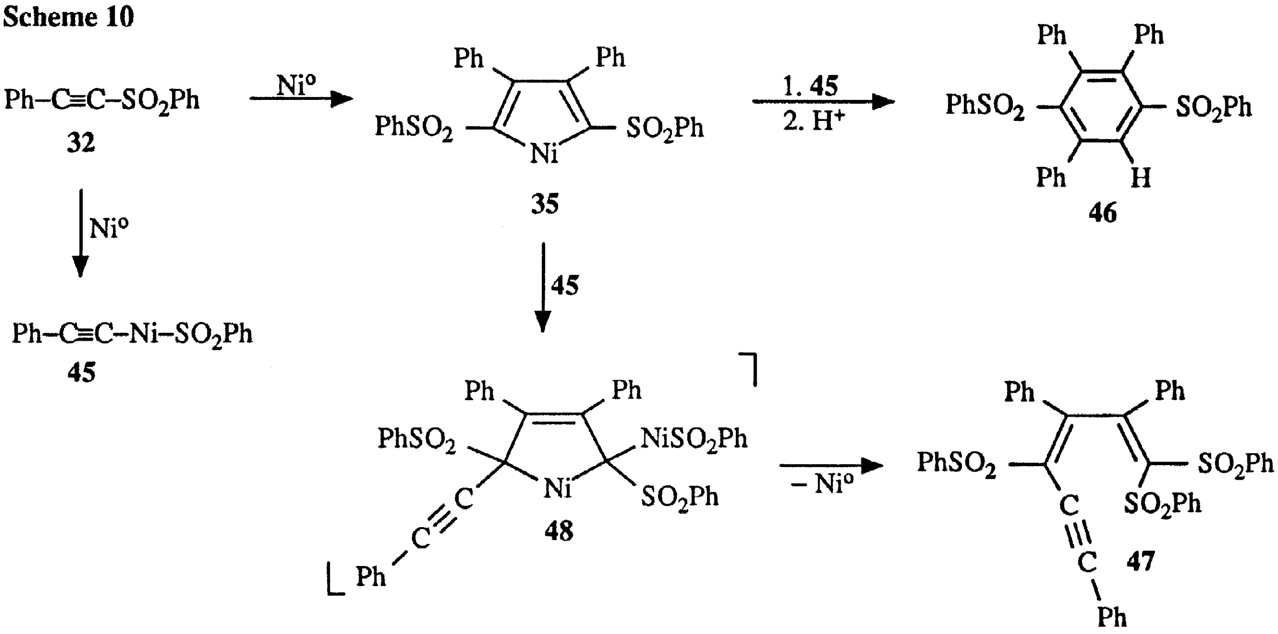
This conclusion is obvious from the finding that nickeloles, such as **26**, generated as depicted in Scheme 4, react stoichiometrically with electrophilic alkynes such as $MeO_2C–C≡C–CO_2Me$ (**43**) and act as catalysts for the cyclotrimerization of alkynes such as Ph–C≡C–Ph (**19**) (Scheme 9).[18,22] The question remains whether such reactions involve intermediates of the type **17a** or **17b**. Here the decision must, at present, be made mainly on the basis of negative evidence. Were **15b** to react with a third alkyne unit by insertion into its C–Ni bond to generate **17b**, there should be no barrier to a fourth or a fifth alkyne inserting into **17b** to yield linear tetramers or pentamers of the alkyne. However, no such higher oligomers are formed in the reaction of **19** with $(\mathrm{Cod})_2\mathrm{Ni}$. Moreover, positive evidence in favor of the Diels-Alder path of converting **15b** into **17a** comes from the anomalous reactions observed in the attempted cyclotrimerization of phenyl phenylethynyl sulfone (**32**).[15] In addition to 15% of dimer **36** (Scheme 6), 69% of **46** and 8% of **47** were formed (Scheme 10). Although the precise stereochemistry of **46** and **47** is assumed, the overall structures of the products are in accord with a retarded Diels-Alder process between dienophile **32** and an electrophilic diene. Because of the slowness of this cyclotrimerization step, a nucleophilic dienophile **45** apparently has time to form and then to interact more favorably with electrophilic diene **35** to produce **46** ultimately (Diels-Alder reaction with inverse electron demand). In a minor side reaction **45** could add 1,4 to diene **35** and reductive elimination of Ni^0 from adduct **48** would yield **47**.

Thus, nickeloles of type **15b** are pivotal intermediates for both the cyclotrimerization and the cyclotetramerization of alkynes. Which pathway will dominate depends upon the relative rates of: 1) the autodimerization of the nickelole intermediate (e.g., **26** in Scheme 8) and 2) the Diels-Alder reaction between the nickelole and the alkyne (e.g., **26** in Scheme 9). It is to be expected that substituents on the alkyne and ligands on the nickel center will have significant and differing influence on these relative rates.[18,21]

Scheme 9



Scheme 10

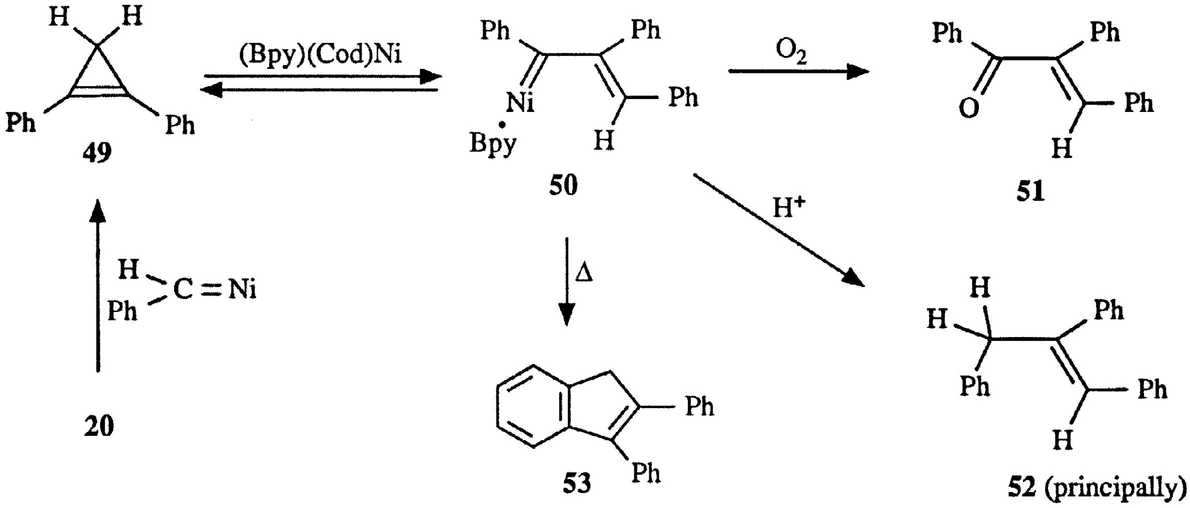


CROSS-CYCLOOLIGOMERIZATIONS OF ALKYNES AND CARBENE SOURCES

The Interaction of Carbene Sources with Nickelacyclopropene 14a Yields Nickel(0)-Vinylcarbene Complex 16b, Rather Than Nickelacyclobutene 16a.

The principal experimental finding favoring the existence of intermediate **16** in form **16b** is the formation of a ketone, rather than a hydroxyketone upon treatment with O_2 (**51** in Scheme 11). In this case, the intermediate is accessible from the reaction of 1,2,3-triphenylcyclopropene (**49**) with (Bpy)(Cod)Ni (Scheme 11).[9,15] The other reactions of **50**, leading with acids to **52** and with heat to **53**, are uniformly in better accord with structure **50**, a nickel-carbene complex of type **16b**, than those of a nickelacyclobutene of type **16a**. Furthermore, although **50** has not yet been isolated pure, its ^{13}C NMR spectrum displays a signal at 251 ppm, a region where authentic nickel(0)-carbene complexes show prominent absorption. Finally, it should be noted that nickelacyclopropene **20** reacts with a source of PhHC=Ni (lithiated benzyl phenyl sulfone + nickel) to produce **49**. This supports the reversible formation of **50** from **49**. We cannot, however, rule out an easily reversible equilibrium between isomeric intermediates of types **16a** and **16b**. (Further evidence of the generation of PhHC=Ni from $PhCHLi–SO_2Ph$ and Ni° is that 1,1,2-triphenyl-cyclopropane can be isolated in 30% by chemical trapping with 1,1-diphenylethene.[15])

Scheme 11

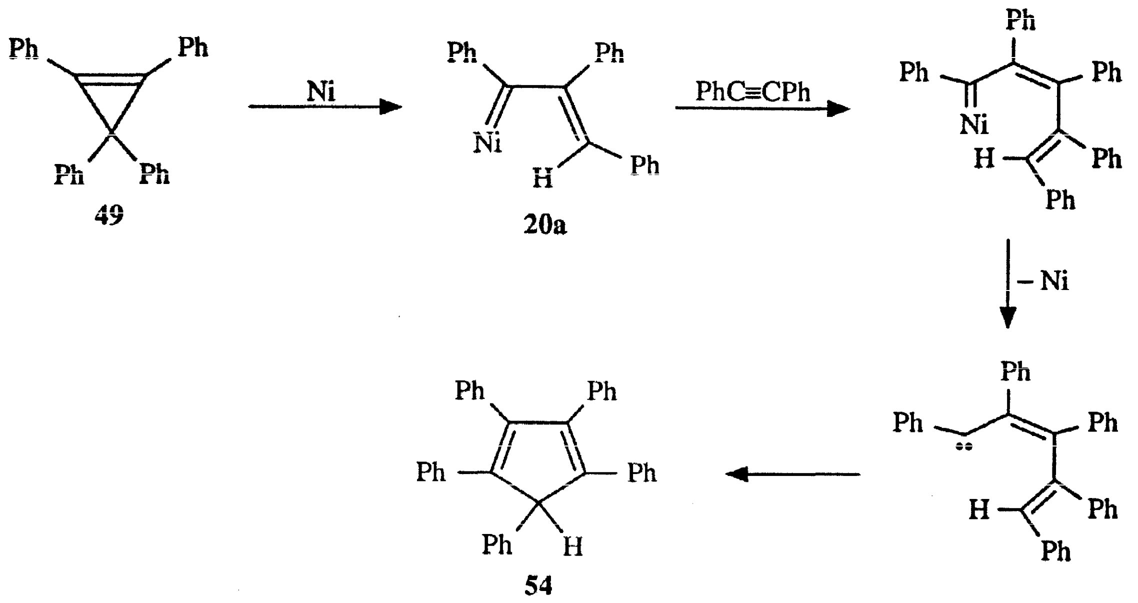


The Reactive Intermediate Formed from Two Alkyne Units and a Carbene Source Is Best Viewed as the Carbene Complex 18b, Rather Than Nickelacyclohexadiene 18a.

In this reaction it should be admitted that there may also be a ready equilibration between **18a** and **18b**, but we favor **18b** as the principal structure of the reaction intermediate. Were a significant amount of **18a** to be present, one would expect further units of alkyne to insert into the C–Ni bonds of **18a**, thereby leading to the formation of C_7, C_9 and higher *cross*-oligomers. Up to now, no such higher oligomers have been observed in these reactions. Instead, we judge that **18b** eliminates Ni° and the resulting carbene cyclizes (Scheme 12). This would explain both the conversion of cyclopropene

49 into cyclopentadiene 54 by diphenylacetylene (19) and the conversion of **50** into **53** (Scheme 11).[9,15]

Scheme 12



SUMMATION AND OUTLOOK

In surveying the lines of evidence that can be marshaled for elucidating the nature of the organonickel intermediates involved in these oligomerizations of alkynes, we hope to have provided chemists interested in organic synthesis with insights into experimental variables whose manipulation may serve to steer the course of organonickel reactions along a desired pathway. Many of these reactions are extraordinarily sensitive to the specific ligands on nickel, the substituents on the organic substrate and even the nature of the aprotic solvent employed. Such experimental sensitivity surely stems from the importance of oxidative addition reactions in nickel(0) chemistry, a process in which considerable electron density is transferred from the nickel center into antibonding orbitals of the organic substrate.

ACKNOWLEDGMENTS

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EXPERIMENTAL SECTION

All transfers, reactions and nonhydrolytic workup procedures of organonickel reagents and intermediates were performed under an anhydrous argon atmosphere. Particular experimental techniques have been previously described.[23]

***cis*-Reduction of Diphenylacetylene by Bis (1,5-cyclooctadiene)nickel-bipyridyl and Protolysis with Phosphoric Acid.** To a suspension of 5.7 mmol of $(Cod)_2Ni$ and 5.7 mol of 2,2′-bipyridyl in 20 ml of THF was added 5.2 mmol of diphenylacetylene. After 20 h reaction at room temperature 10 ml of phosphoric acid (85%) was added to the reaction mixture under an argon atmosphere to give rise to a grey-white precipitate. (The isolated grey white precipitate, after washing with water, with ethanol, and with ether, followed by hydrolysis with 6N HCl and extraction with ether, gave only *cis*-stilbene on GLPC). Continuous stirring at room temperature for 2 h was followed by adding water to dissolve the white precipitate while the solution changed to blue. After ether extraction and solvent removal *cis*-stilbene was obtained in a yield of 95%. The NMR of the crude oil showed only *cis*-stilbene.

Hydrocyanation of Diphenylacetylene via the (Bpy)(Cod)Ni Complex. The $(Cod)_2Ni$ 0.600 g (2.2 mmol), was dissolved in 10 ml of THF. To the resulting yellow solution was added 0.342 g (2.2 mmol) of 2,2′–bipyridyl. The color turned violet-blue. Diphenylacetylene, 0.390 g (2.2 mmol), and trimethylsilyl(iso)cyanide, 0.6 ml (4.4 mmol), were added in succession to give a milky-green complex. The reaction mixture was stirred at room temperature for 24 h and then hydrolyzed with deoxygenated aqueous 6N-HCl. After 12 h the hydrolysate, now a green biphasic mixture, was extracted with ether. On addition of a saturated solution of NaCl, a yellow oily precipitate formed on the sides of the extraction funnel. (This was later hydrolyzed completely with HOAc and subsequent analysis by gas chromatography showed the product to be E–α–phenylcinnamonitrile). Both organic layers were admixed and washed with a saturated solution of $NaHCo_3$/NaCl, dried over $MgSO_4$, and concentrated by rotary evaporation. Analysis by gas chromatography indicated only the following two compounds: 1) diphenylacetylene, 0.054 g (20.5%), and 2) E–α–phenylcinnamonitrile, 0.242 g (79%). The nitrile could be obtained pure and identified by comparison with an authentic sample.

Hydroformylation of the (2,2′–Bipyridyl)(Diphenylacetylene)Nickel Complex with Trimethylsilyl Cyanide (Isocyanide). A mixture of $(Cod)_2Ni$, 2.125 g (7.7 mmol), 2,2′–bipyridyl, 1.208 g (7.7 mmol) and diphenylacetylene, 1.377 g (7.7 mmol), was purged with argon and dissolved in 50 ml of THF. The solution was greenish-blue. After stirring for 24 h at room temperature, 1 ml (7.8 mmol) of trimethylsilyl(iso)cyanide was added, and the solution darkened. After a total of 48 h, deoxygenated 6N-HCl was added and the reaction mixture hydrolyzed overnight. The organic layer was extracted into ether, washed with a saturated solution of $NaHCO_3$/NaCl and dried over $MgSO_4$. The extract was then concentrated by rotary evaporation and separated by column chromatography (silica gel, hexanes/methylene chloride, ether gradient). The earlier fractions eluted were determined by NMR spectroscopy to contain 1,5-cyclooctadiene, *cis*-stilbene, diphenylacetylene and the mixture of α–phenylcinnamonitrile isomers. These were neither isolated nor their yields determined. The product of interest eluted at a higher solvent gradient. Recrystallization from ethanol gave white crystals of (E)–α–phenylcinnamaldehyde, 0.503 g (31%).

An analogous reaction with the only difference being a total of 24 h reaction period gave the aldehyde in an 18% yield.

A third similar reaction with the difference being two equivalents of trimethylsilylnitrile and a hydrolytic work-up with deoxygenated 85% H_3PO_4 gave the aldehyde in an estimated 45% yield. The yield was determined from the integrated NMR spectrum of the crude mixture.

(E)–α–phenylcinnamaldehyde: mp: 92-94°C; ^{1}H NMR ($CDCl_3$): δ7.20(s, 7H), 7.32(m, 4H), 9.62(s, 1H) ppm; IR (Nujol): 1665, 1628, 1600, 1448, 1415, 1380, 1200, 1096, 1072, 1028, 935, 800, 762, 714, 694 cm^{-1}; MS: m/e 208(100), 207(42), 179(63), 178(60), 176(13), 165(22), 152(15), 102(33), 77(15), 76(10), 63(11), 51(24).

Interception of Nickelacyclopentadiene Intermediates in Alkyne Oligomerization Reactions: Synthesis of 2,3,4,5-Tetraphenylcyclopentadienone. The $(Cod)_2Ni$, 1.687 g (6.1 mmol) was dissolved in 10 ml benzene to give a yellow solution. To this was added 1.090 g (6.1 mmol) of diphenylacetylene and 1.2 ml (9.5 mmol) of trimethylsilyl(iso)cyanide. The final color was a dark red. The solution was maintained at reflux for 48 h and then hydrolyzed at room temperature with excess deoxygenated water. After 12 h deoxygenated 6N-HCl was added and hydrolysis continued for another half an hour. Then the organic layer was extracted into ether which became colored intensely red. This was washed with a saturated solution of $NaHCO_4$/NaCl, dried over $MgSO_4$, and concentrated by rotary evaporation. The dark red oil was separated by column chromatography (silica gel, hexanes/20% methylene chloride). The earlier fractions eluted contained 1,5-cyclooctadiene, *cis*-stilbene, diphenylacetylene, and the α–phenylcinnamonitrile isomers. These were identified by GLPC by co-injection of authentic samples from previous experiments, but their yields were not determined. The next compound eluted was intensely red in color. Recrystallization from a ratio of 9:1 ethanol:methylene chloride gave dark red crystals of 2,3,4,5-tetraphenylcyclopentadienone, 0.476 g (43.7%), mp: 217.219°C; ^{1}H NMR ($CDCl_3$): δ6.75-7.08(m, 7H), 7.17(s, 13H) ppm; IR (Nujol): 1715, 1455, 1390, 1370, 1315, 1035, 825, 765, 730, 705 cm^{-1}.

The Reaction of the (2,2′–Bipyridyl)(Diphenylacetylene)Nickel Complex with Benzonitrile. A solution of 0.228 g (0.580 mmol) of (Bpy)(PhC≡CPh)Ni in 10 ml THF was cooled down to -78°C. Then 0.061 ml (0.598 mmol) of benzonitrile was added dropwise. The reaction mixture was then brought up to RT gradually and was stirred at 25°C for 2 days. No apparent change could be observed. The reaction mixture was then refluxed for 6 h, whereupon the reaction was quenched with 20 ml of 2N-HCl. The organic layer was neutralized with sodium bicarbonate and then dried over anhydrous magnesium sulfate. According to GC/MS and coinjection with authentic samples (provided by American Peptid Corp., Sunnyvale, CA), *cis*- and *trans*-1,2,3-triphenylpropen-1-one were found to be the main products. Total yield of the *cis*- and *trans*- isomers was about 38%. *cis*-Stilbene was also one of the main products (yield of 53%). The minor products are

1,2,3,4-tetraphenyl-1,3-butadiene isomers and traces of *trans*-stilbene. Characterization: GC/MS: *cis*- and *trans*-1,2,3-triphenylpropene-1-one: $C_{21}H_{16}O$; m/z: 284 = $[M]^+$; 179 = $[C_{14}H_{11}]^+$; 105 = $[C_7H_5O]^+$; 77 = $[C_6H_5]^+$; isomeric butadiene derivatives: $C_{28}H_{22}$; m/z: 358 = $[M]^+$; 267 = $[C_{21}H_{15}]^+$; 179 = $[C_{14}H_{11}]^+$; 178 = $[C_{14}H_{10}]^+$; 77 = $[C_6H_5]^+$; IR (thin film): carbonyl absorption of 1,2,3-triphenylpropen-1-one is 1652 cm^{-1}.

Reaction of Phenyl Phenylethynyl Sulfone with Bis(1,5-cyclooctadiene)nickel.[24] Phenyl phenylethynyl sulfone (1.30 g 5.4 mmol) was dissolved into 15 ml of dry THF, under argon. This solution was then added to a solution of 0.69 g (2.7 mmol) of $(Cod)_2Ni$ in 35 ml of THF. The color went from yellow to orange during the addition. The reaction stirred for 16 hours, during which time the color became black. The mixture was worked up with 6N-HCl and extracted with ether. The ether portions were dried and the solvent evaporated to give an oil (75% recovery by weight). Recrystallization from 95% ethanol resulted in 15% of 1,1,4-triphenylsulfonyl-2,3,6-triphenyl-1,3-hexadiene-5-yne; mp: 294-295°C (dec); ^{1}H NMR ($CDCl_3$): 7.7-7.0 (br m); IR (Neat): 2250, 1320, 1150 cm^{-1}; MS: (m/e) 726 (M^+).

The filtrate was then concentrated to give an oil, whose recrystallization from diethyl ether gave 8% of 1,4-diphenylsulfonyl-2-3-diphenyl-1,3-butadiene; mp: 173-175°C; ^{1}H NMR ($CDCl_3$): 7.4-7.6 (m); IR (Neat): 1140, 1315 cm^{-1}; MS (m/e) 486 (M^+).

A second concentration of the filtrate and the passing of the resultant oil through a silica gel column (hexane/chloroform) resulted in 69% of 2,5-diphenylsulfonyl-1,3,4-triphenylbenzene, which was isolated as an oil. ^{1}H NMR ($CDCl_3$): 6.7 (s, 1H), 6.8-7.8 (m, 25H); IR (Neat): 1148, 1305 cm^{-1}. MS: (m/e) 586 (M^+).

Reaction of α–Lithiobenzyl Phenyl Sulfone with 1,1-Diphenylethylene, Promoted by Nickel(0). To a solution of 620 mg (2.67 mmol) of benzyl phenyl sulfone in 20 mL THF was added dropwise 1.70 ml (2.67 mmol, 1.6M in hexane) of n-butyllithium at 25°C. The solution immediately changed from colorless to orange. Thereupon a solution of 2 ml of 1,1-diphenylethylene (2.04 g, 11.3 mmol) and 20 mg nickel(II) acetylacetonate (7.79×10^{-5} mol) in 5 ml THF was added. The reaction flask was carefully covered with aluminum foil and the reaction was allowed to proceed at 25°C for 7 days. After the usual hydrolytic work-up and flash column chromatography separation, 200 mg of 1,1,2-triphenylcyclopropane (30%) was isolated. Characterization of 1,1,2-triphenylcyclopropane; ^{1}H NMR ($CDCl_3$): δ(ppm) 1.7 (q, 1H); 1.9 (, 1H); 2.8 (q, 1H), 6.8-7.3 (m, 15H); ^{13}C NMR ($CDCl_3$): δ(ppm) 20.9, 32.4, 39.3, 125.6, 125.9, 126.2, 127.4, 127.9, 128.3, 128.5, 129.2, 131.0, 131.2, 138.7, 140.2, 147.0.

Reaction of (Bpy)(Cod)Ni with 1,2,3-Triphenylcyclopropene. To the violet solution resulting from admixing $(Cod)_2Ni$ (480 mg, 1.75 mmol) with 2,2′–bipyridine (270 mg, 1.75 mmol) in 20 ml THF was added 470 mg of 1,2,3-triphenylcyclopropene (1.75 mmol) in 5 ml THF at 25°C. The solution, which changed to deep green immediately, was allowed to stir at 25°C for 15 hours and then heated at reflux for 1 hour. The reaction mixture was concentrated *in vacuo* and the residue analyzed by ^{13}C NMR in dry C_6D_6 (no $(CH_3)_4Si$ added). A prominent peak appeared at 251 ppm. The reaction mixture was quenched with degassed 6N HCl under argon in the usual manner. The 1,2,3-triphenylcyclopropenes (Z: E = 4:1, estimated from NMR) were isolated by means of flash column chromatography.

Reaction of $(Et_3P)_4Ni$ with 1,2,3-Triphenylcyclopropene in the Presence of Diphenylacetylene
To the mixture of 1,2,3-triphenylcyclopropene (3870 mg, 1.42 mmol) and diphenylacetylene (252 mg, 1.42 mmol) in 30 ml toluene was added 750 mg of $(Et_3P)_4Ni$ (1.42 mmol) at 25°C. The reaction mixture was heated to reflux for 3 hours before quenching with degassed, 6N HCl. The work-up procedure was the same as described above. In addition to the (E)- and (Z)-triphenylcyclopropenes the 2,3-diphenylindene (70 mg, yield of 18%) was isolated by means of flash column chromatography. Some diphenylacetylene was also recovered (230 mg, 91%). Characterization of 2,3-diphenylindene: ^{1}H NMR ($CDCl_3$): δ(ppm) 3.92 (s, 2H), 7.23-7.40 (m, 14H); ^{13}C NMR ($CDCl_3$): δ(ppm) 41.22, 120.39, 123.56, 125.05, 126.50, 126.90, 127.37, 128.15, 128.30, 128.78, 129.38, 136.10, 136.60, 139.96, 141.10, 142.39, 146.95; DEPT-135 ($CDCl_3$, gives $CH\oplus$, $CH_2\ominus$, $CH_3\oplus$): δ(ppm) 41.21 ($CH_2\ominus$), 120.39, 123.57, 125.05, 126.50, 126.91, 127.37, 128.17, 128.30, 128.79, 129.39.

Reaction of 1,2,32-Triphenylcyclopropene with Diphenylacetylene, Catalyzed by Nickel(0). To a mixture of 1,2,3-triphenylcyclopropene (0.36 g, 1.34 mmol), 0.48 g of diphenylacetylene (2.68 mmol) and nickel(II) acetylacetonate (0.01 g, 4×10^{-5} mol) in 30 ml THF was added dropwise 0.13 ml ethylmagnesium chloride (0.27 mmol, 2.0M in Et_2O). The solution, which changed to dark brown immediately, was allowed to stir at 25°C for 3 hours and then heated at reflux for 2 hours. The work-up procedure was the same as described above. The 1,2,3,4,5-pentaphenylcyclopentadiene (100 mg, 17%; 44% based on the unrecovered cyclopropene) and hexaphenylbenzene (20 mg, 4%) were separated by flash column chromatography. Some diphenylacetylene (69%) and 1,2,3-triphenylcyclopropene (61%) were also recovered. Characterization of 1,2,3,4,5-pentaphenylcyclopentadiene: m.p. 253°C; ^{1}H NMR ($CDCl_3$): δ(ppm) 5.06(s), 7.13-7.50 (m); ^{13}C NMR ($CDCl_3$): δ(ppm) 62.62, 126.24, 126.45, 126.60, 127.60, 127.77, 128.37, 128.48, 128.93, 130.03, 135.71, 136.04, 137.99, 143.91, 146.44; MS m/e 446 (M^+), 119.

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