

Mechanistic Comparison of the Nickel(0)-Catalyzed Homo-Oligomerization and Co-Oligomerization of Alkynes and Nitriles^[‡]

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Dedicated on the occasion of his 75th birthday to Professor Günther Wilke, an outstanding pioneer in transition metal catalyzed organic synthesis

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A comparative mechanistic study of the nickel(0)-catalyzed homo-oligomerization and co-oligomerization of alkynes and of nitriles has been undertaken, with diphenylacetylene and benzonitrile, towards an array of nickel(0) reagents, such as finely divided nickel, (COD)₂Ni, (Bpy)(COD)Ni, (Et₃P)₄Ni, (Bpy)(PhC≡CPh)Ni and (COD)₂Ni–MeAlCl₂ combinations in donor (THF) and nondonor (PhMe or neat substrate) solvents. Special attention has been given to the detailed molecular structures of the initial 1:1 adducts, (Bpy)(PhC≡CPh)Ni, (Ph₃P)₃(PhC≡CPh)Ni and [(Ph₃P)(PhC≡N)Ni]₄ by a consideration of XRD and IR data. Data from the single crystal XRD analysis of (Bpy)(PhC≡CPh)Ni, reported here for the first time, are shown to be in excellent accord with the presence of a 2,3-diphenylnickelacyclopentadiene ring for the (PhC≡CPh)Ni moiety with almost coplanar chelating coordination of the bipyridyl ligand, rather than with the presence of simple “side-on” coordination of the alkyne with the metal center. A parallel analysis of XRD and IR data for the two benzonitrile-nickel(0) complexes, which were drawn from previous publications, has concluded that the nickel in (Ph₃P)₃(PhC≡N)Ni is coordinated in an “end-on” fashion and the nickel centers in [(Ph₃P)(PhC≡N)Ni]₄ are coordinated as bridges between nitrile units in both an “end-on” and “side-on” manner. The stereochemistry of the acid hydrolysis of the

nickelacyclopentadiene complex to (E)- or (Z)-alkene was shown to depend on the structure of the cleaving acid; parallel hydrolysis of nitrile-nickel complexes has shown that “end-on” complexes regenerate the nitrile, while “side-on” complexes lead to the aldehyde. In homo-oligomerization of diphenylacetylene or other alkyne the clean cyclotrimerization to the benzene derivative was shown to proceed by way of a nickelacyclopentadiene intermediate, as was evident by chemical trapping. The homo-oligomerization of benzonitrile by nickel(0) was found not to lead to 2,4,6-triphenyl-1,3,5-triazine, as claimed in the literature, but rather solely to benzyl phenyl ketone, the dimeric hydrolysis product. The attempted co-oligomerization of diphenylacetylene and benzonitrile with ordinary nickel(0) complexes led only to the homocyclotrimer of the alkyne. Only when the alkyne was prebonded to the nickel, as in (Bpy)(PhC≡N)Ni, could significant amounts of a codimerization product with the nitrile be observed. The origin of the triazine, claimed in a previous report to form from benzonitrile and Raney nickel, has been traced to the presence of adventitious moisture and air. Other unexpected products formed from nickel(0) complexes and benzonitrile have been shown to arise from oxidative addition reactions of nickel(0) with various σ C–E bonds.

Introduction

The nickel-catalyzed selective cyclooligomerizations of alkynes by Walter Reppe's group in the 1940s^[1] and the analogous cyclooligomerizations of 1,3-alkadienes by Günther Wilke and co-workers^[2] in the succeeding two decades were seminal discoveries in ushering in the current era of transition metal-mediated organic synthesis.^[3] Wilke's studies in particular, with their focus on detecting and trapping reactive intermediates and on probing the steric and electronic effects of metal ligands on reactivity, have pro-

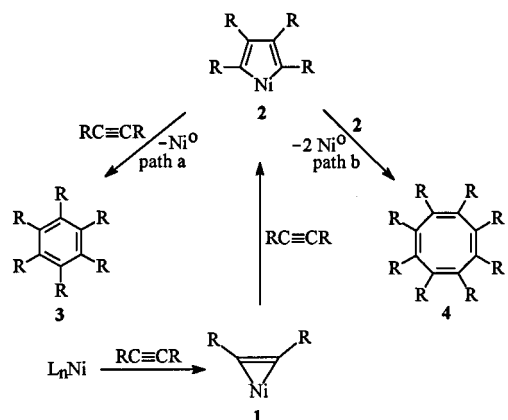
vided researchers in this flourishing field with a stellar paradigm for steering and optimizing such metal-catalyzed organic reactions.

Reppe's empirical findings that acetylene is principally cyclotrimerized into benzene by nickel(0) catalysts, such as (Ph₃P)₂(CO)₂Ni, but is largely cyclotetramerized into the unstable cyclooctatetraene by such nickel(II) salts as Ni(CN)₂^[1a,4] or by nickel(0) complexes having labile ligands [(COD)₂Ni]^[5] have long piqued the curiosity of many chemists. Subsequent detailed mechanistic studies of these oligomerizations have adduced cogent and persuasive evidence that reactive nickelacyclopentadiene (**1**) and nickelacyclopentadiene (**2**) rings are pivotal intermediates in both cyclooligomerizations and that trimerization to **3** or tetramerization to **4** hinges on whether **2** reacts with a third alkyne (path a) or undergoes autodimerization (path b) (Scheme 1).^[2c,6–13]

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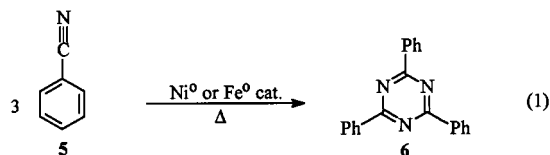


Scheme 1

The varying prevalence of path a or path b has been suggested to depend upon the ligands L_n on nickel and the substituents R on the acetylene monomer.^[12]

In light of the intricate mechanistic features involved in such oligomerizations, we were curious to learn to what extent organic nitriles or azaacetylenes, $R-C\equiv N$, might undergo similar homo-cyclooligomerization or co-cyclo-trimerization with alkynes by nickel metal catalysis. Two brief publications offered encouragement: benzonitrile (**5**) was reported to cyclotrimerize to 2,4,6-triphenyl-1,3,5-triazine (**6**) [Equation (1)] when heated at reflux with $Fe(CO)_5$ or $Fe_2(CO)_9$ ^[14] or when allowed to reflux with Raney nickel for many hours.^[15] However, attempts by other workers to reproduce the formation of triazine **6** over carefully dried and deoxygenated Raney nickel or even on pure nickel surfaces were unsuccessful.^[16] No reports of the nickel-catalyzed co-cyclo-trimerization of alkynes and nitriles have been found, even though such oligomerizations by cobalt catalysis are common and have received much attention.^[17] In the present report we establish that benzonitrile can be co-dimerized with an alkyne but only by intermediacy of an alkyne-nickel(0) complex. Furthermore, benzonitrile can indeed be oligomerized by nickel(0) com-

plexes but in an entirely different manner not involving the formation of triazine **6**. The structural and electronic reasons for these divergent oligomerization pathways followed by alkynes and by nitriles under nickel(0)-mediation will be elucidated in light of the actual and probable organonickel intermediates.



Results and Discussion

Structures of Initial 1:1 Complexes of Nickel(0) with Alkynes or with Nitriles

Such cyclotrimerizations of alkynes have as their common starting intermediate 1:1 adducts with nickel(0) that have been isolated, where appropriate ligands are present, and characterized by spectroscopic and single crystal X-ray structural analyses. Here we present such characterization of 2,2-bipyridyl(η^2 -diphenylacetylene)nickel (**7**), where an essentially planar interaction of both the bipyridyl group and the $C\equiv C$ bond with the nickel center is evident (Figure 1). The average Ni–C (acetylenic) separation of 1.86 ± 0.01 Å is comparable with *sigma* Ni–C bonds involving sp^2 -hybridized carbon centers, such as the Ni–C bond of 1.89 ± 0.01 Å in structure **8**.^[18] Moreover, the supposed acetylenic C–C separation of 1.30 ± 0.005 Å is more congruent with the presence of a C=C rather than a $C\equiv C$ bond in **7**.^[19] (Table 1). Finally, complex **7** displays a sharp absorption at 1770 cm^{-1} in its infrared spectrum, shifted by 330 cm^{-1} to lower frequencies than the $C\equiv C$ stretch of unsymmetrically substituted alkynes such as phenylacetylene. An absorption of 1770 cm^{-1} in complex **7** is in much closer agreement with a C=C bond stretching vibration,

Professor Günther Wilke was born in Heidelberg, Germany, on February 23, 1925, where he was to obtain both the Abitur at the Humanistisches Gymnasium and the doctorate degree in 1951 at the Universität Heidelberg upon completion of structural studies on lignin under the direction of Professor Karl Freudenberg. Shortly thereafter, he joined Karl Ziegler's research group as scientific assistant at the Max-Planck-Institut für Kohlenforschung in Mülheim (Ruhr) and participated in bringing Ziegler's recent discoveries in organoaluminum chemistry and low-pressure ethylene polymerization to economic fruition. Since his curiosity was strongly aroused by the seminal discovery of the Nickel Effect by Ziegler and Holzkamp, he launched his independent research program in 1956 with the systematic investigation of the effect of nickel and other transition metals on reactions of main-group organometallics. Over the next 40 years he pursued the exciting and unforeseen ramifications of such research, which have led to the novel template syntheses of medium-sized carbocycles, the regioselective oligomerizations of alkenes and alkadienes as well as the asymmetric syntheses of carbon skeletons. Interwoven with such discoveries have been many pioneering mechanistic studies that have elucidated the governing roles of the transition metal and its ligands in these novel carbon-carbon bond coupling processes. During the period of 1969–1993 as successor to Karl Ziegler, he directed the MPI during a flourishing period of expansion of its research activities and facilities. In over 220 publications and numerous patents he disseminated the classic research results of his many doctoral students and published with Peter Jolly the authoritative, two-volume treatment of "The Organic Chemistry of Nickel" (1974, Academic Press). Among many honors for his scientific discoveries may be cited the Ruhr-Preis für Kunst und Wissenschaften and both the Emil Fischer Medaille and the Karl-Ziegler-Preis of the Gesellschaft Deutscher Chemiker. His outstanding enthusiasm and skill in the art of laboratory experimentation finds a fitting parallel in his keen interest in and a notable private collection of contemporary art. As a young scientist it was this senior author's pleasure and honor to work closely with Günther Wilke, the master experimentalist, during a yearlong postdoctoral fellowship in Professor Ziegler's institute in 1956.

which in unconjugated disubstituted *cis*-alkenes absorb near 1670 cm^{-1} . Accordingly, a nickelacyclopropene or nickelirene structure seems to be a more important resonance structure contributor (**7a**) with a nickel(II) oxidation state than does resonance structure **7b** where the nickel center is viewed as in a Ni(0) oxidation state and as only accepting electron density from its ligand donors, diphenylacetylene and 2,2-bipyridyl. As will be evident, the nickelirene structure **7a** also proves to be the more useful molecular model for understanding the courses of chemical reactions undergone by **7** with various electrophilic or unsaturated organic reagents.

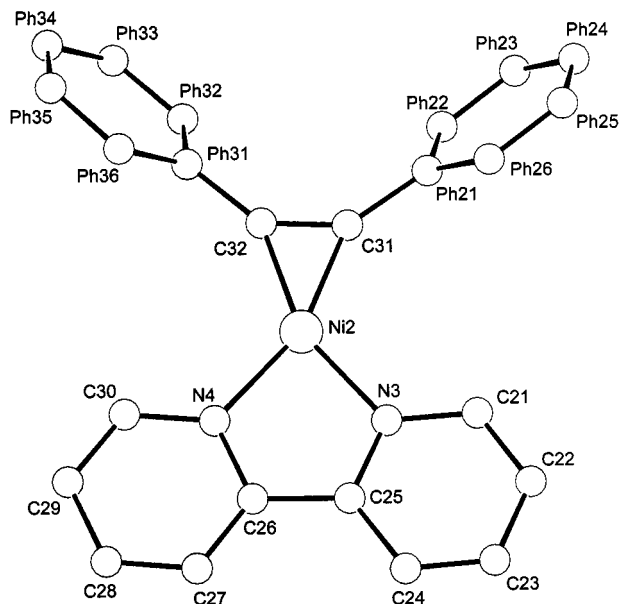
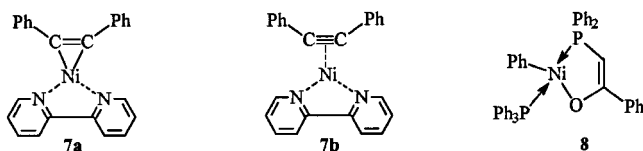
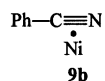
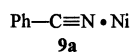


Figure 1. Structure and atom numbering of one of the independent molecules of 2,2-bipyridyl (η^2 -diphenylacetylene)nickel found in the asymmetric unit cell of **7**



A number of spectroscopic and single crystal X-ray structural analyses of 1:1 adducts of benzonitrile with nickel(0) complexes have been published. The two XRD studies are most valuable in establishing that the nickel(0) center can coordinate with the nitrile group in both an “end-on” (**9a**) and a “side-on” (**9b**) manner.



As was established in the structure of (benzonitrile)tris(triphenylphosphane)nickel(0) (**10**), “end-on” coordination of Ni⁰ was evident (Ni–N bond length of $1.89 \pm 0.011\text{ Å}$ and Ni–N–C bond angle of $173 \pm 7^\circ$).^[20] Similarly, the

Table 1. Selected bond lengths and angles of 2,2'-bipyridyl(η^2 -diphenylacetylene)nickel (**7**)

Bond lengths [Å] ^[a]	Min. value	Max. value	Av. value
C ₁₁ –C ₁₂	1.296	1.306	1.301
C ₃₁ –C ₃₂	1.289	1.299	1.294
Ni ₁ –C ₁₁	1.854	1.860	1.857
Ni ₂ –C ₃₁	1.843	1.849	1.846
Ni ₁ –C ₁₂	1.866	1.872	1.869
Ni ₁ –C ₃₂	1.856	1.862	1.859
C ₁₁ –Ph ₁	1.445	1.455	1.450
C ₃₁ –Ph ₂₁	1.458	1.468	1.463
C ₁₂ –Ph ₁₁	1.446	1.456	1.451
C ₃₂ –Ph ₃₁	1.450	1.460	1.455

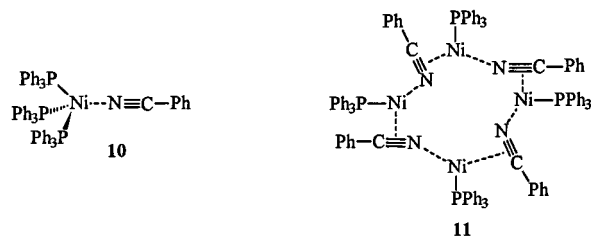
Bond angles [°]

C ₁₁ –Ni ₁ –C ₁₂	40.8	41.0	40.9
C ₃₁ –Ni ₂ –C ₃₂	40.8	41.0	40.9
Ni ₁ –C ₁₁ –C ₁₂	69.9	70.3	70.1
Ni ₂ –C ₃₁ –C ₃₂	69.9	70.3	70.1
Ni ₁ –C ₁₂ –C ₁₁	68.9	69.3	69.1
Ni ₂ –C ₃₂ –C ₃₁	68.8	69.2	69.0

^[a] The pairwise grouping of bond lengths and bond angles in the Table are the measured values for the two independent molecules of **7** found in the asymmetric cell. The first value in each pair is for the molecular and the atom numeration shown in Figure 1. The second value in each pair is that of the second molecule not shown in any figure. However, the atom numeration in the second molecule has the following atom correspondence to molecule one/ C₁₁ = C₃₁; C₁₂ = C₃₂; Ni₁ = Ni₂; Ph₁ = Ph₂₁; Ph₁₁ = Ph₃₁.

structure of the clathrate compound, tetrakis[(benzonitrile)-(triphenylphosphane)nickel(0)] (**11**),^[21] incorporating various hydrocarbon solvent molecules, actually has the Ni⁰ centers simultaneously coordinated to adjacent benzonitrile units in an “end-on” and a “side-on” manner (**11**, schematically drawn). Since complexes **10** and **11** are in equilibrium with each other, one can conclude that “end-on” coordination of the nickel center is the stronger primary binding mode with the nitrile group and that “side-on” bonding is only ancillary to it. The “end-on” Ni–N bond length of 1.90 Å is similar to that in **7** but the Ni–N–C bond angle at 167° deviates more from linearity. The “side-on” Ni–C bond length at 1.85 Å is comparable to Ni–C bonds with sp³-hybridized carbons (vide supra).

Infrared spectral data on complexes **10** and **11** provide a useful insight into such “end-on” and “side-on” coordination. The nitrile stretch in uncomplexed benzonitrile at 2230 cm^{-1} is lowered to 2150 cm^{-1} by “end-on” coordination as in **10**.



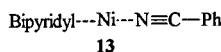
On the other hand, complex **11** displays a strong band at 1850 cm^{-1} . Again, such a stretching frequency lies much closer to a C=N stretch ($1470\text{--}1690\text{ cm}^{-1}$) than to a C≡N

stretch ($2100\text{--}2200\text{ cm}^{-1}$). Thus, it again appears that for such “side-on” coordination, the resonance contribution of a nickel(II) system, namely, azanickelacyclopentene (**12a**) would seem to be more important than that of a nickel(0) *pi*-complex (**12b**).



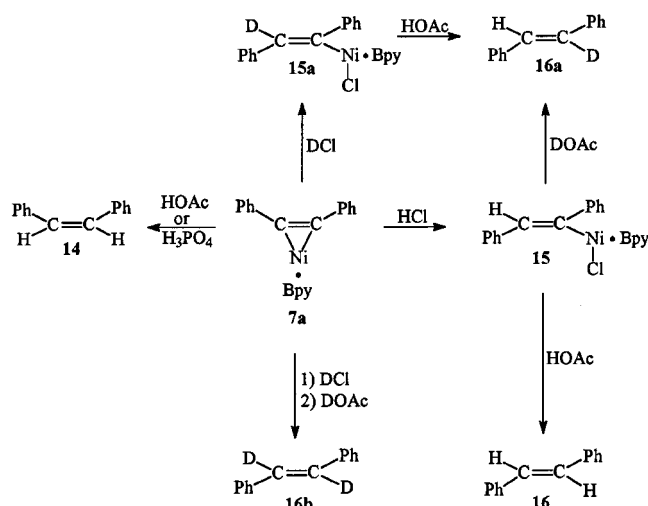
As confirmation of the importance of structure **12a** is the observed C–N bond length of 1.26 Å , considerably longer than the C≡N bond (1.16 Å) and very comparable with those of C=N linkages ($1.26\text{--}1.30\text{ Å}$).^[21]

These infrared data from nickel(0)-benzonitrile complexes of known structure can now conversely be used to evaluate the type of bonding in unknown structures. Thus the complex, (benzonitrile) (2,2-bipyridyl)nickel(0) (**13**), which has a sharp absorption at 2105 cm^{-1} must have “end-on” coordination.^[22] This is undoubtedly the complex formed initially when (2,2-bipyridyl)(1,5-cyclooctadiene) nickel(0) interacts with benzonitrile (vide infra).



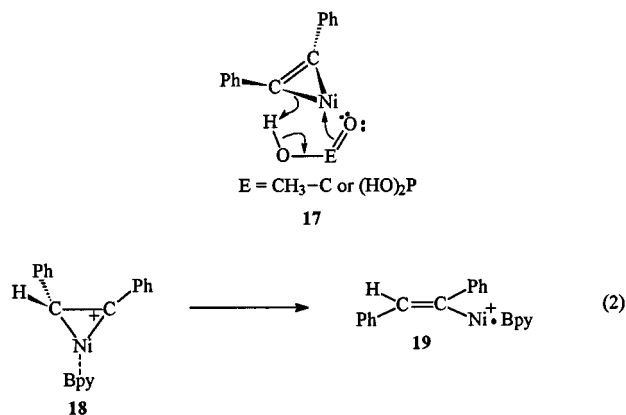
Protonolysis of the Initial 1:1 Complexes of Nickel(0) with Alkynes or with Nitriles

The stereochemical course of the protonolysis of 2,3-diphenylnickelirene-2,2-bipyridyl (**7a**) depends strikingly upon the solvent and the specific nature of the proton source. When **7a** was treated with 85% H_3PO_4 in THF or with glacial HOAc, almost quantitative yields of only *cis*-stilbene (**14**) were obtained. On the other hand, when the protonolysis was conducted with 6N aqueous HCl, a pale red precipitate of $\text{PhCH}=\text{CPh}(\text{NiCl}\cdot\text{Bpy})$ (**15**) was formed almost immediately in 90% yield. The remaining 10% of the starting material had been converted into a 9:1 mixture of *cis*- and *trans*-stilbenes. The stereochemistry of the stilbenyl C–Ni bond in intermediate **15** was established by treating **15** first with HOAc and determining that only *trans*-stilbene (**16**) was produced. Then in a separate experiment **15** was treated with DOAc with the result that *trans*-stilbene- d_1 (**16a**) was formed. Since HOAc did not cause isomerization of the stilbenyl group in the protonolysis of **7a**, it is reasonable that it would not cause isomerization in the protonolysis of intermediate **15**. Therefore, isomerization of the stilbenyl group must have occurred during the formation of **15** from **7a** under the action of HCl. That only one proton is added in the formation of **15** from **7a** was verified by treating **7a** with DCl. The deuteriated **15a** formed was treated in separate experiments with either HOAc or DOAc. Both experiments generated only *trans*-stilbenes but the former experiment gave the d_1 -isotope (**16a**) while the latter only the $\text{d}_{1,2}$ -isotope (**16b**). These interrelated reactions are depicted in Scheme 2.



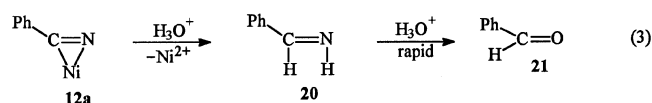
Scheme 2

A congruent explanation for the retention of configuration on the protonolysis of the first C–Ni bond in **7a** by acetic acid or by phosphoric acid may lie in the ability of these acids to deliver a proton via a six-membered coordinated transition state (**17**). By contrast, the ionic transition state **18**, formed by HCl in water, can easily isomerize by ring-opening, to form the sterically most stable ion (**19**) [Equation (2)]:



Up to the present work, little has been known about the course of protonolysis of “end-on” or “side-on” nickel-nitrile complexes. It has been reported that complex **13**, which can now be assigned an “end-on” structure, regenerates benzonitrile essentially quantitatively after being treated with a weak acid like acetylacetone. Even dilute HNO_3 produces only recovered benzonitrile.^[22] Given the known resistance of nitriles to reduction or to hydrolysis, this result may not be surprising. In the present work it is therefore noteworthy to report that the treatment of benzonitrile in THF with nickel complexes, such as $(\text{COD})_2\text{Ni}$, $(\text{Bpy})(\text{COD})\text{Ni}$ or $(\text{Et}_3\text{P})_4\text{Ni}$ and hydrolytic workup produces benzaldehyde in yields of 5–15%. We conclude that such benzaldehyde must have arisen from the hydrolysis of a “side-on”-coordinated nickel complex like **12a**, which can

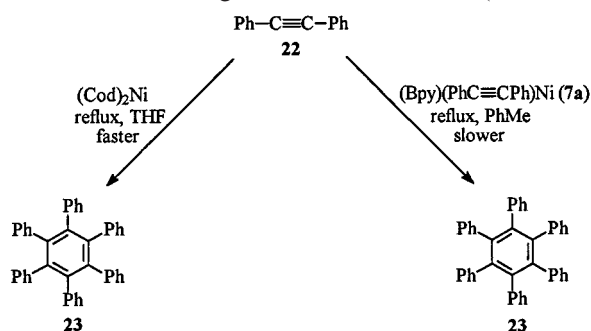
be considered as having much azanickelacyclopropene character (vide supra). The intermediate benzaldehyde imine (**20**) should hydrolyze easily to benzaldehyde (**21**) [Equation (3)].



Oligomerization Reactions of Alkynes and Nitriles by Nickel(0) Complexes

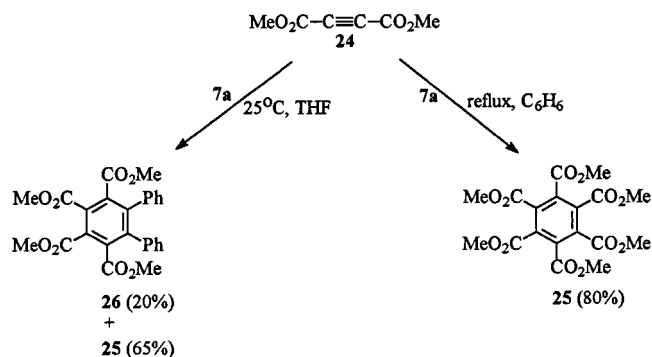
Oligomerizations with (2,2'-Bipyridyl)(diphenylacetylene)-nickel(0) (**7a**)

Complex **7a** catalyzes the cyclotrimerization of diphenylacetylene (**22**) to hexaphenylbenzene (**23**) in refluxing toluene but at a significantly slower rate than with (COD)₂Ni as catalyst, which effects comparable conversions to **23** in refluxing THF in half the time (Scheme 3).



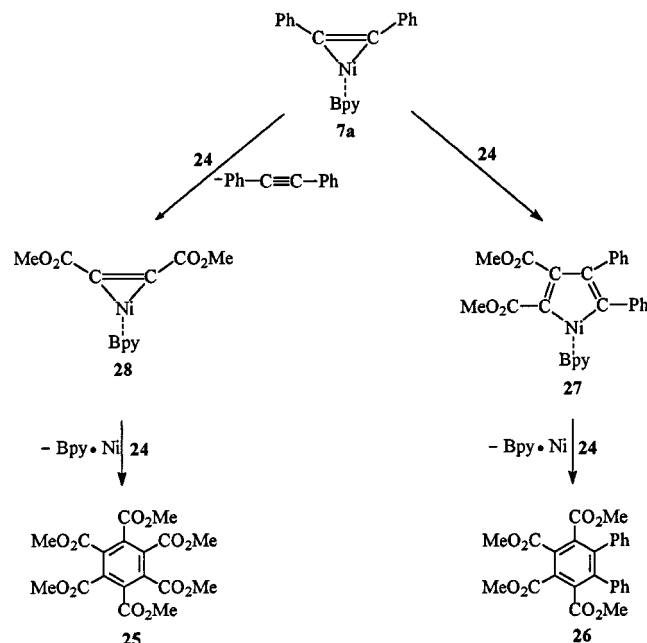
Scheme 3

The cyclotrimerization of dimethyl acetylenedicarboxylate (**24**) catalyzed by **7a** to hexamethyloxycarbonylbenzene (**25**) occurs in refluxing benzene faster than that of **22** in refluxing toluene. When the cyclotrimerization of **24** with **7a** was carried out at 25 °C in THF, up to 20% of the product was the mixed cyclotrimer, 1,2,3,4-tetramethyloxycarbonyl-5,6-diphenylbenzene (**26**) (Scheme 4). This finding supports the conclusion that at lower temperatures some of complex **7a** is stable and undergoes insertions of **24**, ultimately leading via **27** to **26**. At higher temperatures especially, **7a** decomposes with the transfer of Bpy·Ni to **24** with the formation of **28**, which leads to the formation of **25** (Scheme 5). These findings support the previously proposed



Scheme 4

hypothesis that nickelirenes, such as **7a** and **28**, are discrete and crucial intermediates in the cyclooligomerization of alkynes by nickel(0) complexes.^[11–13]



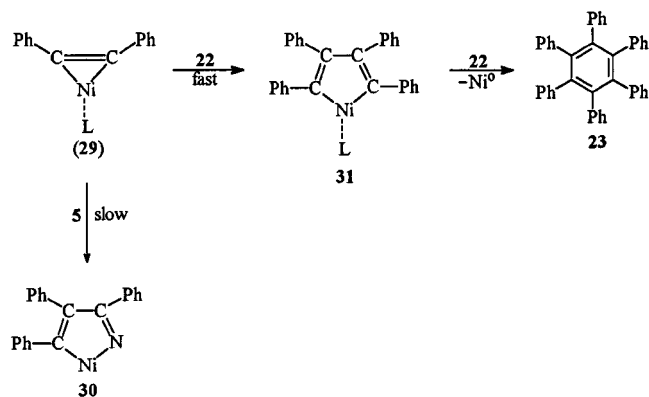
Scheme 5

Attempted Co-oligomerizations of Diphenylacetylene (**22**) and Benzonitrile (**5**) by Nickel(0) Complexes

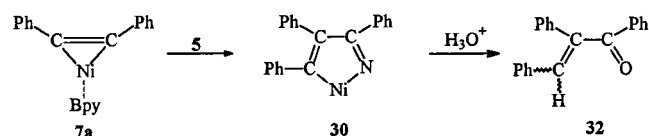
The interaction of a 2:1 mixture of **22** and **5** with one equivalent of (COD)₂Ni in refluxing THF led to a 65% yield of hexaphenylbenzene (**23**) and 3% of *cis*-stilbene (**14**) but no discernible oligomer involving incorporation of benzonitrile, such as pentaphenylpyridine. This result implies that benzonitrile cannot compete with diphenylacetylene in the crucial insertion step with the nickelirene intermediate **29** (L = COD) (Scheme 6 depicting the competitively faster formation of **31** and hence **23** from **7a** and the much slower formation of **30**, which would lead to pentaphenylpyridine). The validity of this inference was substantiated by subjecting the more stable and less reactive nickel complex **7a** to the action of benzonitrile alone in THF at 25 °C, without any competing alkyne. Indeed, hydrolytic workup gave up to 40% of the *cis*- and *trans*-isomeric 1,2,3-triphenylpropen-1-ones (**32**), convincing evidence that azanickelole **30** had formed from **7a** by insertion of benzonitrile (Scheme 7).

Attempted Homo-Oligomerizations of Benzonitrile (**5**) by Nickel(0) Complexes

Many careful and systematic variations have been attempted to reproduce the reported cyclotrimerization of **5** over Raney nickel in refluxing benzonitrile with the formation of 2,4,6-triphenyl-1,3,5-triazine (**6**) [Equation (1)].^[15] To avoid possible contaminants present in the typical samples of Raney nickel, such as aluminum metal and NaOH, as well as moisture and dihydrogen, the attempted



Scheme 6.



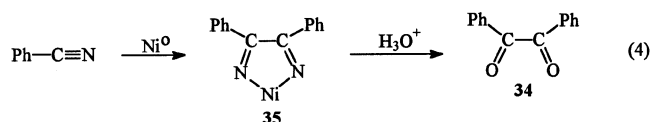
Scheme 7

oligomerizations were also carried out with pure nickel metal powders, prepared under argon by the alkylative reduction of nickel salts with *n*-butyllithium in THF at -78°C . In the complete absence of traces of oxygen and of moisture, such nickel metal led to little or no **6** even after 2 days at 190°C . Only when moist air was admitted during reflux did noticeable amounts of **6** form (5–10% of **5**) and other unusual reaction products appear (vide infra). We are forced to agree with the conclusion of Oehme and Praejeus^[16] that a pure nickel metal surface is incapable of catalyzing the cyclotrimerization of benzonitrile under the conditions reported by Heldt.^[15]

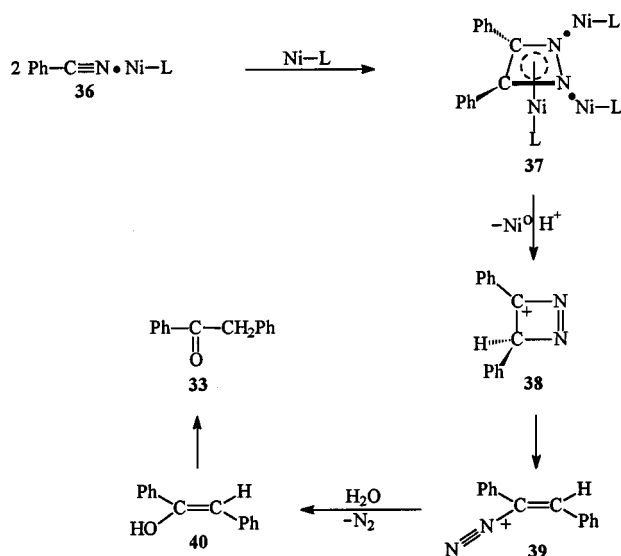
Since our previous experience with the coupling and cleavage reactions of nickel(0) complexes has shown that such reactions are especially favored in donor solvents at or below 25°C , we then undertook a study of the reaction of benzonitrile with nickel(0) complexes in THF. As reported above, protonolysis of such reaction mixtures gave benzaldehyde (**21**), most likely stemming from the protonolysis of a “side-on” complex [Equation (3), **12a**]. But an additional, most surprising hydrolysis product was also isolated, namely benzyl phenyl ketone (**33**). No trace of any other dimeric or trimeric product, such as benzil (**34**) or triazine **6** was detected. The yields of benzaldehyde and benzyl phenyl ketone obtained with different ratios of (COD)₂Ni and nitrile are noteworthy: with a 1:2 (COD)₂Ni:**5** ratio, the yields of **21** and **33** were 13% and 15%, with 70% of nitrile **5** remaining. When a reverse ratio of 2:1 (COD)₂Ni:**5** was employed, all of the benzonitrile was consumed and again only **33** and **21** were found in the reaction products, this time in a ratio of 96:4.

These results show that the formation of ketone **33** is fostered by the stoichiometric action of more than one nickel atom per nitrile. Clearly, when a 1:2 (COD)₂Ni:**5** ratio is employed, (COD)₂Ni is the limiting reagent and hence only about one-third of the benzonitrile can react. In ex-

plaining the origin of ketone **33**, we suggest that the coupling of the nitrile carbons must occur in an unusual manner, certainly not involving a straightforward reductive dimerization as depicted in Equation 4.^[23] Were such an ordinary reductive coupling to have occurred, an intermediate diazanic nickelole (**35**) would have formed and would undoubtedly have hydrolyzed to benzil (**34**), a product noteworthy by its absence in this reaction.



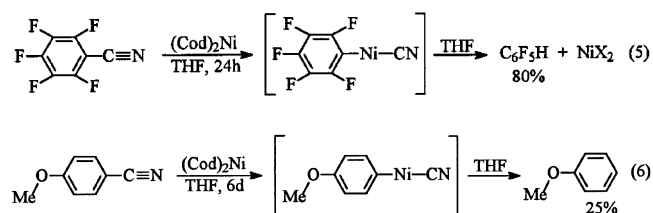
To account for the formation of ketone **33**, therefore, we propose a cyclodimerization of two “end-on”-coordinated nickel(0) complexes of benzonitrile (**36**) by agency of nickel(0) to form a (3,4-diphenyl-1,2-diazacyclobutadiene)nickel(0) complex of type **37**. Protonolytic decomposition of **37** would reasonably be expected to lead via **38**–**40** to ketone **33** (Scheme 8). Currently, our efforts are directed toward isolating a suitably ligated derivative of **37** for confirmatory XRD and protonolysis studies. There is ample precedent for the stable complexation of the cyclobutadiene ring with nickel(0), typified by (η⁴-tetraphenylcyclobutadiene)bis(triethylphosphane)nickel(0), whose structure has been confirmed by an XRD study.^[11] Also, the mode of protonolytic cleavage of this latter structure partly resembles that of **35**: glacial acetic acid leads to the formation of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene.



Scheme 8

Although such complexations between benzonitrile and nickel(0) are relatively stable at 25°C , they are easily disrupted at higher temperatures. For example, conducting the reaction of (Bpy)(COD)Ni with benzonitrile in THF at 25°C gives, upon hydrolysis, 20% of ketone **33**, whereas the same reaction conducted in refluxing THF gives no trace of **33**. Even at room temperature, such reactions can lead to decyanation of the nitrile, especially those nitriles with

electron-withdrawing substituents, as shown in Equation (5). With electron-donating substituents, oxidative addition of C–CN bonds to nickel(0) occurs more slowly [Equation (6)].



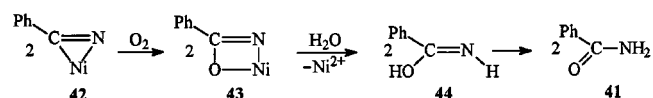
The usual aryl aldehyde and substituted benzyl phenyl ketone were also detected upon hydrolysis of the latter reaction mixture.

During our attempts to reproduce the cyclotrimerization of benzonitrile reported by Heldt^[15] as occurring on nickel metal in refluxing **5**, we did observe significant decyanation, as was evident by low recovery of **5** (<50%) and by the detection of cyanide ion in the hydrolysis products with the “Prussian Blue” test.

Significant, Unexpected Reactions Occurring between Benzonitrile and Nickel(0) Complexes

Formation of Benzamide (41) and 2,4,6-Triphenyl-1,3,5-triazine (6)

From the present study and the previous work of Oehme and Pracejus^[16] it is clear that under a completely inert atmosphere and anhydrous conditions neither a clean nickel surface nor a nickel(0) complex reacts with pure benzonitrile at temperatures up to 200 °C to produce any triazine **6**. However, in the presence of adventitious moist air such nickel(0) complexes convert the nitrile to benzamide (**41**) even at 25 °C. Nickel(II) salts, in turn, have been shown to convert benzamide into the triazine **6** at elevated temperatures.^[16] The so-called catalytic hydration of nitriles to amides, reported over 40 years ago, involves heating aqueous suspensions of amides with nickel metal catalysts of the Raney or Urushibara type under an air atmosphere.^[24] In the light of our present findings, we can now propose a rational reaction mechanism involving the formation of a “side-on” complex on the nickel surface (**42**, with **5**), its air-oxidation to **43** and the hydrolysis via enamine **44** to the amide **41** (Scheme 9). In keeping with the intermediacy of **42**, significant reduction of the nitrile to the amine or even reductive cleavage to ammonia has been observed.

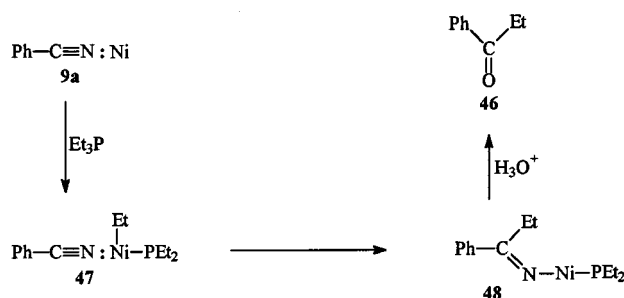


Scheme 9

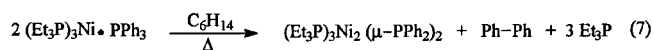
Ethylation of Benzonitrile (5) in the Presence of Tetrakis(triethylphosphane)nickel(0) (45)

As with other nickel(0) complexes, the triethylphosphane complex **45** reacted with benzonitrile to produce small

amounts of benzaldehyde (5%) and benzyl phenyl ketone (10%) upon hydrolysis. But, surprisingly, ethyl phenyl ketone (**46**) was also formed in 60% yield. Since the only discernible source of the ethyl group is the Et₃P ligand, we are led to suggest that the Ni(0) center, in the presence of benzonitrile (**9a**) undergoes an oxidative addition into the ethyl-phosphorus bond of a Et₃P unit (Scheme 10). Decomposition of **47** in either a heterolytic or a homolytic fashion would yield **48**, whose hydrolysis would provide ketone **46**. Although an unusual reaction for phosphane complexes themselves at 25 °C, the following C–P bond cleavage reaction has been observed in refluxing hexane [Equation (7)].^[25] Clearly an oxidative addition to the Ni(0) center must be involved. Pending further study, it remains unclear as to whether such reactions are promoted by light or radical sources.



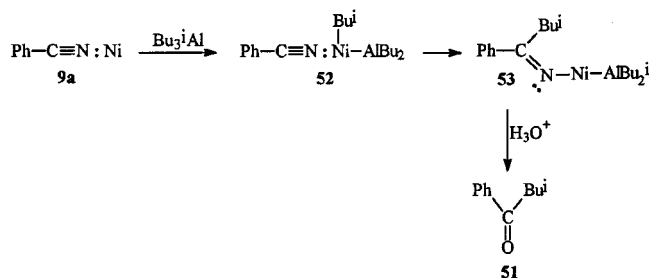
Scheme 10



Isobutylation of Benzonitrile (5) by Triisobutylaluminum (49) in the Presence of Bis(1,5-cyclooctadiene)nickel(0) (50)

Nitriles react with diisobutylaluminum hydride at 20–25 °C to give aldehydes upon hydrolysis but they do not react with triisobutylaluminum at such temperatures. Only when nitriles are heated with Bu₃Al does reaction occur but then hydroalumination, rather than carbalumination, is the observed outcome, leading again to aldehydes or primary amines.^[26] Therefore, the extraordinary reaction of benzonitrile with 1:1 mixture of Bu₃Al and (COD)₂Ni to yield isobutyl phenyl ketone (**51**) in 42% yield deserves particular attention. Such a yield results from reactions of 1:1:1 mixtures of the reactants conducted in toluene either over seven days at 25 °C or 24 hours at reflux. Traces of benzyl phenyl ketone (**33**) and benzophenone (1–5%) were also detected.

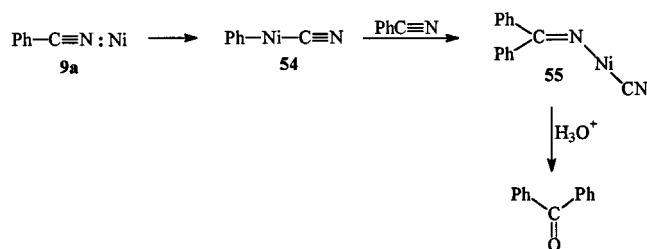
To account for the formation of ketone **51**, an oxidative addition of the Ni(0) center of **9a** into the isobutyl-aluminum bond is reasonable, similar to that depicted in Scheme 10 to form **52** which decomposes in an analogous fashion to **53**, whose hydrolysis would yield **51** (Scheme 11). That the yield of **51** levels off under 50% may be a consequence of strong Lewis base (**53**) complexing with half of



Scheme 11

the available Bu_3iAl and preventing it from reacting with **9a**. As to the mechanism of reaction, there is evidence from the reaction of diphenylacetylene with 1:1 combinations of iBu_3Al and $(\text{COD})_2\text{Ni}$ that both photochemical- and radical-promoted processes may be operative.^[27]

The small but significant yield of benzophenone is noteworthy: the above-mentioned oxidative addition of $\text{Ni}(0)$ into aryl-cyano bonds [Equations (5) and (6)] is undoubtedly the cause. At 25°C the resulting phenylnickel cyanide (**54**) would be sufficiently stable to add to the nitrile **5** to form adduct **55**, whose hydrolysis would lead to benzophenone (Scheme 12):



Scheme 12

Conclusions

These parallel studies of the homo-oligomerization and co-oligomerization of alkynes and nitriles show how pivotal the initial 1:1 adduct of nickel(0) and the triple-bonded substrate is on the course of such oligomerizations. With alkynes the reactive “side-on” complex can best be viewed as a nickelacyclopentene or nickelirene both in terms of its molecular structural properties and its chemical reactions. The 1:1 nickel(0) complex with nitriles can be “end-on” as well as “side-on” (azanickelacyclopentene) with evidence existing that “end-on” complexation is the more stable mode and the more important precursor to the homo-oligomerization, nickelodecyanation and several unusual addition reactions of nitriles. In the co-oligomerization of alkynes and nitriles the greater stability of the “side-on” complex of nickel(0) with the alkyne monomer over the corresponding “side-on” complex of nickel(0) with nitriles results in essentially exclusive homocyclotrimerization of the alkyne. Only in the absence of free alkyne can the nickelacyclopentene apparently be intercepted by the nitrile leading to a co-dimer with the alkyne. In the homo-oligomerization of nitriles the 1:1 “end-on” complexation with nickel(0) appears to lead to an unusual stoichiometric dimerization ap-

parently in the form of an η^4 -1,2-diazacyclobutadiene-nickel(0) precursor complexed in a “corner-on” fashion with two nickel(0) units.

Experimental Section

Instrumentation, Analysis and Starting Reagents: All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal-benzophenone ketyl mixture prior to use.^[28] The IR spectra were recorded with a Perkin–Elmer instrument, model 457 and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^1H and ^{13}C) were recorded with a Bruker spectrometer, model EM-360 and tetramethylsilane (TMS) was used as the internal standard. The chemical shifts reported are expressed in the δ -scale and in parts per million (ppm) from the reference TMS signal. The GC/MS measurements and analyses were performed with a Hewlett-Packard GC 5890/Hewlett-Packard 5970 Mass-Selective-Detector instrument. The gas chromatographic analyses were carried out with a Hewlett-Packard instrument, model 5880, provided with a 6 ft OV-101 packed column or with a Hewlett-Packard instrument, model 5890, having a 30 m SE-30 capillary column, respectively. Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. The $(\text{COD})_2\text{Ni}$ was prepared according to a procedure adapted from those of Semmelhack^[29] and of Schunn.^[30] The yield of product has been improved to 95% by purifying the starting materials with extreme care.

The $(\text{Et}_3\text{P})_4\text{Ni}$ was prepared according to the method of Cundy^[31] and the $(\text{Bpy})(\text{COD})\text{Ni}$ by the procedure of Dinjus et al.^[32] The complex, $(\text{Bpy})(\text{Ph}-\text{C}\equiv\text{C}-\text{Ph})\text{Ni}$ (**7**), was prepared according to the following modified procedure, which is based upon the method of Eisch and Piotrowski.^[33]

A suspension of $(\text{COD})_2\text{Ni}$ (2.91 g, 10.6 mmol) in 40 mL THF was treated with 2,2'-bipyridyl (1.70 g, 10.7 mmol) in 10 mL THF at 25°C and the reaction mixture stirred for 1 h. After the solvent was removed under reduced pressure, the viscous dark purple residue was dried under vacuum overnight. Then 50 mL of THF was introduced to dissolve this black-purple solid and diphenylacetylene (1.89 g, 10.6 mmol) in 20 mL of THF was then added dropwise. The reaction mixture was then stirred at 25°C for 15 h, after which time THF was removed under reduced pressure and the black viscous residue dried under vacuum for 16 h in order to remove the cyclooctadiene. Then 50 mL of THF was used to extract the residue and the mixture filtered. The filtrate was concentrated to about 20 mL and pentane was then introduced in small portions. After the first precipitation was observed, another 15 mL of pentane was added. The mixture was allowed to stand at 25°C for 2 h to complete the crystallization. The black crystalline solid was then filtered off and was washed with small portions of pentane three times and then dried under vacuum for 4 h. The yield of the product was 3.00 g (72%). Such crystals were employed for X-ray crystallographic structure determination. — IR (mineral oil): $\tilde{\nu}$ = 710(s), 730(s), 755(s), 765(m), 775(m), 850(w), 1025(s), 1490(m), 1570(w), 1590(s), 1740(br, w), 1770(m).

General Procedures: All steps in the preparation, transfer, and main reactions of the metal salts and organometallic reagents studied here were conducted under an atmosphere of anhydrous and oxygen-free argon. All solvents and apparatus were likewise freed of

traces of dissolved or adsorbed moisture and oxygen by published procedures and then maintained under argon. Methods and techniques for working under anhydrous and anaerobic conditions have been described previously.^[28] In the hydrolysis procedure employed for the workup of all nickel(0) reaction mixtures, it proved essential that the aqueous HCl be thoroughly free of oxygen and that both freeze-thaw cycles in vacuum and readmission of argon be conducted to that end. Because of the small-scale runs the presence of oxygen during hydrolysis greatly reduced the amounts of benzaldehyde and benzyl phenyl ketone isolated.

Protonolysis of (Bpy)(Ph–C≡C–Ph)Ni (7): A solution of **7** (1.00 g, 2.55 mmol) in 20 mL of THF under argon was treated with 10 mL of degassed 85% H₃PO₄ at 25 °C for 4 h to form an off-white precipitate and a blue solution. Hydrolytic workup gave an organic extract containing only *cis*-stilbene (**14**) (0.73 g, 95%), as determined by IR, ¹H and ¹³C NMR spectroscopy.

A similar solution of **7** was treated with degassed 6 N aqueous HCl with prompt formation of a pale red-colored precipitate, which corresponded to a 90% yield of PhCH=CPh(NiCl·Bpy) (**15**) based upon a Ni analysis of 14.0% (calcd. 13.63%), as well as a positive test for Cl anion upon sodium fusion, and IR spectroscopy: $\tilde{\nu}$ = 700(s), 740(s), 790(s), 910(m), 1040(m), 1080(m), 1500 (m, occurring in C=C–M groupings), 1540 (vw), 1580(w), 1600(m). The filtrate was shown by GC/MS analysis to contain *cis*- and *trans*-stilbenes (**14** and **16**) in a 9:1 ratio.

Treatment of the pale red solid **15** with glacial acetic acid in THF gave, upon hydrolytic workup, a quantitative yield of only *trans*-stilbene.

Finally, a 1.00-g sample of **7** in THF was treated with degassed 6 N DCl in D₂O to give the deuteriated pale red solid, PhCD=CPh(NiCl·Bpy) (**15a**). In separate reactions then, **15a** was treated either with HOAc in THF or with DOAc in THF. In the former reaction, only *trans*-stilbene-d₁, C₆H₅CD=CHC₆H₅ (**16a**), was formed. In the latter reaction, only *trans*-stilbene-d_{1,2}, C₆H₅CD=CDC₆H₅ (**16b**), was found.

Cyclotrimerization of Diphenylacetylene (22) by (Bpy)(Ph–C≡C–Ph)Ni (7): A sample of **7** (395 mg, 1.0 mmol) and diphenylacetylene (1.00 g, 5.6 mmol) was heated in refluxing toluene for 2 days. During this time a white precipitate formed in the dark red solution. After hydrolytic workup the solid was filtered off and shown to be hexaphenylbenzene (**23**) (0.75 g, 75%). – IR (mineral oil): $\tilde{\nu}$ = 700(m), 735(w), 790(w), 1380(m), 1465(s). – m.p. >400°C. The organic layer contained mainly unchanged **22** and traces of stilbenes **14** and **16**.

Cyclotrimerization of Dimethyl Acetylenedicarboxylate (24) by (Bpy)(Ph–C≡C–Ph)Ni(0): A sample of **7** (5.5 mmol, 2.17 g) and **24** (15 mmol, 2.13 g) was heated in refluxing benzene for 36 h. Usual hydrolytic workup provided an 80% yield (1.70 g) of hexamethyloxycarbonylbenzene (**25**), m.p. 186–188°C (from THF/H₂O), identified by MS and ¹H NMR spectroscopic data. Traces of stilbenes, but no hexamethylbenzene, were observed.

Co-cyclotrimerization of Dimethyl Acetylenedicarboxylate (24) and Diphenylacetylene Derived from (Bpy)(Ph–C≡C–Ph)Ni (7): A sample of **7** (5.9 mmol, 2.33 g) and **24** (13 mmol 1.85 g) dissolved in 30 mL of THF was stirred for 18 h at 25 °C. After hydrolytic workup and column chromatographic separation of the organic products on silica gel (40–60 mesh) with ethyl ether/hexane as the eluting solvent, the following products were obtained and identified by MS and ¹H NMR spectroscopic data: hexamethyloxycarbonyl-

benzene (65%) (**25**); 1,2,3,4-tetramethyloxycarbonyl-5,6-diphenylbenzene (**26**) (20%), m.p. 221–222°C. – ¹H NMR (CDCl₃): δ = 3.42 (s, 6 H), 7.03 (s, 5 H). – IR (mineral oil): $\tilde{\nu}$ = 710(s), 1000(m), 1100(s), 1210(m), 1460(s). – dimethyl fumarate (10%). – m.p. 102–103°C. – ¹H NMR (CDCl₃): δ = 3.78 (s, 6 H), 6.80 (s, 2 H); and *trans*-stilbene (5%).

Attempted Co-oligomerization of Diphenylacetylene (22) and Benzonitrile (5) in the Presence of (COD)₂Ni: To a solution of (COD)₂Ni (62.0 mg, 0.226 mmol) in 5 mL THF was added a mixture of benzonitrile (232 mg, 2.26 mmol) and diphenylacetylene (805 mg, 4.52 mmol) in 10 mL of THF. The reaction mixture was then stirred at 25 °C for 24 h. A 2-mL sample of the reaction mixture was hydrolyzed with 4 mL of 3N HCl. The organic layer was then neutralized with sodium bicarbonate and dried over magnesium sulfate. The solvent was removed under reduced pressure and the product mixture was analyzed by GC. Diphenylacetylene (conversion of 5%), benzonitrile (conversion of less than 1%) and *cis*-stilbene (yield of 3%) were identified by the co-injection of authentic samples.

The rest of the reaction mixture was heated at reflux for 24 h. After one hour of reflux a white solid separated and the color of the solution turned brown. When the reaction mixture was cooled to 25 °C, the crystalline solid was filtered off from the solution and washed twice with small amounts of THF. The organic layer was hydrolyzed with 20 mL of 3 N aqueous HCl and neutralized with aqueous NaHCO₃. The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. Analysis by GC showed the presence of diphenylacetylene (**22**) (33%), benzonitrile (**5**) (85%) and *cis*-stilbene (3%) (**14**). The white solid, 512 mg (65%), was confirmed to be hexaphenylbenzene (**23**) by the following spectral characterization: ¹H NMR (CDCl₃, TMS): δ = 6.84 (m). – ¹³C NMR (CDCl₃): δ = 125.13, 126.54, 131.36, 140.28 and 140.60 (m). – IR (KBr): $\tilde{\nu}$ = 559(vs), 690(vs), 728(vs), 780(vs), 1028(s), 1072(s), 1406(vs), 1448(vs), 1500(vs), 1607(vs), 3040(vs), 3070(s), 3090 (m) cm^{–1}. – MS (70eV): *m/z* = 534 [M]⁺. A mass spectral search for the parent ion of pentaphenylpyridine, 548, was negative.

Reaction of (Bpy)(PhC≡CPh)Ni (7) with Benzonitrile (5): A solution of (Bpy)(PhC≡CPh)Ni (228 mg, 0.580 mmol) in 10 mL THF was cooled to –78 °C, after which pure benzonitrile (107 mg, 0.598 mmol) was added dropwise. The reaction mixture was warmed to 25 °C and stirred at this temperature for 2 days. The reaction mixture was then heated at reflux for 6 h and then quenched with 20 mL of 2N aqueous HCl. The organic layer was neutralized with aqueous NaHCO₃ and dried over anhydrous MgSO₄. According to GC/MS analysis and co-injection with authentic samples (provided by American Peptid Corp., Sunnyvale, CA), the *cis*- and *trans*-1,2,3-triphenylpropen-1-ones (**32**) were found to be the main products. Total yield of the *cis*- and *trans*-isomers was 40%. *cis*-Stilbene (**14**) (53%) was also one of the main products. Minor products (≈2%) were 1,2,3,4-tetraphenyl-1,3-butadiene isomers and *trans*-stilbene. Spectral characterization of the products by GC-MS analysis follows: *cis*- and *trans*-1,2,3-triphenylpropen-1-ones: C₂₁H₁₆O: *m/z* = 284 [M]⁺, 179 [C₁₄H₁₁]⁺, 105 [C₇H₅O]⁺, 77 [C₆H₅]⁺, isomeric butadiene derivatives of MF, C₂₈H₂₂: *m/z* = 358 [M]⁺, 267 [C₂₁H₁₅]⁺, 179 [C₁₄H₁₁]⁺, 178 [C₁₄H₁₀]⁺. – IR spectrum (thin film): C=O absorption of 1,2,3-triphenylpropen-1-one at 1652 cm^{–1}.

Similar reactions were carried out in toluene both at 25 °C and under reflux. The workup procedures were identical with that of the reaction carried out in THF. For the reaction in toluene at 25 °C for 8 days, the *cis*- and *trans*-stilbenes **14** and **16** were the main

products with a *cis*- to *trans* ratio of 1.3:1.0 and the total yield in stilbenes of 68%. Also 31% of diphenylacetylene was recovered from the nickel complex. The reaction carried out in toluene under reflux for 8 h gave only 10% of *cis*-stilbene with 85% of the diphenylacetylene recovered. Traces (<2%) of hexaphenylbenzene were found but neither the 1,2,3-triphenylpropen-1-ones nor the 1,2,3,4-tetraphenyl-1,3-butadienes were detected.

Oligomerization of Benzonitrile (5) Mediated by Various Nickel(0) Complexes

By (COD)₂Ni: To a solution of (COD)₂Ni (289 mg, 1.05 mmol) in 10 mL THF was added benzonitrile (0.215 mL, 216 mg, 2.10 mmol) dropwise at 25 °C and the reaction mixture then stirred for 7 days. The color of the solution changed immediately from yellow to red and then slowly to dark-brown. Samples withdrawn at reaction times of 24 h, 48 h and 7 days were hydrolyzed with 3 N aqueous HCl, neutralized with aqueous NaHCO₃ and finally dried over anhydrous MgSO₄. The resulting product mixtures were analyzed by GC and GC-MS. After 7 days at 25 °C the main products were identified as benzaldehyde (**21**) (13%) and benzyl phenyl ketone (**33**) (15%) with the conversion of benzonitrile at about 30%. When small amounts of dry air were slowly admitted to the reaction mixture, variable amounts of benzamide were detected in the hydrolysis products. Characterization of benzyl phenyl ketone by GC:MS: C₁₄H₁₂O: *m/z* = 196 [M]⁺, 105 [C₇H₅]⁺, 91 [C₇C₇]⁺, 77 [C₆H₅]⁺.

A similar reaction run to the foregoing was conducted, except that a 2:1 ratio of (COD)₂Ni:5 was allowed to react in THF for 24 h. Hydrolytic workup showed that an 80% material recovery was obtained with the complete consumption of benzonitrile and the formation of a 96:4 molar ratio of **33:21**.

The reaction of benzonitrile with (COD)₂Ni was also conducted in neat benzonitrile. Thus, freshly distilled and degassed benzonitrile (3 mL, 29.4 mmol) was added to (COD)₂Ni (245 mg, 0.892 mmol) at 0 °C whereupon the reaction mixture changed immediately from yellow to bright red. After 10 min at 0 °C 15 mL of 3N hydrochloric acid was added. The usual workup procedure showed that 10% of benzaldehyde but less than 5% of benzyl phenyl ketone was formed. The same reaction carried out at 25 °C over 24 h yielded no **33** and only 10% of benzaldehyde.

By (COD)₂Ni and *i*Bu₃Al: The dropwise addition of *i*Bu₃Al (0.25 mL, 1.00 mmol) to a solution of (COD)₂Ni (275 mg, 1.00 mmol) in 10 mL of toluene turned the initially yellow solution brown. Subsequent introduction of benzonitrile (0.10 mL, 1.00 mmol) caused the gradual development of a red color. The resulting mixture was stirred for 7 days, hydrolyzed and after the usual workup analyzed by GC-MS procedures. A 42% yield (68 mg) of isobutyl phenyl ketone (**49**) was obtained: MS (70 eV): *m/z* = 162 [M]⁺, 120 [C₈H₈O]⁺, 105 [C₆H₅CO]⁺, 77 [C₆H₅]⁺. – IR (Film): $\tilde{\nu}$ = 1680 cm⁻¹. Benzyl phenyl ketone (5%) and benzophenone (1%) were also identified.

By (Et₃P)₄Ni: To a solution of the phosphane complex (458 mg, 0.914 mmol) in 15 mL of THF was added benzonitrile (0.186 mL, 188 mg, 1.83 mmol) of. The color of the solution changed from red-purple to green immediately. The reaction mixture was stirred at 25 °C for 7 days. Usual hydrolytic workup and a GC/MS analysis of the organic products showed that ethyl phenyl ketone (**44**) was the main product (60%, 130 mg) and **21** (5%) and **33** (10%) were minor products.

44: MS: *m/z* = 134 [M]⁺, 105 [PhCO]⁺, 77 [C₆H₅]⁺. – IR (film): $\tilde{\nu}$ = 1684 cm⁻¹.

By (Bpy)(COD)Ni: To the freshly made complex **7** (0.82 mmol) were added 15 mL of THF and benzonitrile (0.166 mL, 168 mg, 1.63 mmol). The reaction mixture was stirred at 25 °C for 7 days with no apparent color change of the dark solution. The reaction was quenched with 20 mL of 2 N aqueous HCl and then neutralized with aqueous NaHCO₃. The GC analysis of the dried organic layer showed that benzyl phenyl ketone **33** had formed in 20% yield, but benzaldehyde was found in only 5% yield. The conversion of benzonitrile was 30%.

The same reaction carried out at reflux for 24 h, but only benzaldehyde was obtained in a yield less than 5%; no deoxybenzoin was detected.

By Ni(acac)₂/Et₃Al: To a mixture of Ni(acac)₂ (203 mg, 0.791 mmol) and benzonitrile (0.161 mL, 163 mg, 1.58 mmol) in 15 mL of toluene was added slowly triethylaluminum (0.216 mL, 180 mg, 1.58 mmol). The color of the solution turned immediately from green to dark brown. After the reaction mixture had been stirred at 25 °C for 24 h, hydrolytic workup and analysis showed that **33** was formed in 15% yield.

By (COD)₂Ni/MeAlCl₂: a) **Adding Benzonitrile to the Mixture of (COD)₂Ni-MeAlCl₂ in Toluene:** One milliliter of a 1 M hexane solution of MeAlCl₂ was added dropwise to a solution of (COD)₂Ni (276 mg, 1.00 mmol) in 10 mL of toluene. The formation of a nickel mirror and a black precipitate were immediately formed. To this mixture was added benzonitrile (0.10 mL, 1 mmol) and the reaction mixture stirred at 25 °C for 24 h. The usual workup procedure and subsequent GC analysis showed that no reaction between benzonitrile and the nickel complex had occurred. Of interest is that about 90% of the 1,5-cyclooctadiene had been isomerized to its 1,3-isomer.

b) **Adding (COD)₂Ni to the Mixture of Benzonitrile and MeAlCl₂ in Toluene:** A solution of (COD)₂Ni (291 mg, 1.06 mmol) in 8 mL of toluene was added to a mixture of benzonitrile (0.11 mL, 1.06 mmol) and 1.06 mL of a 1 M hexane solution of MeAlCl₂ in 7 mL toluene and the reaction mixture then stirred for 24 h at 25 °C. After hydrolysis and GC analysis benzyl phenyl ketone (**33**) was found in 20% yield but no trace of benzaldehyde was detected.

By comparison, a similar reaction run in which the MeAlCl₂ was added to a mixture of (COD)₂Ni and benzonitrile in toluene led to the formation of no organic products.

Oligomerization of Substituted Benzonitriles by (COD)₂Ni

Pentafluorobenzonitrile: A reddish solution of (COD)₂Ni (1.27 mmol) and 2.54 mmol of the nitrile in 10 mL of THF was stirred at 25 °C for 24 h, during which time it turned pale yellow. Usual hydrolytic workup permitted the recovery of only 20% of the nitrile and yielded only pentafluorobenzene and no other organic products. It is assumed that any nickel(0) complex with the nitrile underwent decyanation with the loss of the C₆F₅ group (vide infra).

4-Methoxybenzonitrile: A red solution of (COD)₂Ni (1.00 mmol) and 2.0 mmol of the nitrile in 10 mL of THF was stirred at 25 °C for 24 h, during which time it turned dark brown. Usual hydrolytic workup and GC-MS and NMR analysis showed the presence of 75% of the nitrile, 15% of 4-methoxybenzyl 4-methoxyphenyl ketone and 10% of 4-methoxybenzaldehyde with only a trace of anisole (material balance of 90%).

In an identical reaction extended over 6 days, the material balance fell to 60% and anisole was now a significant product (25%).

Reaction of Nickel Metal with Benzonitrile at Reflux: To a solution of Ni(acac)₂ (2.56 g 10.0 mmol) in 30 mL of THF was added *n*-

butyllithium (12.5 mL, 20.0 mmol, 1.6 M in hexane) at -78°C , and the resulting mixture was allowed to come to 25°C over 2 hours. The black suspension was then evaporated to dryness under reduced pressure. Under argon dry benzonitrile (degassed under Ar and freshly distilled from P_2O_5 , 13 mL, 0.13 mol) was added and the reaction mixture was heated at reflux (190 – 195°C) for 40 hours. The resulting dark gray suspension was evaporated to dryness under vacuum and the solid residue was then slurried with toluene and hydrolyzed with 3 N aqueous HCl. Concentration of the dried toluene extract led to the deposition of 2,4,6-triphenyltriazine (**6**) (50 mg, 0.5%): ^1H NMR (CDCl_3): δ = 7.61–7.58 (m, 9 H), 8.80–8.77 (d of d, 6 H). – ^{13}C NMR (CDCl_3): δ = 128.64, 128.99, 132.49, 136.31, 171.71. Evaporation of the toluene filtrate left a residue of 45% of recovered benzonitrile.

The reaction of nickel metal with refluxing benzonitrile was repeated six times, with the nickel metal being generated initially from either NiBr_2 or $\text{Ni}(\text{acac})_2$ and two equivalents of *n*-butyllithium in THF, as described above. In each case, only traces of **6**, or none at all, were detected in the benzonitrile residue.

The low recovery of benzonitrile in certain runs (<50%) was an indication of decomposition of **5** by catalytic decyanation.^[34] Verification of this side reaction was obtained by cooling the unhydrolyzed reaction mixture and filtering off the yellow brown precipitate. This solid was freed of organic matter by extraction with toluene to leave a residue of nickel metal and $\text{Ni}(\text{CN})_2$. The presence of $\text{Ni}(\text{CN})_2$ was established by a “Prussian Blue” test. The addition of aqueous ammonium hydroxide dissolved the $\text{Ni}(\text{CN})_2$, leaving the Ni metal residue. To this ammoniacal extract were added, successively, aqueous FeSO_4 and then aqueous FeCl_3 , whereupon a deep blue precipitate formed.

Reaction of Nickel Metal with Benzonitrile at Reflux (Presence of Oxygen and Moisture): In conducting the foregoing reaction it was observed in certain runs that the initially dark gray nickel suspensions turned to a yellow-green color. This color change was shown to be caused by adventitious entry of moist air into the reaction vessel. In such runs, 2,4,6-triphenyl-1,3,5-triazine and other reaction products were found upon hydrolysis. Thus a reaction run as the foregoing with $\text{Ni}(\text{acac})_2$ as the source of Ni metal gave a yellow-brown suspension after 50 h at 195°C under an argon atmosphere. The toluene extract was concentrated to 25 mL and then was allowed to stand at -10°C for several days to allow crystallization. After the supernatant liquid was removed with a cannula the cluster of deposited red crystals, which proved unsuitable for XRD analysis, was quenched with degassed 6 N HCl. After Et_2O extraction the organic layer was neutralized with sodium bicarbonate, dried over anhydrous magnesium sulfate and evaporated under reduced pressure. The major organic product proved to be 1,3-diphenyl-1,3-propanedione (30 mg, 5%). – ^1H NMR (CDCl_3) δ = 4.63 (s, 2 H, diketone tautomer), 6.86 (s, 1 H, enolate vinyl hydrogen), 7.57–7.47 (m, 6 H), 8.11 (d, 4 H), 16.85 (s, 1 H, enolate OH). – ^{13}C NMR (CDCl_3): δ = 93.17, 127.17, 128.68, 132.47, 135.61, 185.78. – MS (Positive Ion Electrospray): m/z = 225 $[\text{MH}]^+$, 105.

After the usual hydrolytic workup of the supernatant liquid the organic residue obtained was purified by flash chromatography [silica gel, gradient elution with hexanes, hexanes/dichloromethane (4:1), and hexanes/ethyl acetate (3:1)] to give 2,4,6-triphenyl-1,3,5-triazine (**6**, 2%, based on starting **5**) and 4,5,6-triphenylpyrimidine (0.3%), for which latter product the following spectral data were obtained: ^1H NMR (CDCl_3): δ = 7.60–7.52 (m, 9 H), 8.03 (s, 1 H), 8.31–8.29 (d of d, 4 H), 8.74–8.72 (d of d, 2 H). – ^{13}C NMR (CDCl_3): δ = 110.31, 127.31, 128.45, 128.50, 128.92, 130.62,

130.76, 137.63, 164.82. – DEPT (CH only): δ = 110.30, 127.29, 128.44, 128.49, 128.92, 130.63, 130.76. – CIMS: 309 $[\text{MH}]^+$, 205, 102).

The product mixture from the last chromatographic fraction was concentrated and the residue was analyzed by ^1H and ^{13}C NMR spectroscopy. Small amounts of hexaphenylbenzene and benzamide (<1%) were observed. The origin of these products can be reasonably ascribed to the benzamide formed from benzonitrile by adventitious moist air^[35] and detailed consideration of their generation will be the subject of future publications.

X-ray Crystallographic Study of 2,2'-Bipyridyl(η^2 -diphenylacetylene)nickel (7**):** Crystal Mounting and Data Collection: A black crystal of **7**, $0.58 \times 0.58 \times 0.14$ mm in size, was mounted with a perfluorinated polyether oil on the tip of a glass fiber on the goniometer head and cooled immediately by an argon current to -173°C . Intensity data were collected with an Enraf–Nonius CAD4 diffractometer by a coupled ω - 2θ scan technique with speeds varying from 1.0 to $10.0^{\circ}/\text{min}$ depending on the standard deviation to intensity ratio of a preliminary $10^{\circ}/\text{min}$ scan. The radiation employed was Mo-K_α with a graphite monochromator. The crystals of molecular weight 393.1 g mol^{-1} have two independent molecules per unit cell and have a calculated density of 1.35 Mg m^{-3} ; they belong to the monoclinic crystal system and the space group of $P2_1/c$, No. 14. The two independent molecules in the asymmetric unit cell of **7** have the same atom separations within the margin of experimental error. They differ only with respect to their torsion angles. Both Ni centers are absolutely planar (sum of angles equals 360°). All other geometrical data correspond to expected values.

The absorption corrections were made by the ψ -scan method. Observed reflections were defined as those reflections with $I \geq 2\sigma(I)$. Only these were used in the solution and refinement of the structure (F refinement). For refinement based on F^2 all reflections were used. Refinement was done by least-squares; the quantity minimized was $\sum w(|Y_o| - |Y_c|)^2$, with $Y = F$ or F^2 . Computations were done using VAX, Sun4, and Silicon Graphics computers. In addition to several locally written programs, the following software was used: S. L. Lawton, R. A. Jacobson, TRACER (cell reduction), United States Energy Commission, Report IS-1141, Iowa State University, USA, 1965. P. Coppens, L. Leiserowitz, D. Rabinovich, DATAP (data reduction), *Acta Crystallogr.* **1965**, *18*, 1035. G. M. Sheldrick, SHELXS-86 (crystal structure determination), *Crystallographic Computing 3* (Eds: G. M. Sheldrick, C. Krüger, R. Goddard), Clarendon Press, Oxford, **1985**, dp. 185. G. M. Sheldrick, SHELXL-93 (least-squares refinement), University of Göttingen, **1993**. E. Egert, G. M. Sheldrick, PATSEE (structure solution), *Acta Crystallogr.* **1985**, *A41*, 262. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson, MULTAN80 (structure solution), University of York, England and Louvain, Belgium, **1980**. W. R. Busing, K. O. Martin, H. A. Levy, GFMLX a highly modified version of ORFLS (full-matrix least-squares refinement), Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee, USA, **1962**; H. D. Flack, (enantiomorph-polarity estimation), *Acta Crystallogr.* **1983**, *A39*, 876. P. Roberts, G. M. Sheldrick, XANADU (calculation of best planes, torsion angles and idealized hydrogen atom positions), University of Cambridge, England, **1976**. R. E. Davis, D. R. Harris, DAESD (calculation of distances and angles), Roswell Park Mem. Inst., USA, **1970**. V. Schomaker, K. N. Trueblood, RIGID (rigid-body analysis) *Acta Crystallogr.* **1968**, *B24*, 63. C. K. Johnson, ORTEP (thermal ellipsoid plot program), Report ORNL-5138, Oak Ridge National Lab., Tennessee, USA, **1976**. E. Keller, SCHAKAL (molecular drawing), *Chem. Unserer Zeit* **1986**, *20*, 178. B. W. van der Waal, FSYN (slant

plane Fourier syntheses), Technical University of Enschede, Netherlands, 1975. *SYBYL* (molecular calculations), Tripos Associates, Inc., St. Louis. *INSIGHT/DISCOVER*, Biosym Technologies, San Diego, USA.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144795. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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- [1] Leading literature citations: [1a] W. Reppe, O. Schlichting, K. Klager, T. Toepel, *Justus Liebigs Ann. Chem.* **1948**, 560, 1. — [1b] W. Reppe, O. Schlichting, H. Meister, *Justus Liebigs Ann. Chem.* **1948**, 560, 93. — [1c] W. Reppe, W. Schweckendiek, *Justus Liebigs Ann. Chem.* **1948**, 560, 104.
- [2] Comprehensive reviews of such oligomerizations: [2a] B. Bogdanovic, B. Henc, A. Lösler, B. Meister, H. Pauling, G. Wilke, *Angew. Chem.* **1974**, 85, 39. — [2b] G. Wilke, *J. Organomet. Chem.* **1980**, 200, 349. — [2c] J. J. Eisch, S. R. Sexsmith, *Res. Chem. Intermed.* **1990**, 13, 149.
- [3] *Comprehensive Organometallic Chemistry II*, Vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**.
- [4] Overviews: [4a] J. W. Copenhaver, M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, Reinhold, New York, **1960**. — [4b] G. N. Schrauzer, *Adv. Organomet. Chem.* **1964**, 2, 1.
- [5] The actual catalyst for the cyclotetramerization of acetylene is thought to be "naked" nickel(0) in all cases ("naked" meaning, in G. Wilke's view, that the ligands available to nickel, such as COD, are easily displaced by the alkyne.) The induction period observed for the oligomerization with nickel(II) salts is thought to entail the necessary reduction of nickel(II) to nickel(0), the actual catalyst. If nickel(0) is added at the start, there is no induction period and the oligomerization starts promptly (Professor Günther Wilke, observations and views communicated personally to J. J. E., **1985**). In addition, cf. G. Wilke, *Pure Appl. Chem.* **1978**, 50, 677.
- [6] J. J. Eisch, J. E. Galle, *J. Organomet. Chem.* **1975**, 96, C23.
- [7] J. J. Eisch, G. A. Damesevitz, *J. Organomet. Chem.* **1975**, 96, C19.
- [8] J. J. Eisch, A. A. Aradi, K. I. Han, *Tetrahedron Lett.* **1983**, 24, 2073.
- [9] J. J. Eisch, A. M. Piotrowski, K. I. Han, C. Krüger, Y. H. Tsay, *Organometallics* **1985**, 4, 225.
- [10] J. J. Eisch, *Pure & Applied Chem.* **1984**, 56, 35.
- [11] J. J. Eisch, A. M. Piotrowski, A. A. Aradi, C. Krüger, M. J. Romano, *Z. Naturforsch.* **1985**, 40b, 624.
- [12] J. J. Eisch, J. E. Galle, A. A. Aradi, M. P. Boleslawski, *J. Organomet. Chem.* **1987**, 312, 399.
- [13] J. J. Eisch, A. A. Aradi, M. A. Lucarelli, Y. Qian, *Tetrahedron Symposium-in-Print* **1998**, 54, 1169.
- [14] S. F. A. Kettle, L. E. Orgel, *Proc. Chem. Soc.* **1959**, 307.
- [15] W. Z. Heldt, *J. Organomet. Chem.* **1966**, 6, 292.
- [16] G. Oehme, H. Pracejus, *Z. Chem.* **1969**, 9, 140.
- [17] Leading references: ^{17a}H. Yamazaki, Y. Wakatsuki, *Tetrahedron Lett.* **1973**, 3383. — ^{17b}Y. Wakatsuki, H. Yamazaki, *Synthesis* **1976**, 26. — ^{17c}H. Bönemann, R. Brinkmann, H. Schlenkluhn, *Synthesis* **1974**, 575.
- [18] W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem.* **1978**, 90, 493.
- [19] The reported C=C separation in cyclopropene is 1.304 ± 0.003 Å: L. V. Vilkov, V. S. Mastryukov, N. I. Sadova, *Determination of the Geometrical Structure of Free Molecules*, Mir Publishers, Moscow, **1983**, p. 122.
- [20] I. W. Bassi, C. Benedicenti, M. Calcaterra, G. Rucci, *J. Organomet. Chem.* **1976**, 117, 285.
- [21] I. W. Bassi, C. Benedicenti, M. Calcaterra, R. Intrito, G. Rucci, C. Santini, *J. Organomet. Chem.* **1978**, 144, 225.
- [22] M. Uchino and S. Ikeda, *J. Organomet. Chem.* **1971**, 33, C41.
- [23] J. J. Eisch, Y. Qian, M. Singh, *J. Organomet. Chem.* **1996**, 512, 207: 9-Fluorenone reacts with Ni(0) complexes to yield, upon hydrolysis, a 25% yield of the dimeric pinacol, 9,9-dihydroxy-9,9'-bifluoreneol.
- [24] [24a] K. I. Watanabe, *Bull. Chem. Soc. Japan* **1959**, 32, 1290. — [24b] K. I. Watanabe, *Bull. Chem. Soc. Japan* **1964**, 37, 1325. — [24c] K. I. Watanabe, K. Saki, *Bull. Chem. Soc. Japan* **1966**, 39, 8.
- [25] D. R. Fahey, J. E. Mahan, *J. Am. Chem. Soc.* **1976**, 98, 4499.
- [26] H. Lehmkuhl, K. Ziegler, H. G. Gellert in *Methoden der Organischen Chemie*, E. Müller, ed., Thieme Verlag, Stuttgart, vol. XIII/4, 1970, pp. 239–241.
- [27] J. J. Eisch, X. Ma, M. Singh, G. Wilke, *J. Organomet. Chem.* **1997**, 527, 301. This communication was put into print without the Elsevier Publishers sending the galley proofs to the senior author for his approval as they had promised. As a result, the published communication contains many errors in typography and layout. Since Elsevier has declined to publish this version as a corrigendum, the senior author (JJE) has been forced to prepare a completely corrected and emended version of this communication. Interested researchers can receive a copy of this corrected version by writing to the senior author.
- [28] J. J. Eisch, *Organometallic Syntheses*, Vol. 2, Academic Press, New York, **1981**.
- [29] M. F. Semmelhack, *Organic Reactions*, Vol. 19, Wiley, New York **1972**, p. 178.
- [30] R. A. Schunn, *Inorganic Syntheses*, Vol. 15, Wiley, New York, **1974**, p. 5.
- [31] C. S. Cundy, *J. Organomet. Chem.* **1974**, 69, 305.
- [32] E. Dinjus, I. Gorski, E. Uhlig, H. Walther, *Z. Anorg. Allg. Chem.* **1976**, 75, 422.
- [33] J. J. Eisch, A. M. Piotrowski, unpublished studies.
- [34] For leading references to reductive cyanation by main-group and transition metal reagents, cf. J. March, *Advanced Organic Chemistry*, 4th ed., Wiley, New York, **1992**, p. 634.
- [35] Precedents for the transformations of benzamide into the products observed in this reaction have been observed: 1) into triazine **6**: ref. [16]; 2) into diphenylacetylene (**22**) by subvalent titanium reagents: R. Dams, M. Malinowski, H. J. Geise, *Recl. Trav. Chim. Pays-Bas* **1982**, 101, 112; 3) the co-oligomerization of benzonitrile, diphenylacetylene and possibly Ni(CN)₂ into 4,5,6-triphenylpyrimidine: Scheme 7, the present work; 4) the cyclotrimerization of **22** into hexaphenylbenzene (**23**) by nickel(0): ref. [11] and the present work; and 5) the possible coupling of two molecules of benzonitrile and Ni(CN)₂ by nickel(0) to form precursors to 1,3-diphenyl-1,3-propanedione coupling related to that in Scheme 8, the present work.

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