

## ORGANIC CHEMISTRY OF SUBVALENT TRANSITION METAL COMPLEXES

### XI \*. OXIDATIVE ADDITIONS OF NICKEL(0) COMPLEXES TO CARBON–CARBON BONDS IN ALKYNES: NICKELIRENES AND NICKELOLES AS CATALYTIC CARRIERS IN THE OLIGOMERIZATION OF ALKYNES

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#### Summary

The formation of 2,3,4,5-tetraphenylnickelole-bis(triphenylphosphine) (IIIa) and 2,3,4,5-tetraphenylnickelole-bis(1,2-diphenylphosphino)ethane (IIIb), either from (*E, E*)-1,2,3,4-tetraphenyl-1,3-butadien-1,4-ylidenedilithium (I) and the corresponding nickel(II) chloride-phosphine complexes (II) or from the reduction of  $\eta^4$ -tetraphenylcyclobutadienenickel(II) bromide dimer (XII) in the presence of phosphines, proceeds in good yields. Nickelole IIIa displays physical and chemical properties consistent with its structure and is a catalyst for the trimerization of diphenylacetylene. Nickelole IIIb is a highly associated structure but in its chemical response to alkynes, HOAc, O<sub>2</sub>, Br<sub>2</sub>, NaAlEt<sub>2</sub>H<sub>2</sub> and heat displays the properties of a nickelole, rather than a cyclobutadienenickel(0) complex. Attempts to generate IIIb photochemically from  $\eta^4$ -1,5-cyclooctadiene( $\eta^4$ -tetraphenylcyclopentadienone)nickel and diphos failed, but it was shown that structural types, such as  $\eta^4$ -tetraphenylcyclopentadienone(diphos)nickel (a model for the structure suggested by Hoberg and Richter for IIIb), are unstable.

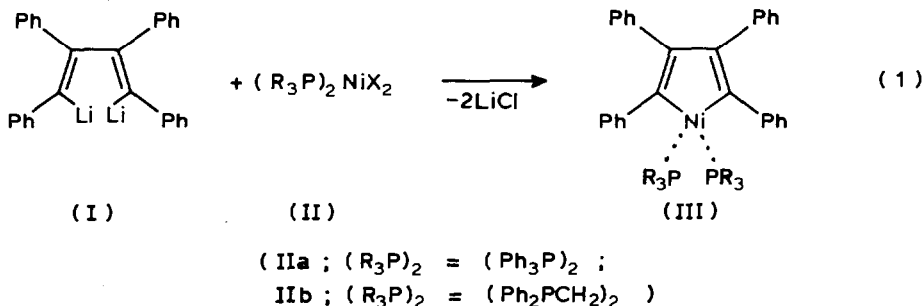
Oligomerizations of diphenylacetylene by bis(1,5-cyclooctadiene)nickel were retarded by conducting the reaction in THF or in the presence of diphos. This retardation permitted the interception of products (*cis*-stilbene and (*E, E*)-1,2,3,4-tetraphenyl-1,3-butadiene) diagnostic for the intermediacy of nickelirenes and nickeloles. Deuterium labeling verified the presence of carbon–nickel bonds. These trapping experiments, together with findings on the thermal behavior of nickeloles, are combined into a comprehensive view of the cyclotrimerization, cyclotetramerization and linear polymerization of alkynes by nickel(0).

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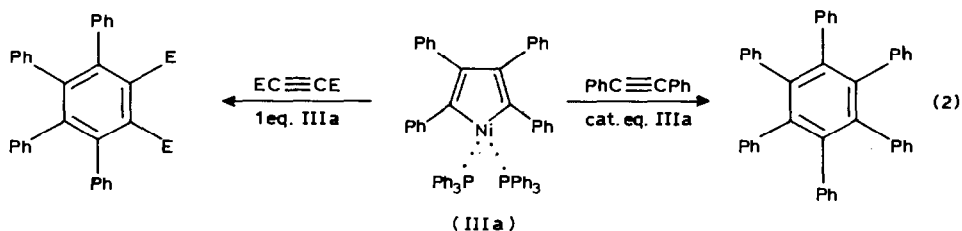
\* For Part X, see ref. 3.

## Introduction

Over 10 years ago, the first evidence was reported that implicated nickelole intermediates in the cyclotrimerization of alkynes [1]. Indeed, nickeloles (III) bearing triphenylphosphine or bis(1,2-diphenylphosphino)ethane ligands were independently synthesized from (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadien-1,4-ylidenedilithium (I) and nickel(II) halide-phosphine complexes (II) (eq. 1) and such nickeloles



were shown to have chemical properties appropriate for their intermediacy in the cyclotrimerization of alkynes [2]. Thus, they underwent a rapid reaction with alkynes to yield benzene derivatives, either stoichiometrically or catalytically [2] (eq. 2). Subsequently, such nickelole intermediates bearing trialkylphosphine or bis(1,2-

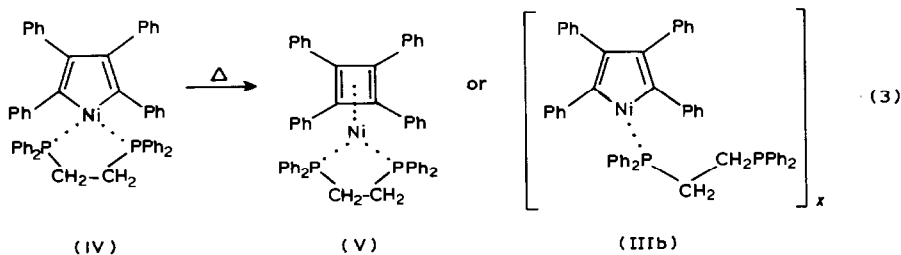


dialkylphosphino)ethane ligands were prepared both by the use of the dilithium reagent I, as in eq. 1 and by the oxidative addition of nickel(0) into the carbon-carbon bond of tetraphenylbutadiene [3]. Finally, dibenzonickeloles proved to be readily accessible by the oxidative addition of nickel(0) into the  $\text{C}_4$ -ring bond of biphenylene [4].

In the intervening time, nickel-catalyzed cyclotrimerization of labeled alkynes has ruled out the role of any cyclobutadiene-nickel intermediates in such catalysis [5,6]. In fact, our studies have demonstrated that cyclobutadienenickel(0) complexes tend to isomerize to the corresponding nickeloles but that nickeloles do not isomerize to the cyclobutadienenickel(0) system [3]. Instead, nickeloles undergo a thermal dimerization to dinickelecin rings and ultimately to cyclooctatetraenes and nickel metal [3,4].

In all the foregoing studies, the properties of the nickelole obtained from the dilithium reagent I and  $\text{NiCl}_2 \cdot (\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  (IIb) at  $25^\circ\text{C}$  were the most unusual and anomalous. Besides its complete insolubility and high decomposition range, this brick-red solid (IIIb) was less reactive than all the other nickeloles synthesized [2,3] and thus was inert to CO at  $25^\circ\text{C}$ . Carbonylation of the other nickeloles proceeds smoothly, even at low temperatures, to yield tetraphenylcyclopentadienone.

Subsequent to our report [2], Hoberg and Richter studied the reaction of I and IIb at  $-30^{\circ}\text{C}$  and were able to obtain a very soluble orange-yellow isomer IV, which they were able to characterize satisfactorily, by chemical reactions, spectral properties and mass spectral molecular weight, as a genuine nickelole [7]. They then found that IV is converted into our brick-red IIIb upon warming (eq. 3).



Because of the lack of any parent ion in the mass spectrum of IIIb and its complete insolubility, we suggested that IIIb is a polymeric nickelole, possibly with a nickelole/phosphine ratio of  $> 1/1$  [2]. Based upon chemical analysis, and some tentative assignments of Raman bands, Hoberg and Richter concluded that V was the cyclobutadienenickel(0) isomer of IV and that thermal reductive elimination of nickel(0) had occurred. Since such an interpretation contradicted what we had observed in our previous studies [3], we have reexamined the preparation and behavior of IIIb in a searching manner.

In this article we present a thorough investigation of the nickeloles obtained from I and nickel(II) chloride-phosphines, we reach an unambiguous decision on the ring structure of IIIb and we adduce cogent evidence on the role of nickelirenes and nickeloles in the cyclooligomerization of diphenylacetylene.

## Results

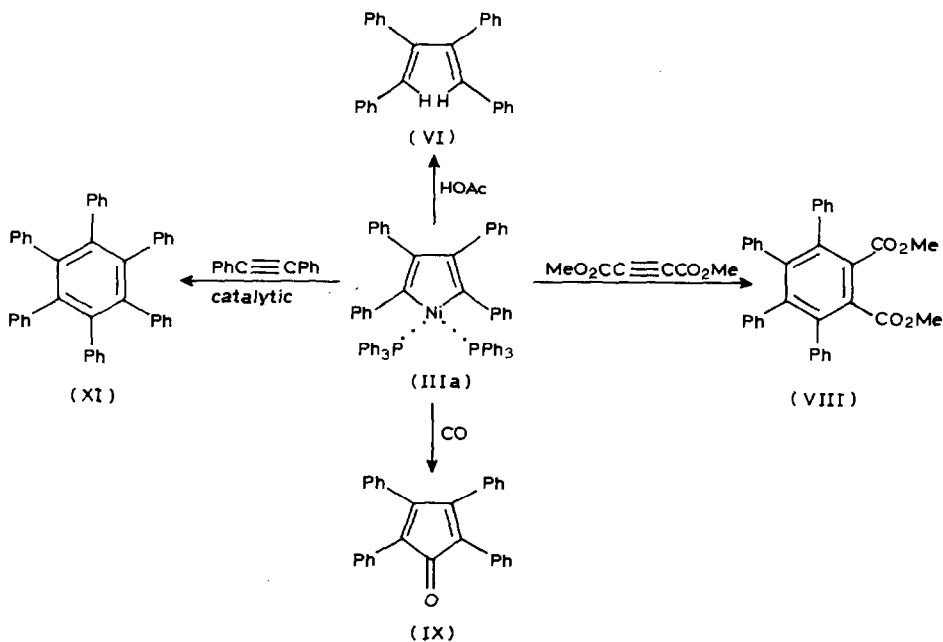
### *Formation and reactions of 2,3,4,5-tetraphenylnickelole-bis(triphenylphosphine) (IIIa)*

The formation of this nickelole from dilithium reagent I and nickel complex IIa proceeded readily at  $-78^{\circ}\text{C}$  to yield the product as a red-brown solid or a dark red solution in toluene. Since it displayed the expected aryl multiplet between 6.5–7.5 ppm in the  $^1\text{H}$  NMR spectrum, it was diamagnetic. Upon standing at  $25^{\circ}\text{C}$  its color and crystal habit changed, even under argon.

However, its chemical response to a variety of reagents was prompt and unambiguous: (1) cleavage by glacial acetic acid at  $-78^{\circ}\text{C}$  gave 82% of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (VI); (2) addition of dimethyl acetylenedicarboxylate (VII) at  $25^{\circ}\text{C}$  led to 69% of dimethyl tetraphenylphthalate (VIII); (3) carbonylation at  $25^{\circ}\text{C}$  produced 76% of tetraphenylcyclopentadienone (IX); and (4) diphenylacetylene (X) was converted into hexaphenylbenzene (XI) at  $110^{\circ}\text{C}$  catalytically with a turn-over number of 27. These reaction results are summarized in Scheme 1.

### *Formation and reactions of associated 2,3,4,5-tetraphenylnickelole-bis(1,2-diphenylphosphino)ethane (IIIb)*

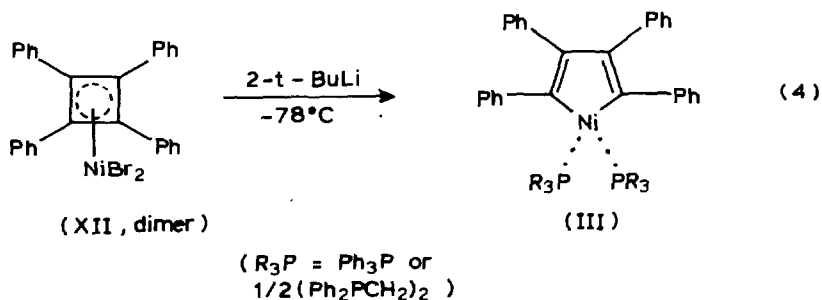
This compound was prepared, as previously reported [2], from dilithium reagent I and nickel complex IIb in methylene chloride solution at  $25^{\circ}\text{C}$  (eq. 1). Because it slowly decomposes when warmed (cf. the following paragraph), the thermal decom-



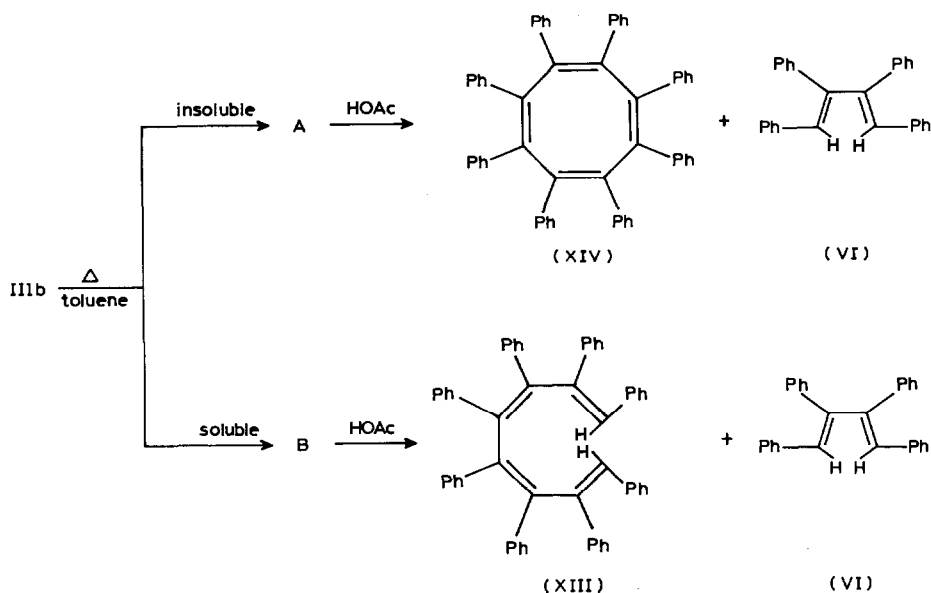
SCHEME 1

position range and elemental analyses exhibited by a sample of *IIIb* depend upon its method of purification. If samples are washed promptly and temperatures over 35–40°C avoided, satisfactory elemental values for  $\text{C}_{54}\text{C}_{44}\text{NiP}$  are obtainable.

Both *IIIb* and nickelole *IIIa* can also be prepared by the reduction of  $\eta^4$ -tetraphenylcyclobutadienenickel(II) bromide dimer (*XII*) with *t*-butyllithium in the presence of the appropriate phosphine (eq. 4):



Since *IIIb* is insoluble in, or decomposed by, a gamut of hot solvents, no electronic or magnetic spectra could be obtained. Its infrared spectrum in a mineral oil or KBr suspension, however, was well-resolved and showed a particularly intense band at  $1585\text{ cm}^{-1}$ , an absorption found in a wide variety of metalloles [8–10]. The decrease in the intensity of this band served to signal the onset of thermal decomposition, when *IIIb* was warmed in toluene suspension between 50–110°C. After 15–48 h of such heating *IIIb* went partially into solution in the toluene (B) and the undissolved remainder (A) lightened in color. The infrared spectra of A and

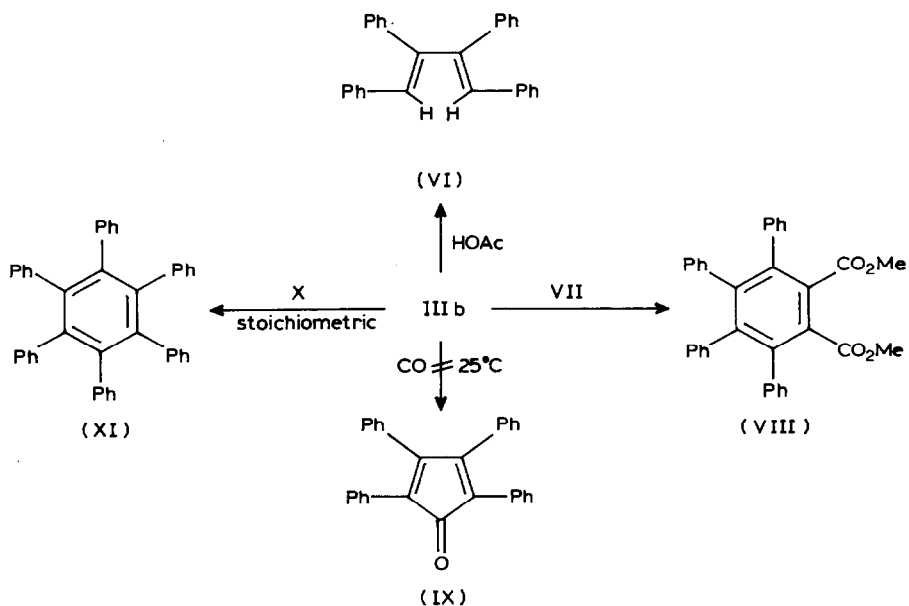


SCHEME 2

B differed from that of IIIb, as did their mass spectra. Whereas the mass spectrum of IIIb (70 eV, inlet temperature of 350°C) displayed only weak peaks above 700 ( $m/e$ ), the spectra of A and B display intense peaks at 712 and 714, respectively. Finally, treatment of A and B individually with glacial acetic acid resulted in a mixture of octaphenylcyclooctatetraene (XIV) and some tetraphenylbutadiene (VI) from A, and a mixture of principally octaphenylcyclooctatetraene (XIII) and some tetraphenylbutadiene (VI) from B (Scheme 2).

Accordingly, in order to characterize the nature of IIIb chemically, it was subjected to a battery of diverse reagents. Toward the four reagents used to characterize nickelole IIIa, namely, HOAc,  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ , CO and  $\text{PhC}\equiv\text{CPh}$ , it displayed a markedly lower reactivity. However, this may stem from its extreme insolubility. Cleavage by HOAc to yield 88% of the butadiene VI occurs at 25°C, but reaction with either alkyne VII or alkyne X requires refluxing toluene to give benzene derivatives VIII and XI in yields of 70 and 60%, respectively. On the other hand, IIIb did not react with CO at 25°C, nor did it show any significant catalytic activity in trimerizing diphenylacetylene (X) into hexaphenylbenzene (XI) (Scheme 3). IIIb did yield octaphenylcyclooctatetraene (XIV) when heated to 90°C in the presence of CO. However, since it also yields XIV merely upon heating, the CO simply serves as a CO scavenger and not as a causative agent for XIV.

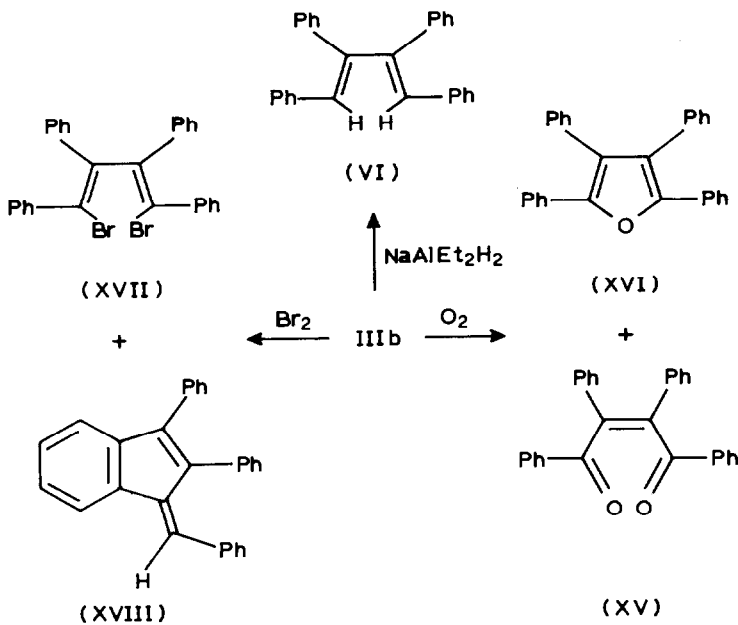
In the foregoing reactions, IIIb displays a chemical behavior completely consistent with its having a nickelole structure, albeit of reduced reactivity. Furthermore, toward three other reagents IIIb responds in a manner typical of nickeloles and not in keeping with the hypothesis that it be a cyclobutadienenickel(0) complex: (1) with dry oxygen it yields a 3/1 mixture of *cis*-1,2,3,4-tetraphenyl-2-buten-1,4-dione (XV) and tetraphenylfuran (XVI); (2) with bromine it forms a mixture of 1,4-dibromo-1,2,3,4-tetraphenyl-1,3-butadiene (XVII) and 3-benzylidene-1,2-diphen-



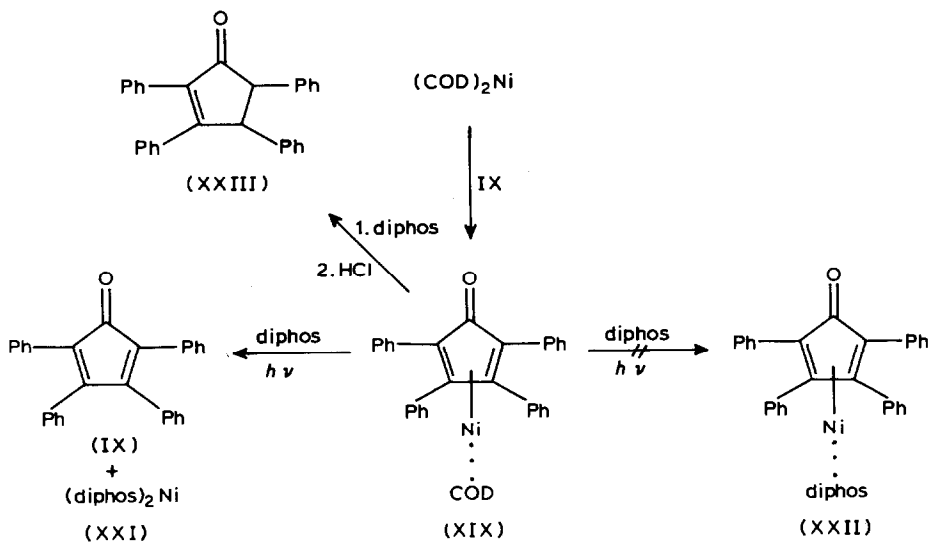
SCHEME 3

ylindene (XVIII); and (3) with sodium diethylaluminum hydride it produces essentially only (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (VI) (Scheme 4).

The outcome of all three of these reactions with the corresponding cyclo-

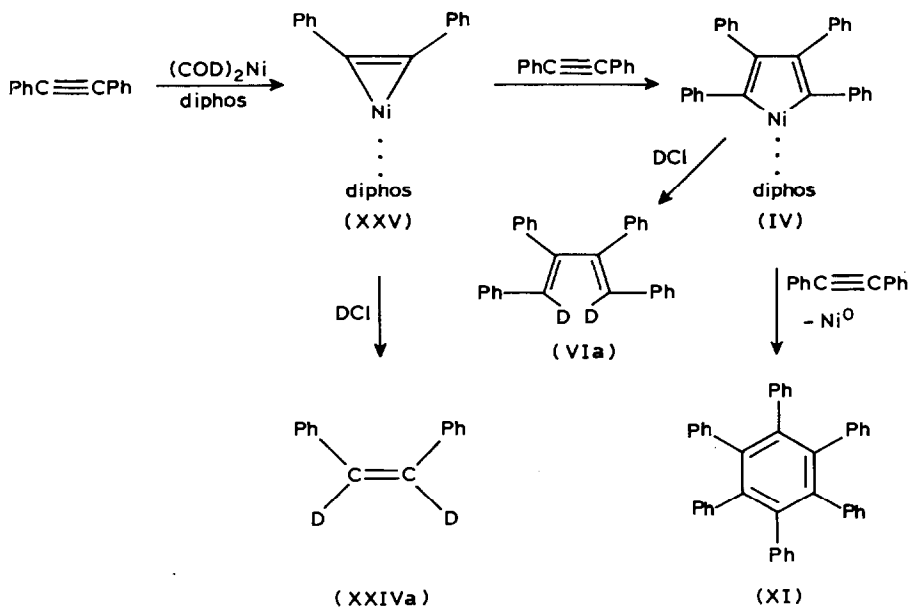


SCHEME 4



SCHEME 5

butadienenickel(0) complex is known to be different [11]: (1) oxygen yields only XV; (2) metal hydrides give only the more stable (*E,Z*)-isomer of tetraphenylbutadiene (VI); and (3) bromine yields smoothly  $\eta^4$ -tetraphenylcyclobutadiene-nickel(II) bromide dimer (XII).



SCHEME 6

*Formation and reactions of  $\eta^4$ -1,5-cyclooctadiene( $\eta^4$ -tetraphenylcyclopentadienone)-nickel (XIX)*

Since Hoberg and Richter had suggested structure V as an alternative isomeric structure for IIIb, an attempt was made to synthesize V or a similar complex. Thus heating bis(1,5-cyclooctadiene)nickel (XX) and tetracyclone IX in THF led to the formation of XIX in 78% yield. Then an attempt was made to displace the cyclooctadiene by diphos and to effect decarbonylation photochemically to produce IIIb or V. However, not only did no decarbonylation occur, but both the tetracyclone and the COD were displaced from XIX to yield the bis(diphos)nickel complex XXI. This result suggests that diphos complexes of the type suggested by Hoberg and Richter (V or XXII) may be unstable with respect to XXI (Scheme 5).

*Oligomerization of diphenylacetylene with bis(1,5-cyclooctadiene)nickel (XX)*

In hydrocarbon media (COD)<sub>2</sub>Ni is an efficient cyclotrimerization catalyst for diphenylacetylene. But to permit the interception of precursors, it was found advantageous to employ THF or diphos donors that slow down the cyclotrimerization. Thus although XX in toluene trimerized X at 110°C in 78% yield with a turn-over number of 260, in THF solution at 25°C a 5% yield of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene(VI) was isolated. With a 1/1 mixture of XX and diphos at 30°C a 3% yield of diene VI was obtained, together with 40% of *cis*-stilbene and 27% of trimer XI. Work-up with DCl led to 1,4-dideuterated VI and 1,2-dideuterated *cis*-stilbene (XXIV). These products show that nickelirene XXV and nickelole IV are the precursors to XXIV and VI, respectively (Scheme 6).

## Discussion

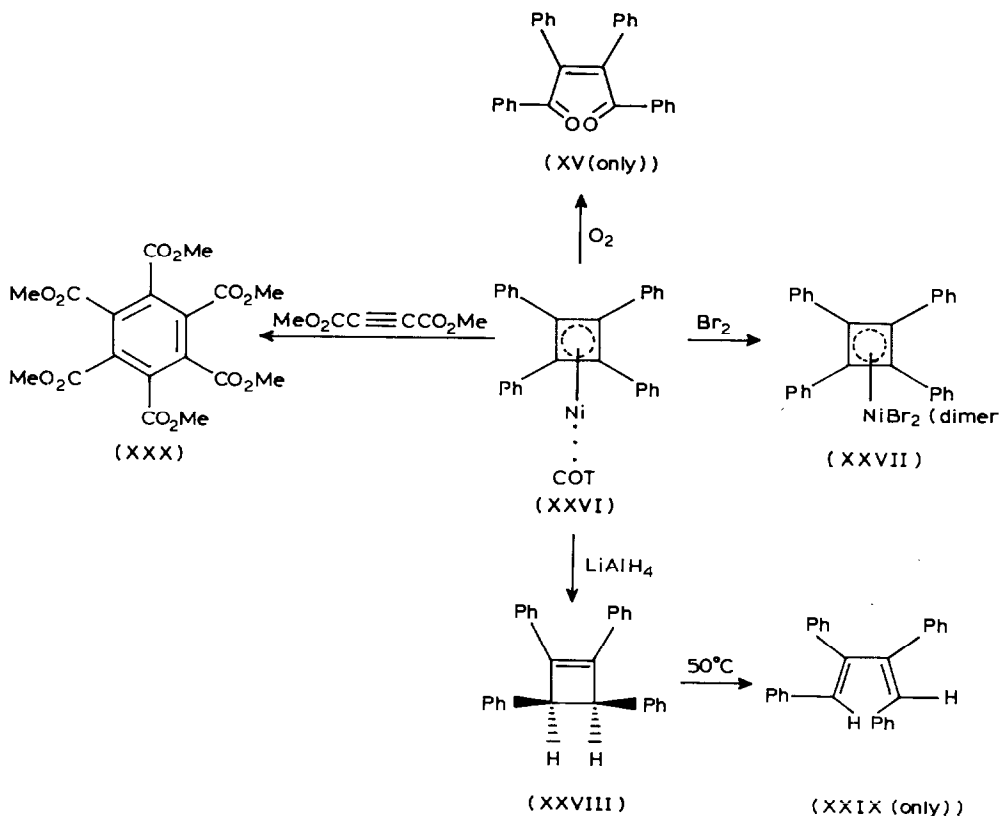
*Structure of the nickeloles IIIa and IIIb*

Both on the basis of their formation according to eq. 1 and on the outcome of their reactions summarized in Schemes 1–4, compounds IIIa and IIIb can confidently be assigned structures as nickeloles. Both in its reactivity and mode of reaction, IIIb must be considered as a nickelole rather than as a cyclobutadiene-nickel(0) isomer V. Despite its low solubility, IIIb is much more reactive toward MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me and PhC≡CPh than is tetraphenylcyclobutadiene( $\eta^4$ -cyclooctatetraene)nickel (XXVI) toward the same reagents [11]. Furthermore, the mode of response of XXVI toward O<sub>2</sub>, Br<sub>2</sub>, MAIH<sub>4</sub> and MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me differs sharply from that of IIIb (Scheme 7, [11]). The formation of diene XXIX from XXVI is especially decisive\*, for this *E,Z*-isomer is more stable than the *E,E*-isomer formed from IIIa and NaAlEt<sub>2</sub>H<sub>2</sub>. Hence, the *E,Z*-isomer could not have formed from IIIb and isomerized into the *E,E*-isomer in the course of reducing IIIb.

Because of its chemical behavior and its intense IR band at 1585 cm<sup>-1</sup>, IIIb definitely possesses the nickelole nucleus. However, its low solubility and high melting point show that it is very different from the soluble nickelole IV characterized by Hoberg and Richter. Accordingly, IIIb should be viewed as a highly associated nickelole, most likely formed by diphos units linking between nickelole

\* Even a phosphine-bearing tetraphenylcyclobutadienenickel(0) complex, C<sub>4</sub>Ph<sub>4</sub>Ni(PEt<sub>3</sub>)<sub>2</sub>, is reduced by LiAlH<sub>4</sub> to give principally XXVIII [3].





SCHEME 7

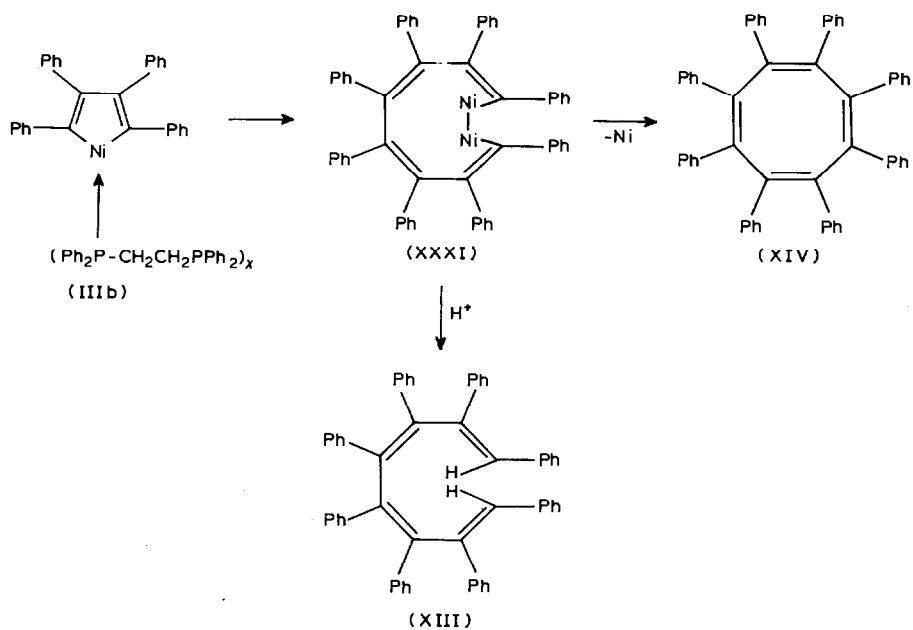
rings. The formation of IIIb from IV is a polymerization caused by the conversion of the chelating diphos unit into an internuclear bridge. Thus, there is no evidence that a nickelole undergoes thermal conversion into its cyclobutadienenickel(0) isomer.

#### *Thermal rearrangements of nickeloles*

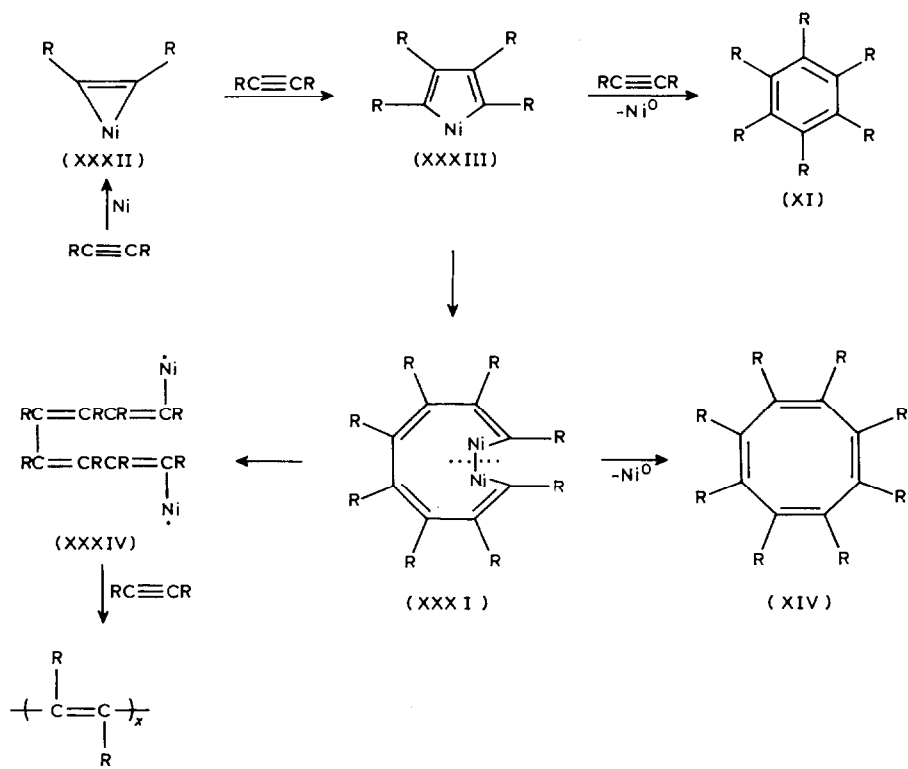
Our cumulative experience on the thermal behavior of both nickeloles [3] and dibenzonickeloles [4] is that they dimerize to dinickelecins XXXI, rather than isomerize to cyclobutadienenickel(0) complexes. At somewhat higher temperatures, XXXI eliminates nickel(0) and forms cyclooctatetraenes. The thermal behavior of IIIb conforms to this pattern: heating between  $60\text{--}110^\circ\text{C}$  leads to the formation of the open-chain (XIII) and cyclic (XIV) octatetraenes (Schemes 2 and 8).

#### *Oligomerization of alkynes*

The pattern of thermal behavior for nickeloles, as depicted in Scheme 8, and the chemical trapping of nickelirene and nickelole intermediates in the oligomerization of alkynes, as shown in Scheme 6, permit a coherent view of how nickel(0) predisposes alkynes to cyclotrimerization, cyclotetramerization or polymerization. The first step can be viewed as the formation of a 1/1 alkyne-nickel(0) complex or a nickelirene (XXXII). A number of such complexes bearing phosphines or amines



SCHEME 8



SCHEME 9

have been isolated [12] and in fact, the crystal structure of the 2,2'-bipyridyl(diphenylacetylene)nickel(0) complex has recently been determined [13].

In the next step, such nickelirenes combine with a second alkyne to form a nickelole (XXXIII). The chemical trapping of nickeloles from alkyne-nickel(0) systems as dienes (VIa, Scheme 6) or as cyclopentadienones [14] assure their presence as intermediates.

The reactions of the intermediate nickeloles constitute a branching point. Depending upon their stability and the reactivity of the alkyne, they can either dimerize, as depicted in Scheme 8, ultimately leading to open-chain or cyclic tetramers, or they can react readily with a further alkyne to yield a cyclotrimer (Scheme 1). In either case, nickel(0) is regenerated for repetition of the catalytic cycle.

Finally, such dinickelecons as in Scheme 8 could undergo Ni-Ni bond cleavage and function as a nickel(I)  $\alpha,\omega$ -dinickeladecatetraene oligomerizing agent (XXXIV) and thus propagate the polymerization of alkynes [15]. The overall summary of these key steps is portrayed in Scheme 9.

## Experimental

### *Starting materials*

Stilbene-free diphenylacetylene was prepared from benzil and triethyl phosphite and recrystallized from methanol, m.p. 62–63°C [16]. This was then treated with lithium foil, according to published directions [17], and the resulting (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene-1,4-ylidenedilithium isolated as the yellow granular bis(diethyl etherate). This reagent was subsequently allowed to react with dimethyltin dichloride to form 1,1-dimethyl-2,3,4,5-tetraphenylstannole [18] and with the phosphine complexes of the nickel halides, as described in this article.

$\eta^4$ -Tetraphenylcyclobutadiene-nickel(II) bromide dimer was synthesized from the stannole in two steps, namely bromination and subsequent addition of NiBr<sub>2</sub>, m.p. 298–300°C (dec.) [19]. Bis(1,5-cyclooctadiene)nickel was produced by following modifications of a previously tested procedure [20]. Nickel(II) chloride complexes of triphenylphosphine and bis(1,2-diphenylphosphino)ethane were obtained by the reaction of NiCl<sub>2</sub> with the individual purified phosphine in 1-butanol [21].

*t*-Butyllithium in pentane solution was purchased from Aldrich Chemical Company and was analyzed just before use by the Gilman double-titration procedure [22].

Reaction media for organometallic reactions (diethyl ether, tetrahydrofuran, toluene and methylene chloride) were purified by standard procedures [23] and then made anhydrous and deoxygenated by final distillation from appropriate drying agents [4] under an argon atmosphere.

### *Instrumentation and analyses*

All melting points were measured with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on Perkin-Elmer spectrophotometers, Models 457 and 283B, which were equipped with sodium chloride optics. Proton magnetic resonance spectra (<sup>1</sup>H NMR) were obtained with a Varian spectrometer, Model EM-360, on pure samples or on 10% solutions in pure

deuterated solvents. The  $^1\text{H}$  NMR data are reported on the  $\delta$ -scale in parts per million with reference to internal tetramethylsilane, followed by peak multiplicities, relative proton intensities and coupling constants in hertz. Mass spectral data (MS) were collected either with a Dupont instrument, Model 21-491B, or with a MS-902/CIS. 2 instrument. The latter spectrometer was provided with a V6 Datasystem 2040 computerized recorder.

Gas-liquid phase chromatographic analyses (GC) were carried out with an F&M temperature-programmed chromatograph, Model 720, equipped with dual 12-ft columns of a 10% UC-298 phase on a Chromosorb W support and with an electronic peak-area integrator. Unless otherwise indicated, column chromatographic separations (CC) were effected on silica gel columns with solvent eluting gradients of hexane/methylene chloride. Thin layer chromatographic analysis (TLC) were done on Eastman Chromagram Sheets, no. 13181, consisting of silica gel with fluorescent indicator.

#### *General procedures*

All steps in the preparation, transfer and main reactions of the 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 and then maintained under argon. Methods and techniques for working under anhydrous and anaerobic conditions have been described previously [4].

#### *Formation of associated 2,3,4,5-tetraphenylnickelole-bis(1,2-diphenylphosphino)ethane (IIIb)*

*Method A: Reaction of bis(1,2-diphenylphosphino)ethanenickel(II) chloride (IIb) with (E,E)-1,2,3,4-tetraphenyl-1,3-butadiene-1,4-ylidenedilithium (I).* A solution of 1.79 g (3.64 mmol) of the lithium reagent I in 75 ml of pure methylene chloride was prepared just before use (I is stable in such solutions for short periods). Then a stirred suspension of 1.72 g (3.30 mmol) of the phosphine-nickel chloride complex IIb in 25 ml of  $\text{CH}_2\text{Cl}_2$  was treated dropwise at  $20^\circ\text{C}$  with the solution of the lithium reagent over the course of 15 min. The addition funnel was rinsed with another 25 ml of  $\text{CH}_2\text{Cl}_2$ , in order to ensure that all of I was introduced into the reaction medium. The momentarily homogeneous yellow reaction solution slowly began to deposit a brick-red solid. After an additional 30-min stirring period, approximately 50 ml of the  $\text{CH}_2\text{Cl}_2$  was evaporated from the reaction mixture under reduced pressure. Thereafter, 75 ml of deoxygenated, anhydrous methanol was introduced dropwise over 15 min into the stirred red suspension. The red precipitate was filtered and maintained under argon as it was successively washed and digested with deoxygenated methanol (25 ml), toluene (25 ml) and anhydrous diethyl ether. After extensive drying in vacuo the red IIIb weighed 1.80 g (67%).

Anal. Found: C, 79.48; H, 5.53;  $\text{C}_{54}\text{H}_{44}\text{NiP}_2$  calcd.: C, 79.72; H, 5.45; Ni, 7.22; P, 7.61%. The product gave a negative flame test for Li (red) and a negative copper wire flame test for chloride (green). Furthermore, digestion of a sample with nitric acid and addition of aqueous  $\text{AgNO}_3$  to filtered aqueous layer also proved negative for chloride. However, elemental analyses for phosphorus and nickel resulted in low (6–7%) and high (9–10%) values, respectively. Although initially the elemental analyses seemed to point to a 2/1 nickelole-diphosphine complex, we now conclude

that IIIb probably underwent a thermal change after its formation and prior to its analysis (cf. *infra*).

The nickelole complex IIIb proved to be completely insoluble in all common solvents at room temperature under argon: ethers, halocarbons, hydrocarbons and nitriles. Only in hot solvents did it show any solubility, but in these instances IIIb underwent chemical change. As is discussed below, its slight solubility in warm toluene is accompanied by reaction and it dissolves in hot chlorobenzene only to redeposit a yellowish powder upon cooling. Hence, solutions of IIIb could not be obtained for desired spectroscopic measurements. Its IR spectrum in a mineral oil mull, however, displayed the following bands ( $\text{cm}^{-1}$ , intensity): 609w, 671m, 698s, 701s, 711s, 732w, 746m, 750w, 779w, 837m, 877m, 1025w, 1090m, 1155w, 1175w, 1305w, 1342w, 1432s, 1435m, 1491s, 1496m, 1530w, 1568w, 1585s, 1591m and 1600m.

*Method B: Reaction of  $\eta^4$ -tetraphenylcyclobutadiene-nickel(II) bromide dimer (XII) with *t*-butyllithium in the presence of bis(1,2-diphenylphosphino)ethane.* A suspension of 0.80 g (1.4 mmol) of the purified complexed nickel(II) bromide XI and 0.80 g (2.0 mmol) of the phosphine in 45 ml of toluene was stirred at  $-78^\circ\text{C}$  until a blue, partial solution was attained. Then, through a rubber septum on the reaction flask 1.4 ml (2.8 mmol) of 2-*M* *t*-butyllithium in hexane were added dropwise, by means of a gastight syringe, to the blue suspension. After 6 h of stirring at  $-78^\circ\text{C}$  the resulting orange-red suspension was allowed to warm to room temperature over 24 h. The solvent was then evaporated from the dark red reaction residue at  $20$ – $30^\circ\text{C}$  under reduced pressure. A 30-ml portion of deoxygenated methanol was added to the reaction residue and by magnetic stirring all product sticking to the flask wall was thoroughly eluted. The methanolic extract was siphoned off by syringe and the residue washed successively with two 30-ml portions of methanol. The brick-red residue was finally washed thrice with 30-ml portions of dry, deoxygenated diethyl ether and dried over several hours at  $25^\circ\text{C}$  under reduced pressure. The yield of IIIb was 0.85 g (75%). Its IR spectrum in mineral oil was identical with product IIIb that resulted from method A.

Anal. Found: Ni, 7.50; P, 7.36.  $\text{C}_{54}\text{H}_{44}\text{NiP}$  calcd.: Ni, 7.22; P, 7.61%.

#### *Formation of 2,3,4,5-tetraphenylnickelole-bis(triphenylphosphine) (IIa)*

*Isolation of the solid.* A suspension of 1.65 g (4.5 mmol) of lithium reagent I in 30 ml of pure methylene chloride was stirring at  $-78^\circ\text{C}$  while 2.94 g (4.5 mmol) of powdered bis(triphenylphosphine)-nickel(II) chloride (IIa) was introduced in one portion. The resulting solution was allowed to warm to room temperature over 1 h and then the methylene chloride was evaporated under reduced pressure. The reaction residue was digested successively with three 30-ml portions of deoxygenated toluene and the combined dark-red-brown toluene extracts were filtered under argon. The toluene filtrate was cooled to  $-78^\circ\text{C}$  and slowly diluted with 150 ml of deoxygenated hexane, whereupon a red solid precipitated. Filtration at  $-78^\circ\text{C}$  with a siphon connected with a medium-porosity frit left 2.5 g of red-brown solid in the flask. This nickelole (III) could be redissolved in ethyl ether and reprecipitated with hexane at  $-78^\circ\text{C}$ . Since IIIa proved to be extremely air- and moisture-sensitive and at  $25^\circ\text{C}$  changed in appearance, even under argon, it was not sent for analysis. However, a sample treated in  $\text{CH}_2\text{Cl}_2$  solution with glacial acetic acid and then worked up as in section (2) (cf. *infra*) yielded a mixture of (*E,E*)-

1,2,3,4-tetraphenyl-1,3-butadiene and triphenylphosphine oxide. This compound can also be prepared in a manner similar to Method B for IIIb [3].

*Formation in solution.* Because of its reactivity, therefore, nickelole III was prepared in solution and used immediately in subsequent reactions. Thus, the lithium reagent I (1.90 g, 5.2 mmol) was suspended at 25–30°C in 50 ml of anhydrous diethyl ether and then 3.40 g (5.2 mmol) of the powdered phosphine-nickel chloride complex IIa was added in one portion. After 30 min of stirring a 25-ml portion of benzene was introduced and the red reaction mixture used directly for further reaction of reagent IIIa.

*Formation of  $\eta^4$ -1,5-cyclooctadiene( $\eta^4$ -tetraphenylcyclopentadienone)nickel (XIX)*

A solution of 1.79 g (6.5 mmol) of bis(1,5-cyclooctadiene)nickel (XX) and 2.29 g (6.5 mmol) of tetraphenylcyclopentadienone (IX) in 30 ml of anhydrous tetrahydrofuran was warmed to 50°C for 72 h. Addition of deoxygenated H<sub>2</sub>O and then 6 *N* aqueous HCl, followed by column chromatography under argon, allowed the isolation of 2.80 g (78%) of the dark green complex XIX, m.p. 216–217°C, black crystals: <sup>1</sup>H NMR (CDCl<sub>3</sub>) 1.75–3.00 (m, 8H), 3.90–4.50 (d, 4H), 6.67–7.40 (m, 16H) and 7.40–7.90 (m, 4H); IR (mineral oil) 635, 695, 710, 720, 752, 760, 800, 1029, 1075, 1300, 1448, 1512 and 1618; MS (70 eV, *m/e*) 551, 550, 387, 386, 385, 358, 357, 179.

Anal. Found: C, 80.18; H, 5.85; Ni, 10.79; O, 2.90. C<sub>37</sub>H<sub>32</sub>ONi calcd.: C, 80.6; H, 5.85; Ni, 10.65; O, 2.90%.

*Reactions of associated 2,3,4,5-tetraphenylnickelole-bis(1,2-diphenylphosphino)ethane (IIIb)*

(1) *Thermal treatment.* Brick-red solid IIIb proved to be sensitive to heat; this may explain why two very different melting ranges have been observed: 265–270°C [2] and 215°C [7], both with decomposition. Thus, the heating at reflux under argon of 0.5–1.0-mmol samples of IIIb suspended in 25 ml of toluene caused a dark brown solution to form and a lightening of the color of the undissolved solid. After 48 h the cooled dark suspension was filtered under argon. The recovered solid A was a much lighter brown, almost tan in color. The filtrate was evaporated in vacuo to leave brown solid B.

The infrared spectra of solids A and B were distinctly different in several bands from each other and from starting IIIb. For example, the characteristic, intense band of IIIb at 1585 cm<sup>-1</sup> (MC=C, [8–10]) was greatly diminished or absent in A and B.

In contrast with the starting solid IIIb, which gave a MS at 70 eV (inlet temperature at 350°C) having its highest mass at 534 (other mass peaks at 398, 356, and 178), both solids A and B had their highest prominent mass peak at 770 (C<sub>8</sub>Ph<sub>8</sub>Ni). In addition, A had enhanced peaks at 712, 534, 356 and 178 and B at 714, 398, 534 and 356.

Then solids A and B were heated individually in refluxing glacial acetic acid under argon; the samples were then diluted with water and neutralized with aqueous NaOH. Separation of the organic products was effected by filtration or extraction with benzene. Such treatment of solid A gave an insoluble solid that was shown to be principally octaphenylcyclooctatetraene and some tetraphenylbutadiene by IR, MS and TLC comparisons.

From such a treatment of solid B the organic product proved to be a mixture of octaphenyloctatetraene, the dioxide of the phosphine and some (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene, as supported by IR, MS and TLC evidence.

(2) *Glacial acetic acid.* A 0.5-mmol sample of IIIb was suspended in 10 ml of pure toluene was treated with 2 ml of glacial acetic acid, whereupon a red-brown solution was formed immediately. After a 12-h period of stirring the volatiles were removed in vacuo and the solid residue was introduced onto a column of neutral alumina. Development with a hexane/methylene chloride gradient yielded 88% of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (VI), m.p. 180–181°C, as confirmed by mixture m.p. and IR spectroscopy.

(3) *Dimethyl acetylenedicarboxylate.* A 0.95-mmol sample of IIIb was suspended in 20 ml of toluene and then treated with 1.0 ml of the acetylenic ester VII. After 5 h at reflux the resulting yellow solution was concentrated in vacuo and the residue then dissolved in 150 ml of a 1/1 (v/v) mixture of benzene and hexane, whereupon air was passed through the resulting solution. The suspension was filtered through solid anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was chromatographed on silica gel and developed with a benzene-methylene chloride gradient. A 70% yield of dimethyl tetraphenylphthalate was isolated, m.p. 245–250°C. Recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH, this product melted at 255–257°C. Its identity was confirmed by a mixture m.p. and IR spectral comparison with an authentic sample. The latter sample was obtained by treating tetraphenylcyclopentadienone with dimethyl acetylenedicarboxylate at reflux.

(4) *Carbon monoxide.* A 0.77-mole sample of IIIb suspended in 20 ml of toluene did not absorb any CO at 25°C. After 15 h at 90°C the red suspension had turned cream-colored and about 2 molar equiv. of CO had been taken up. Filtration of the suspension yielded 75% of octaphenylcyclooctatetraene (XIV), m.p. > 400°C and IR spectral comparison.

(5) *Oxygen.* A 0.5-mmol sample of IIIb suspended in 30 ml of toluene was treated with pure, dry oxygen at 25°C, and after 15 min the suspension turned green-brown. Addition of water and diethyl ether and subsequent separation of the ether layer and its drying over anhydrous Na<sub>2</sub>SO<sub>4</sub> yielded a dry organic extract of reaction products. Removal of solvent and column chromatography of the residue gave 25% of tetraphenylfuran (XVI), m.p. 171–172°C after recrystallization from an ethanol/methylene chloride pair, and 70% of *cis*-1,2,3,4-tetraphenyl-2-buten-1,4-dione (XV), m.p. 210–211°C after recrystallization from ethanol. Both products were identified by comparison with authentic samples.

(6) *Bromine.* In separate experiments, 1.0–1.5 mmol samples of IIIb were suspended in 10 ml of pure methylene chloride and then cooled to –78°C. In separate runs, then, 1.0, 3.0 or 4.0 molar equivalents of Br<sub>2</sub> dissolved in CH<sub>2</sub>Cl<sub>2</sub> were slowly introduced. In all cases, a red-brown color, but no blue color, developed. After warming to room temperature the reaction solution was washed with aqueous Na<sub>2</sub>SO<sub>3</sub> and then 6 *N* aqueous HCl. Column chromatography yielded about a 60% yield of a mixture of 1,4-dibromo-1,2,3,4-tetraphenyl-1,3-butadiene (XVII) and 3-benzylidene-1,2-diphenylindene (XVIII) (m.p. 185–186°C), whose formation was verified by TLC, MS and IR data. Elution of insoluble organic material from the top of the column yielded bis(diphenylphosphino)ethane dioxide, m.p. 268–270°C (90%), which was identified by mixture m.p. and IR spectral comparison with an authentic sample.

(7) *Sodium diethylaluminum hydride*. A suspension of 0.643 g (0.80 mmol) of IIIb in 50 ml of toluene was treated with 0.74 ml (1.0 mmol) of  $\text{NaAlEt}_2\text{H}_2$  in toluene. Since no color change was observed, the mixture was stirred for 17 h at  $50^\circ\text{C}$  and for 7 h at  $75^\circ\text{C}$ . After cooling the reaction mixture was treated with dry air, in order to destroy any residual nickelole. A mixture of diethyl ether and aqueous  $\text{NaHCO}_3$  solution was added. The organic layer was separated, dried and evaporated to give an organic residue, which was subjected to column chromatography to yield (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (30%) (VI), *cis*-1,2,3,4-tetraphenyl-2-buten-1,4-dione (30%) (XV), tetraphenylfuran (10%) (XVI) and traces of (*E,Z*)- and (*Z,Z*)-1,2,3,4-tetraphenyl-1,3-butadienes, as verified by TLC, IR, MS and mixture m.p. comparisons. Also, 0.6 mmol of the diphosphine dioxide was recovered.

(8) *Diphenylacetylene (stoichiometric)*. The red nickelole was prepared from 1.0 mmol of XII and 1.0 mmol of diphos in 40 ml of toluene, which was treated with 2.0 mmol of *t*-butyllithium. After 6 h at  $-78^\circ\text{C}$  and 12 h coming to  $25^\circ\text{C}$ , the mixture was treated with 0.42 g (2.3 mmol) of diphenylacetylene and then heated to reflux for 18 h. Hydrolysis with deoxygenated 6 *N* aqueous HCl gave an orange precipitate of the diphos- $\text{NiCl}_2$ , which was filtered off. The organic filtrate was washed with aqueous  $\text{NaHCO}_3$  solution, dried over anhydrous  $\text{MgSO}_4$  and then evaporated to a smaller volume. Eventually 0.25 g (60%) of hexaphenylbenzene (XI) precipitated, as IR and MS data verified.

#### *Reactions of 2,3,4,5-tetraphenylnickelole-bis(triphenyl)phosphine (IIIa)*

(1) *Glacial acetic acid*. A 1.0-mmol sample of IIIa dissolved in 40 ml of toluene was cooled to  $-78^\circ\text{C}$  and treated with 3 ml of glacial acetic acid. After slowly being warmed to room temperature, the reaction mixture was freed of volatiles in vacuo and the residue worked up as in section (2) above. An 82% yield of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (VI) was isolated (mixture m.p. and IR comparison).

(2) *Dimethyl acetylenedicarboxylate*. The nickelole IIIa was formed from 3.84 mmol of dillithium reagent and 3.84 mmol of  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  in 75 ml of diethyl ether. The acetylenic ester (10.5 mmol) was added to the aforementioned reaction solution and the mixture stirred 16 h at  $25^\circ\text{C}$ . Work-up as in section (3) above yielded 1.32 g of dimethyl tetraphenylphthalate, m.p.  $259\text{--}261^\circ\text{C}$  (69%).

(3) *Carbon monoxide*. The nickelole IIIa was formed in an ether/benzene medium (2/1 v/v) on a 2.00-mmol scale. Treatment with 1 atmosphere of CO led to the absorption of 6 mmol of gas. After being stirred for 16 h at  $25^\circ\text{C}$ , the mixture was oxidized with dry air and the mixture was subjected to column chromatography. A total yield of 0.588 (76%) of pure tetraphenylcyclopentadienone (IX), m.p.  $217\text{--}219^\circ\text{C}$ , was isolated.

(4) *Diphenylacetylene*. The nickelole IIIa was formed in toluene on a 1.28 mmol scale. Addition of 40 mmol of the acetylene and heating at reflux for 18 h led to the formation of a yellow suspension. The yellow solid was filtered off and then washed successively with ethanol, acetone and ether. The crude yield was 93% and after this solid was extracted in Soxhlet extractor with  $\text{CHCl}_3$ , 6.45 g (87%) of pure hexaphenylbenzene was obtained. Thus, a turn-over number of 27 was achieved in the catalysis.



*Reactions of  $\eta^4$ -1,5-cyclooctadiene( $\eta^4$ -tetraphenylcyclopentadienone)nickel (XIX)*

(1) *Stability to heat and light.* A 0.40-mmol sample of XIX was heated for 72 h in 20 ml of refluxing toluene. After removal of the solvent, the  $^1\text{H}$  NMR and IR spectra of the residue showed the presence of only XIX.

A 0.70-mmol samples of XIX in 30 ml of benzene was irradiated for 20 h in a Rayonet photochemical reactor, Model RPR-100, which was equipped with lamps giving 254-nm light. Flash chromatography on silica gel with a hexane-methylene chloride gradient yielded 78% of recovered XIX, 5% of tetraphenylcyclopentadienone and traces of the latter's dihydro derivative, m.p. 162–163°C.

(2) *Reduction with bis(1,5-cyclooctadiene)nickel (XX).* A solution of 1.1 mmol of XIX and 1.1 mmol of XX in 30 ml of THF was allowed to stand for 90 min at 25°C. Thereafter, an excess of deoxygenated, aqueous 6 *N* HCl was introduced; an exothermic reaction occurred as the dark green color became light green. Work-up by ether extraction, drying of the organic layer over anhydrous  $\text{MgSO}_4$  and solvent removal gave a residue that was almost exclusively dihydrotetraphenylcyclopentadiene (XXIII, 65%), which melted at 162–163°C after recrystallization from ethanol-methylene chloride.

On the other hand, treatment of XIX itself in THF solution with deoxygenated 6*N*-aqueous HCl over 16 h gave no sign of the formation of the dihydro derivative.

(3) *Attempted displacement of 1,5-cyclooctadiene by bis(1,2-diphenylphosphino)ethane.* (a) *Thermal promotion.* An equimolar mixture of XIX and the phosphine on a 0.3-mmol scale was dissolved in 20 ml of toluene. After 72 h at 25–30°C there was neither color nor spectral change. The dark green solution was thereafter heated at reflux for 4 d, whereupon it became dark red. Removal of solvent in vacuo and column chromatographic separation under argon yielded the bis(bis(1,2-diphenylphosphino)ethane)nickel complex (XXI) m.p. 254–256°C, starting complex XIX, tetraphenylcyclopentadienone (55%), and bis (tetraphenylcyclopentadienone)nickel, m.p. 256–257°C, as black crystals (5%). The last product exhibited the following spectral properties: MS, *m/e* at 827, 826 (P), 444, 443, 442; IR, 1610  $\text{cm}^{-1}$  br.

(b) *Photochemical promotion.* A mixture of 0.9 mmol of XIX and 1.5 mmol of the phosphine was dissolved in 30 ml of benzene and the solution irradiated at 254 nm for 48 h. Work-up with deoxygenated aqueous HCl led to the deposition of the  $\text{diphos} \cdot \text{NiCl}_2$ , which was filtered off. Column chromatography of the dried organic layer led to the isolation of 58% of dihydrotetraphenylcyclopentadienone.

*Reactions of diphenylacetylene with bis(1,5-cyclooctadiene)nickel*

(1) *Trapping of the cis-stilbene precursor.* A solution of 2.34 g (8.5 mmol) of the diene-nickel complex XX and 2.82 g (15.8 mmol) of the acetylene X was formed in 25 ml toluene to yield a burgundy-red color. Addition of 3.39 g (8.5 mmol) of diphos led to a yellow precipitate. The suspension was stirred for 18 h at 25–30°C and then at 95°C for 1 h. The cooled black reaction mixture had no obvious precipitate. Addition of deoxygenated, 6 *N* aqueous HCl led to the deposition of the  $\text{NiCl}_2$  complex with diphos. The separated organic layer was washed with aqueous  $\text{NaHCO}_3/\text{NaCl}$  and dried over anhydrous  $\text{MgSO}_4$ . Concentration of this layer led to the deposition of 764 mg (27%) of hexaphenylbenzene. Column chromatography of the filtrate yielded 1.23 g of *cis*-stilbene (40%) and 82 mg of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene (3%).

(2) *Interception of (*E,E*)-1,2,3,4-tetraphenyl-1,3-butadiene.* A suspension of 4.30 g (1.56 mmol) of diene-nickel complex XX in 30 ml of THF was cooled to 0°C and

then a solution of 5.55 g (31.2 mmol) of diphenylacetylene in 30 ml of THF was added dropwise over 15 min. Thereby a red solution was attained and stirring was continued for another 15 min. Then 30 ml of 6 *N* aqueous HCl were added, the mixture exposed to air as it rose to 25°C and then ether added to extract the organic products. The organic extract was washed thoroughly with water, dried over anhydrous MgSO<sub>4</sub> and evaporated in vacuo. The residue was subjected to column chromatography on neutral alumina with an eluent gradient of benzene/hexane. A 2.0-g recovery of the acetylene was obtained (36%) and 276 mg of the butadiene were isolated (5%). Some hexaphenylbenzene was recovered from the top of the column.

(3) *Catalytic trimerization of diphenylacetylene.* A mixture of 400 mg of the diene-nickel complex XX, 8.90 g of diphenylacetylene and 30 ml of toluene was heated at reflux for 4 h. The precipitate formed was filtered off and washed with ethanol, acetone and ether to give 6.93 g of fairly pure hexaphenylbenzene (78%). Highly pure product was obtained by a Soxhlet extraction with CHCl<sub>3</sub>, 5.96 g (67%).

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