Oxidative Addition of Nickel(0) Complexes to Carbon–Carbon Bonds in Biphenylene: Formation of Nickelole and 1,2-Dinickelecin Intermediates[1,2]

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The dependence of the ease of oxidative insertion of various nickel(0) complexes into the central bond of biphenylene was examined as a function of the ligands attached to nickel. The complexes $(COD)_2Ni$ and $(Et_3P)_4Ni$ represent two extremes in reactivity: the former was unreactive toward biphenylene, whereas the latter reacted rapidly and completely even at 0 °C. The reactivity of the other nickel complexes increased in the sequence: $(COD)(bpy)Ni < (Ph_3P)_4Ni < (C_2H_4)(Ph_3P)_2Ni < (Et_3P)_4Ni$. The cleavage of the four-membered ring of biphenylene was also brought about by $(COD)_2Ni$ and $LiAlH_4$. The reaction product from the $(Et_3P)_4Ni$, dibenzonickelole–bis(triethylphosphine), was isolated in high yield and allowed to react, in turn, with DOAc, O_2, CO, and PhC≡CPh. Upon standing at 25 °C, this nickelole lost Et_3P and dimerized to tetrabenzo-1,2-dinickelecin-1,2-bis(triethylphosphine), whose structure was determined by an X-ray analysis. This macrocycle was allowed to react, in turn, with DOAc, $LiAlH_4$, and CO. Its thermolysis over 150 °C led to tetraphenylene and nickel metal. The thermal behavior of the aforementioned nickelole and dinickelecin is employed to develop a unified mechanistic scheme for interpreting the nickel-catalyzed Reppe trimerization and tetramerization processes for acetylenes.

Introduction

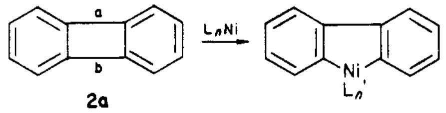
The insertion of low-valent transition metals into σ or the π carbon–carbon bonds is a process basic to many types of hydrocarbon transformations, such as hydrogenation,[4] skeletal rearrangement,[5] oligomerization,[6] and polymerization.[7] These oxidative additions generate carbon–metal bonds (eq 1) at which the hydrocarbon transformations can then take place (eq 2). Essential to the catalytic nature of such a process, however, is that such insertions be reversible (eq 3). In this step a reductive elimination regenerates the transition-metal catalyst.

$$R\text{-}R' + M^0 \rightarrow R\text{-}M\text{-}R' \quad (1)$$

$$R\text{-}M\text{-}R' \rightarrow R\text{-}M\text{-}R'' \quad (2)$$

$$R\text{-}M\text{-}R'' \rightarrow R\text{-}R'' + M^0 \quad (3)$$

The present study has sought to examine the factors fostering the oxidative addition of various nickel(0) complexes (L_nNi, 1) into the strained σ carbon–carbon bond of biphenylene (bonds a in 2). Since nickel(0) complexes have attained a commanding position in hydrocarbon technology,[8] we considered it essential to understand how the ligands (L) on the nickel alter its reactivity in such insertions. Furthermore, we chose biphenylene as the hydrocarbon substrate, since it is known that the central ring possesses considerable strain and since it was expected that the resulting insertion product dibenzonickelole (3) might be stabilized by the annulated benzene rings (eq 4).



(4)

2a **3**

1a–e

a, L_n = 2COD;
b, L = bpy, L = COD;
c, L_n = $4Et_3P$;
d, L_n = $4Ph_3P$;
e, L = C_2H_4, L = $2Ph_3P$

Two prior studies have addressed the question of transition-metal-promoted reactions of 2. In a limited examination, $Cr(CO)_6$ was found to convert 2 into 9-fluorenone,[9] a product that could be viewed as arising from the insertion of Cr^0 into 2 (cf. 3) and subsequent carbonylation. In a more extensive investigation, the carbonyls of Mo, Fe, and Ni were heated with 2 but no ring cleavage products were noted.[10] From 2 and $Mo(CO)_3$(diglyme), however, either a bis(molybdenum) $[(Mo(CO)_3)_2(C_{12}H_8)]$ or a mono(molybdenum) $[Mo(CO)_3(C_{12}H_8)]$ π complex of 2 was isolable. Only when 2 was heated at 100 °C with $Ni(CO)_2(Ph_3P)_2$ could a small amount of cleavage product, tetraphenylene, be identified. Thus, previous work had not proved the formation of metalloles, such as 3, from 2, but the latter work did show that the ligands on the nickel(0) complex might change the reactivity in oxidative addition.

Results

Cleavage of Biphenylene by Nickel(0) Complexes. Treatment of biphenylene (2) with $(COD)_2Ni$ in THF solution at 25–50 °C for 20 h and subsequent workup with O_2, CO, or aqueous 6 N HCl produced no cleavage products; only 2 was recovered unchanged. However, the combined action of an admixture of $(COD)_2Ni$ with $LiAlH_4$ (1:2) in THF solution readily cleaved 2 in a quantitative

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[1] On the occasion of his sixtieth birthday, dedicated to Professor Günther Wilke, whose marvelous chemical touch has transmuted the base metal, nickel, into a golden realm of research.

[2] Part 9 of the series "Organic Chemistry of Subvalent Transition Metal Complexes". Part 8: Eisch, J. J.; Aradi, A. A.; Han, K. I. *Tetrahedron Lett.* 1983, *24*, 2073.

[3] (a) State University of New York at Binghamton. (b) Max-Planck-Institut für Kohlenforschung.

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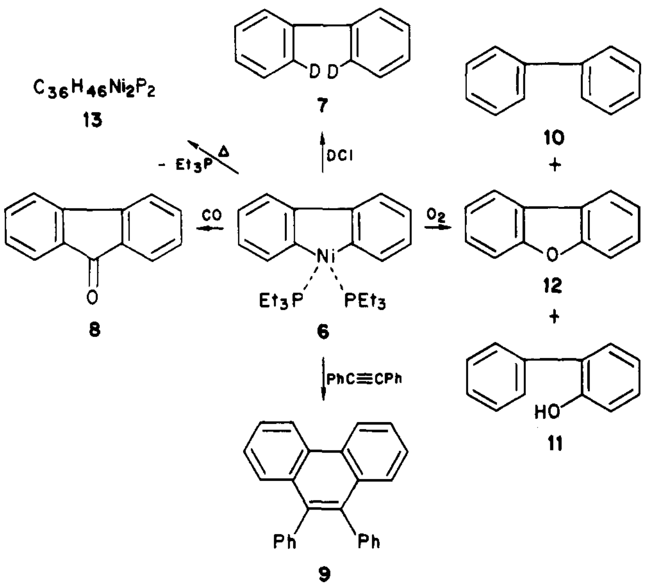
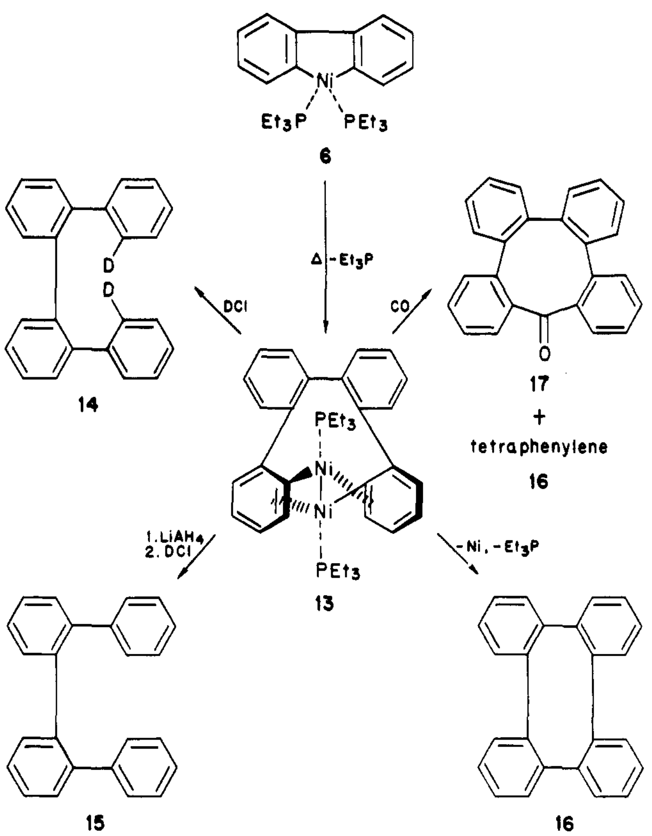
Scheme I



Scheme II



manner. According to a literature report,[11] such a mixture of reagents is said to lead to an anionic nickel complex of the type shown in 4 (eq 5).

$$(COD)_2Ni + 2LiAlH_4 \rightarrow \underset{4}{Li_2Ni(AlH_3)_2} + H_2 + COD \quad (5)$$

On the other hand, when one or both of the 1,5-cyclooctadiene ligands was replaced by 2,2′-bipyridyl or a triorganophosphine, the resulting nickel(0) complex inserted into the central carbon–carbon bond of 2. The ease of such oxidative addition (cf. eq 4), as judged by the proportion of 2 converted into cleavage products, increased in the following order for the ligands on nickel: bipyridyl < triphenylphosphine ≪ triethylphosphine. If the reaction product was carbonylated, 9-fluorenone was a major product; in the case of a hydrolytic workup, 1,1′:2′,1″:2″,1‴-quaterphenyl was the principal cleavage product.

Isolation and Reactivity of Dibenzonickelole–Bis(triethylphosphine) (6). Tetrakis(triethylphosphine)nickel (5) reacted with biphenylene (2) so readily that the reaction could be conducted at ~0 °C and the unstable dibenzonickelole 6 isolated in high yield. Although the thermal lability of 6, especially in solution, precluded a measurement of its molecular weight, its elemental analyses, spectral properties, and chemical reactions are in excellent agreement with the structure of 6 given in Scheme I. Its ^{1}H NMR spectrum, for example, displays the two deshielded aromatic protons expected for the protons ortho to a carbon–metal bond.[12] The ready solubility of 6 in diethyl ether at 0 °C is in better accord with a monomeric nickelole as depicted, rather than with a dimeric or some more highly associated form of nickelole monomers (cf. the solubility of dinickelecin 13).

Decisive evidence for the nickelole ring in 6 emerges from the reactions depicted in Scheme I. Cleavage with 12 N DCl in D_2O at 25 °C gave a 92% yield of 2,2′-dideuteriobiphenyl (7). Treatment with CO between -78 and 25 °C provided an 89% yield of 9-fluorenone (8). Even the unreactive alkyne, diphenylacetylene at 70 °C converted 6 into 9,10-diphenylphenanthrene (9) in over 50% yield. Oxidation with O_2 at 25 °C and subsequent hydrolysis gave an array of products, prominent among which were biphenyl (10), 2-hydroxybiphenyl (11), and dibenzofuran (12). Finally, 6 underwent a facile and remarkable dimerization, even at 25 °C, to yield tetrabenzo-1,2-dinickelecin–1,2-bis(triethylphosphine) (13) (cf. infra).

Isolation and Reactivity of Tetrabenzo-1,2-dinickelecin–1,2-Bis(triethylphosphine) (13). Upon standing at 25 °C, a rust-brown solution of nickelole 6 in various ethers gradually turned dark green as 13 was formed. Since the conversion involves the loss of one mole of Et_3P from 6, the dimerization could be retarded by adding excess Et_3P to the original solution of 6.

The structure of 13 was determined by the X-ray crystallographic analysis on a sample that gave acceptable elemental analyses for all four elements present. The unusual features of the bonding in this dinickelecin (13) are discussed in the next section.

The chemical properties of this nickel heterocycle are summarized in Scheme II. The carbon–nickel bonds in 13 are smoothly cleaved at 25 °C by either 12 N DCl in D_2O or $LiAlH_4$ to give high yields of 1,1′:2′,1″:2″,1‴-quaterphenyl-d_2 (14) or 1,1′:2′,1″:2″,1‴-quaterphenyl (15), respectively. Treatment of 13 with CO at 25 °C led to ~50:50 mixture of tetraphenylene (16) and the novel cyclic ketone tetrabenzo-2,4,6,8-cyclononatetraenone (17). The structure of 17 was established by satisfactory elemental analytical and mass spectral data. Furthermore, the IR spectrum displayed an intense C=O stretch at 1640 cm^{-1}, while the ^{1}H NMR spectrum exhibited two relatively deshielded aromatic protons at 6.9–7.2 ppm, which are in accord with two ortho protons deshielded relative to the aromatic multiplet between 6.2 and 6.8 ppm.

The further thermal transformation of 13 is of particular interest. Above 150 °C 13 decomposed rapidly with the separation of metallic nickel and the release of tetraphenylene (16).

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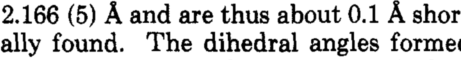
X-ray Crystal Structure of Tetrabenzo-1,2-dinickelecin-1,2-Bis(triethylphosphine) (13). The two independent molecules within the asymmetric unit differ mainly in the relative orientations of the ethyl groups. The molecular structure consists of two bis(triethylphosphine)nickel moieties linked by one 1,1′:2′,1″:2′,1‴-quaterphenylene unit. Each nickel atom is π-bonded to two adjacent carbon atoms of one terminal ring and σ bonded to one of these carbon atoms. Thus, each part of the hydrocarbon ligand supplies three electrons to the system. Without considering metal–metal interactions, the nickel atoms show a trigonal-planar coordination geometry. The Ni(1)–Ni(2) bond lengths of 2.323 (4) and 2.314 (4) Å, respectively, are considerably shorter than those found typically for Ni–Ni single bonds.[13a] They compare favorably with distances found in isoelectronic phosphido-bridge nickel–nickel systems and in similar molecules in which a double bond between the metals might be anticipated.[13b]

The nickel–phosphorus bond lengths lie between 2.142 (6) and 2.166 (5) Å and are thus about 0.1 Å shorter than are usually found. The dihedral angles formed by P–Ni–Ni–P atoms are 78.1 and 78.8°, respectively. Known Ni–C bond lengths usually vary between 1.87 (1) and 1.97 (2) Å for σ-bonded and between 1.93 (1) and 2.27 (2) Å for π-bonded atoms.

Due to disorder of thermal vibrations of all the ethyl groups, the P–C bond distances are rather poorly determined and range between 1.71 (5) and 2.00 (4) Å. The phenylene groups are planar within ±0.03 Å. As is observed in biphenylene,[14] and tetrabenzo[*a*,*c*,*e*,*g*]cyclooctatetraene,[13c] the C–C bridge bond lengths between the two rings are substantially longer (1.49 (2) and 1.54 (2) Å) than the C–C distances within the benzene rings. Dihedral angles between two adjacent phenylene rings range between 73.9 and 88.9 Å.

Discussion

By X-ray diffraction, the C–C bond distance for bonds a of biphenylene is 1.52 Å; the other four-membered ring bonds are 1.46 Å (b in **2b**).[14] In valence bond terms, structure **2a** is considered to be the single, most important resonance contributor. That others, such as **2b** and **2c**,



2b **2c**

are much less important, implies that there is little cyclobutadienoid character in the central ring. Experimental heats of combustion[15] and approximate quantum mechanical calculations[15,16] ascribe a relatively low resonance energy to **2**, of about 9–22 kcal/mol. Such a small stabilization is attributed to the high strain energy of the four-membered ring, ranging from 59 to 66 kcal/mol, depending on the particular MO approximation.

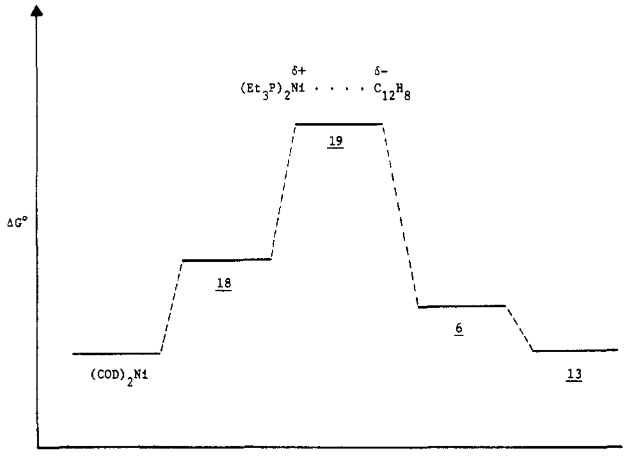
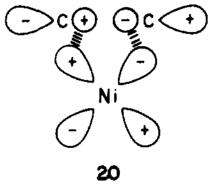


Figure 1. Schematic representation of $\Delta G°$ changes in the course of oxidations between biphenylene and nickel(0) complexes (example shown for $(Et_3P)_4Ni$).

However, the key observations in this investigation have been the rapidity with which nickel(0) complexes oxidatively insert into bond a of **2** and the dependence of such insertions on the ligands attached to nickel. As extremes can be cited the relative reactivities of $(COD)_2Ni$ and $(Et_3P)_4Ni$: at 25 °C, the former gave no sign of cleaving **2**, while the latter converted **2** quantitatively into nickelole **6**. That the replacement of one or both COD ligands successively by bipyridyl, by Ph_3P, and finally by Et_3P increased the extent of cleaving **2** suggests that more basic ligands promote oxidative addition. That $(CH_2{=}CH_2)(Ph_3P)_2Ni$ proved to be more reactive than $(PH_3P)_4Ni$ seems to indicate that biphenylene must coordinate with nickel for insertion (**18**) and thus must compete with ligands initially present on nickel. It is reasonable that **2** competes more effectively with ethylene than with Ph_3P (eq 6).

$$\underset{\mathbf{18}}{(Ph_3P)_2Ni\cdot 2} \underset{L\,=\,2Et_3P}{\rightleftharpoons} (Ph_3P)_2NiL \underset{L\,=\,COD}{\rightleftharpoons} \underset{\mathbf{18}}{(Ph_3P)_2Ni\cdot 2} \qquad (6)$$

The fostering influence of more basic ligands on the oxidative insertion of nickel(0) into biphenylene is clearly both kinetic and thermodynamic in nature. Such a kinetic effect can be rationalized by viewing more donor ligands as increasing the electron density on the nickel(0) center and thereby raising the energy levels of the metal's unshared d electrons. When the energy of the nickel's d electrons is raised in the new complex **18**, the activation energy required for the electron transfer involved in the oxidative insertion, **18** → **19**, is lowered (Figure 1). It might be further noted that the interaction of nickel(0) with the central carbon–carbon bond of biphenylene can be viewed as symmetry allowed and hence concerted under thermal conditions.[21] The symmetry of a filled d_{xy} orbital and the antibonding σ orbital of the C–C bond permit net overlap to be maintained from ground-state **18** through transition state **19** (cf. **20**).



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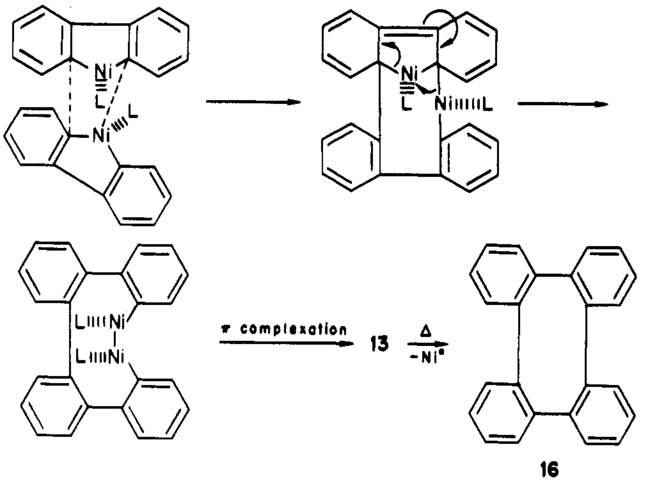
[19] In unpublished work (J. J. Eisch and A. Piotrowski) combinations of Ni(0) complexes and $LiAlH_4$ have been found to remove fluorine from organic fluorides and reduce aromatic ketones to diarylmethanes.

[20] A combination of $(COD)_2Ni$, bipyridyl, and $LiAlH_4$ is a potent desulfurizing agent for aryl sulfides and aromatic sulfur heterocycles: Eisch, J. J.; Hallenbeck, L. E.; Han, K. I. *J. Org. Chem.* **1983**, *26*, 2963.

Scheme III



The thermodynamic promotion of oxidative addition by basic ligands is more straightforward: the higher positive charge on the resulting nickel(II) complex would increase the bond energy between the positive nickel and the more donating ligand (eq 7). Although it might be thought that

$$L_nNi{:}D_m \rightleftharpoons L'^{2-}_n Ni^{2+}{:}D_m \qquad (7)$$

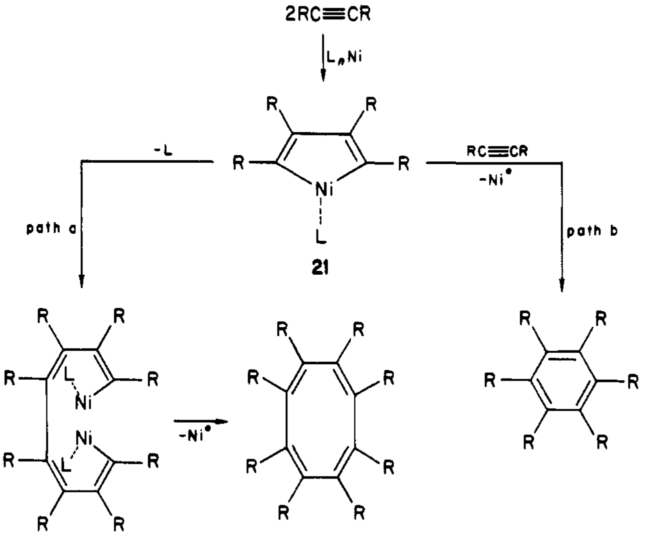
more basic ligands like Et_3P would retard oxidative addition because requisite, coordinatively unsaturated $(Et_3P)_3Ni$ or $(Et_3P)_2Ni$ is less readily formed from $(Et_3P)_4Ni$, such is not the case. Even though olefin ligands are readily displaced from nickel(0) by phosphines (witness the preparation of $(Et_3P)_4Ni$ from $(COD)_2Ni$), these olefin complexes are decidedly less reactive.

However, although the formation of nickelole **6** is favored by both such kinetic and thermodynamic considerations, it is a metastable, highly labile product. Even at 25 °C it gradually loses Et_3P and dimerizes into the unusual dinickelin **13**, which is more stable but is itself metastable with respect to tetraphenylene and nickel(0) (Scheme II). The mechanism by which **6** dimerizes to yield **13** apparently involves the initial loss of one Et_3P from **6**. This conclusion follows from two observations: (a) addition of extra Et_3P to **6** strongly retards the formation of **13** and (b) in the reaction of biphenylene with either $(Ph_3P)_4Ni$ or $(CH_2{=}CH_2)(Ph_3P)_2Ni$ the same rust-brown intermediate is formed (analogous to **6**), but this intermediate is much less stable and readily forms the dark green dinickelecin. The latter point implies that the intermediate nickelole is much less stable with Ph_3P ligands because the latter, for steric reasons, dissociates more extensively than Et_3P and thus initiates dimerization to a dinickelecin.

The actual dimerization step for the dibenzonickelole monophosphine (**21**) could be viewed as a variant of a Diels–Alder reaction between one nickelole functioning as a diene and the other nickelole providing its C–Ni bond as a dienophile (Scheme III). As a chemical precedent for this interpretation, the Diels–Alder reaction between **6** and diphenylacetylene to produce 9,10-diphenylphenanthrene (**9**) can be cited. Furthermore, it should be noted that a σ C–Ni bond orbital can interact with the LUMO of a diene system with conservation of orbital overlap and hence is symmetry allowed[21] (cf. a similar argument depicted in **20** supra).

However, at least one other dimerization pathway deserves serious consideration, namely, a nickel–nickel interaction between two coordinatively unsaturated dibenzonickeloles, followed by a variant of reductive elimination involving two nickel centers. Such reductive elimination would ensue with the formation of a carbon–carbon bond between the two biphenylene units and a nickel–nickel bond. At the present, evidence does not permit a choice between the Diels–Alder view and this type of cycloaddition.

Scheme IV



Finally, in the unusual transformation represented in Scheme III, namely, the dimerization of two nickeloles with the ultimate formation of a cyclooctatetraene (**16**), we may have identified a possible mechanistic route by which acetylenes are converted into cyclooctatetraenes by nickel catalysts in the Reppe process.[22-24] Our previous work[25,26] and that of Hoberg[27] have demonstrated that acetylenes are trimerized by nickel(0) catalysts via the intermediate formation of nickeloles. The present work raises the possibility that such trimerization or tetramerization of acetylenes may possess an underlying mechanistic unity, in that both processes involve the formation of nickeloles (**21**, Scheme IV). The mechanistic pathways for the nickelole to the final oligomer would diverge, depending upon whether the nickelole would dimerize (path a to tetramer) or react preferentially with alkyne (path b to trimer). It is reasonable to suppose that preference for path a or path b would be highly dependent upon the substituents (R) and ligands (L) on nickelole **21**. In the present study, for example, it was shown that the ease of dimerization of the dibenzonickelole to the dibenzodinickelecin increased as L was changed from Et_3P to Ph_3P.

Experimental Section

Instrumentation. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are corrected. Infrared spectra (IR) were recorded on a Perkin-Elmer spectrometer, Model 457, equipped with sodium chloride optics. Proton magnetic resonance spectra (^{1}H NMR) were obtained with

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[25] (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1975**, *96*, C23; (b) Eisch, J. J.; Damasevitz, G. A. *J. Organomet. Chem.* **1975**, *96*, C19.

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[27] Hoberg, H.; Richter, W. *J. Organomet. Chem.* **1980**, *195*, 355.

a Varian spectrometer, Model EM-360, on neat samples or on 10% solutions in pure solvents, and ^{13}C NMR spectra were recorded with a Varian FT 80-MHz multinuclear spectrometer. The values are reported on the δ scale in parts per million with reference to internal or external tetramethylsilane, followed by the relative proton intensities and, for ^{1}H NMR spectra, the coupling constants (J) in hertz. Vapor phase chromatographic analysis (VPC) and isolations were carried out on an F & M chromatograph, Model 720, equipped with a 12 ft × 0.25 in. column of 10% UC-298 on Chromosorb W. Mass spectra of solids and liquids were initially obtained with Du Pont spectrometer, Model 21-491B, and subsequently through the mass spectral facility at Cornell University. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

General Procedures. All preparations and reactions involving air- and moisture-sensitive organometallic compounds were conducted under an anhydrous, oxygen-free atmosphere, which was nitrogen for organolithium compounds and argon for organonickel reagents. The appropriate techniques for the transfer reaction, analysis, and purification of such reagents have been recently described in detail.[28]

The yields of organic degradation products from organonickel reactions were determined by the isolation and weighing of the crude products and the analysis of the mixture by GLPC. *p,p′*-Bitolyl was employed as an internal standard. Response factors were determined on pure samples of all compounds encountered in such analyses. For identification and spectral analyses the individual components were separated or collected by column or gas–liquid chromatography.

Starting Materials. Solvents. Commercial solvents were purified according to recommended published procedures.[29] Tetrahydrofuran (THF), ethyl ether, benzene, and toluene were distilled under nitrogen after being heated at reflux over sodium–potassium alloy.

Reagents. The biphenylene was synthesized from diazotized anthranilic acid in general accordance with a published method.[30] It was found advantageous to carry out the reaction on a 0.25-mol scale, combine the crude product mixtures, and separate the biphenylene by codistillation with ethylene glycol. In this manner, a product of mp 110–112 °C was obtained.

Bis(1,5-cyclooctadiene)nickel was prepared by a modification[20] of a known procedure.[31] This complex was used, in turn for the preparation of tetrakis(triethylphosphine)nickel[32] by admixing $(COD)_2Ni$ with triethylphosphine in diethyl ether solution and filtering off the precipitated $(Et_3P)_4Ni$ (85% yield). Ethylene[bis(triphenylphosphine)]nickel was prepared by the reduction of nickel(II) acetylacetonate by triethylaluminum in the presence of 2 equiv of triphenylphosphine. the ether solution was then saturated with ethylene. During all operations an argon–ethylene atmosphere had to be maintained and the yellow complex was never subjected to reduced pressure, in order to avoid decomposition of the product. Tetrakis(triphenylphosphine)nickel was prepared in a conventional manner.[31]

The deuterated reagents were obtained from the Aldrich Chemical Co: deuterium oxide (99.8% D_2O), deuterium chloride (37%, 99.8% D), *O*-deuterioacetic acid (98% CH_3CO_2D), and $LiAlD_4$ (98%).

Products. 2,2′-Dideuteriobiphenyl was prepared by treating a solution of 1.3 mmol of 2,2′-diiododiphenyl in 4 mL of anhydrous THF at 0 °C with 2.9 mmol of butyllithium in hexane–THF. After being warmed to 25 °C, the mixture was treated with D_2O and worked up in the usual manner. The deuterated biphenyl was collected by GLPC: MS, *m/e* (relative intensity) 157 (M + 1, 15.1), 156 (M, 100), 155 (44.8), 154 (46.3), 153 (19.5); IR (CS_2) 785 (0.22), 740 (0.15), 705 (0.05), 640 (0.34) cm^{-1}. The infrared spectral band at 640 cm^{-1} served to distinguish this compound from undeuterated biphenyl, which does not absorb in this region. Also, the weak band at 705 cm^{-1} distinguishes it from 2-deuteriobiphenyl, which has a strong band at this position.

9-Fluorenone (Aldrich) was recrystallized from ethanol, mp 84–85 °C. 9,10-Diphenylphenanthrene was prepared by rearrangement and dehydrogenation of 9,9-diphenyl-9,10-dihydrophenanthrene by *n*-butyllithium, mp 235.0–235.5 °C, after recrystallization from a hexane–methylene chloride pair.

Reaction of Biphenylene (2) with Nickel(0) Complexes. (a) Bis(1,5-cyclooctadiene)nickel (1a) with and without $LiAlH_4$. A yellow solution of 245 mg (0.93 mmol) of **1a** in 8 mL of anhydrous THF was treated with 120 mg (0.78 mmol) of **2**. During a reaction time of 20 h at 25 °C, the initially bright yellow solution turned green-yellow and deposited a black solid. Aliquots of the reaction mixture were treated in three different ways: passing dry air through a sample; passing CO through a sample and the hydrolyzing; and finally, treating a sample with aqueous 6 N HCl. In each case, only **2** was detected in the organic residue; no biphenyl was formed.

However, when a similar reaction between **1a** and **2** was conducted but an excess of $LiAlH_4$ (>4.0 mmol) was added after 20 h, then a workup with aqueous 6 N HCl and a gas chromatographic analysis showed the presence of a 7:3 ratio of biphenyl and **2**. The components were collected individually and their identities verified by spectral data.

A control experiment in which **2** in THF was exposed to $LiAlH_4$ for 45 h yielded only biphenylene upon hydrolytic workup. But prior admixing of 1.0 mmol of $LiAlH_4$ with 0.52 mmol of **1** in 10 mL of THF at −40 °C gave a dark red solution, which readily cleaved **2**. Adding 0.40 mmol of **2** at −40 °C, bringing the mixture to 25 ± 5 °C over 5 h, stirring it for an additional 13 h, and then hydrolyzing gave only biphenyl and no trace of **2**.

(b) (2,2′-Bipyridyl)(1,5-cyclooctadiene)nickel (1b). This dark purple complex was prepared by admixing 9.13 g (34.8 mmol) of **1a** with 4.0 g (25.6 mmol) of 2,2′-bipyridyl in 100 mL of THF. After being stirred for 2 h, much of the THF was removed under reduced pressure. Deoxygenated ethyl ether was added and **1b** crystallized out at −76 °C; 604 g (73%). This complex (18.7 mmol) was dissolved in 100 mL of THF. Then 2.85 g (18.7 mmol) of **2** was introduced and the resulting dark mixture stirred for 24 h at 25 ± 5 °C and, finally, for 24 h at 50–55 °C. The reaction mixture was treated with dry CO at 25 °C and subsequently hydrolyzed with aqueous 6 N HCl. Column chromatographic separation on silica gel and elution with a hexane–benzene pair gave 2.07 g (73%) of recovered **2** (mp 110.5–112 °C) and 4.04 mg (12%) of 9-fluorenone (mp 82–83 °C).

(c) Tetrakis(triethylphosphine)nickel (1c). A purple solution of 266 mg (0.50 mmol) of **1c** in 10 mL of THF was treated with 61 mg (0.40 mmol) of **2**. The color slowly changed to a greenish brown during 24 h at 20 ± 5 °C. Either treatment with an excess of $LiAlH_4$ (followed later by H_2O) or hydrolysis with 6 N HCl gave 25% of biphenyl and 62% of 1,1′:2′,1″:2″,1‴-quaterphenyl (cf. infra). No biphenylene was detected.

(d) Tetrakis(triphenylphosphine)nickel (1d). A red-brown solution of 4.0 g (3.81 mmol) of **1d** in 100 mL of THF, upon treatment with 533 mg (3.50 mmol) of **2**, turned dark green within 10 min at 25 °C. After 12 h the reaction mixture was hydrolyzed with aqueous 6 N HCl. No biphenyl was found; only triphenylphosphine and 1,1″:2′,1″:2″,1‴-quaterphenyl (mp 117–118 °C) were isolated.

(e) Ethylene[bis(triphenylphosphine)] (1e). An orange-brown solution of 3.36 g (5.48 mmol) of **1e** in 100 mL of THF turned brown upon adding 669 mg (4.40 mmol) of **2**. After 3-h stirring period at 25 ± 5 °C, the mixture had turned dark green. As the THF was removed under reduced pressure, the residual solution turned dark brown. The dark brown residue was suspended in pentane and filtered on a glass frit. The brown solid was washed several times with pentane and with cold ether. Part of this brown solid was dissolved in warm ether, and the resulting solution kept at −78 °C to deposit a solid. The other portion of the solid was washed repeatedly with small portions of toluene, until the solution coming through the frit was greenish in color. Maintaining the filtrate at −20 °C eventually gave dark green crystals. These crystals gave only Ph_3P and 1,1′:2′,2″:2″,1‴-quaterphenyl upon hydrolysis with aqueous 6 N HCl (cf. infra).

Isolation of Organonickel Intermediates from Biphenylene and Tetrakis(triethylphosphine)nickel. (a)

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Dibenzonickelole–Bis(triethylphosphine) (6). A solution of 7.5 g (14.1 mmol) of **1c** and 1.71 g (11.2 mmol) of **2** in 50 mL of ethyl ether was stirred for 18 h at 0 °C. Temperature control was essential to retard the nickelole from rearranging to the green dinickelecin. Some solvent was then removed at 5 °C under reduced pressure, and the rust-brown product was crystallized from the solution at −78 °C. An 82% yield of **6** was obtained: ^{1}H NMR (C_6D_6) δ 0.6–1.7 (br d, 30 H), 6.9–7.3 (br m, 6 H), 7.35–7.6 (br m, 2 H). Anal. Calcd for $C_{24}H_{38}NiP_2$: C, 64.46; H, 8.56; Ni, 13.12. Found: C, 64.32; H, 8.50; Ni, 13.01. (Sample had to be kept cold until analyses, in order to prevent loss of Et_3P and rearrangement to the green dinickelecin **13**.)

(b) Tetrabenzo-1,2-nickelecin-1,2-Bis(triethylphosphine) (13). A solution of 7.5 g (14.1 mmol) of **1c** and 1.71 g (11.2 mmol) of **2** in 100 mL of THF was stirred for 5 h at 18 °C and for 15 h at 0 °C. Thereupon, the solvent was removed at 10 °C under reduced pressure and the residual solid washed with three 20-mL portions of cold pentane (~0 °C). The product was suspended in a mixture of 60 mL of pentane and 30 mL of ethyl ether for a period of 15 h at 20 °C. Then about half of the solvent was evaporated. Some Et_3P was added to the residual solution, and the solution was stored at −78 °C overnight. Dark green crystals of **13** were deposited (88% yield): ^{1}H NMR (C_6D_6) δ 0.5–1.5 (br m, 30 H), 6.2 (d, 2 H, 7.0 Hz), 6.7 (t, 2 H, 7.0 Hz), 6.82 (d of d, 2 H, 7.0 and 2.0 Hz), 7.1 (m, 10 H). Anal. Calcd for $C_{36}H_{46}Ni_2P_2$: C, 65.70; H, 7.04; Ni, 17.84; P, 9.41. Found: C, 65.49; H, 7.13; Ni, 17.83; P, 9.55.

Chemical Reactions of Dibenzonickelole–Bis(triethylphosphine) (6). (a) Thermal Rearrangement. The rust-brown complex **6**, when dissolved in THF or Et_2O and kept at 25 °C, was converted completely into the dark green dinickelecin after 12–15 h.

(b) Deuterium Chloride. Treatment of complex **6** with 12 N DCl in D_2O at 25 °C and separation of the organic products on a silica gel column gave traces of 1,1′:2′,1″:2″,1‴-quaterphenyl (mp 117–118 °C) and tetraphenylene (mp 232–232.5 °C), as comparison with authentic samples verified. The main component, obtained in 92% yield, was biphenyl. Mass spectral and infrared spectral analyses showed that it was 2,2′-dideuteriobiphenyl in >95% purity.

(c) Carbon Monoxide. A 1.97-g sample of **6** (4.4 mmol) in 25 mL of THF was cooled at −78 °C and treated with CO. Over several hours the temperature was allowed to reach 25 °C. Evaporation of the solvent and column chromatographic separation of the residue on silica gel with a hexane–benzene eluting pair gave 0.71 g (89%) of 9-fluorenone, mp 81–83 °C.

(d) Diphenylacetylene. A 1.79-g sample of **6** (4.0 mmol) in 20 mL of THF was treated with 0.71 g of diphenylacetylene for 12 h at 0 °C, 2 h at 25 °C, and 12 h at 70 °C. Workup with aqueous 6 N HCl, separation of the organic products with benzene, drying of the organic layer with $MgSO_4$, and solvent removal gave a solid residue. Recrystallization of the latter from a hexane–methylene chloride pair yielded 630 mg (52%) of 9,10-diphenylphenanthrene: mp 235–235.5 °C; MS, *m/e* 330 (M$^+$).

(e) Oxygen. Treatment of a 1.5 g sample of **6** in 20 mL of THF with a slow stream of dry O_2 at 20–25 °C for 2 h and hydrolytic workup with water gave a complicated mixture of products: more than 7 were detected by TLC and GC analyses. However, the presence of 2-hydroxybiphenyl, biphenyl, and dibenzofuran was confirmed by isolation and both infrared and mass spectral analysis.

Chemical Reactions of Tetrabenzo-1,2-dinickelecin–1,2-Bis(triethylphosphine) (13). (a) Thermolysis. In a sealed capillary under an argon atmosphere **13** has an apparent melting point of 146 °C. Heating of the green crystals between 150 and 200 °C led to the deposition of a nickel mirror on the glass vessel and the formation of tetraphenylene.

(b) Deuterium Chloride. Treatment of 4.0 mmol of **13** in mL of THF with an excess of 12 N DCl in D_2O for 24 h at 25 °C led to the isolation of 85% of 1,1′:2′,1″:2″,1‴-quaterphenyl-d_2'. MS, *m/e* 308 (M$^+$).

(c) Carbon Monoxide. Treatment of 5.5 mmol of **13** in 25 mL of THF with dry CO at 25 °C for 3 h and then hydrolysis with aqueous 6 N HCl gave an organic layer, from which tetraphenylene and a new compound, **17**, were isolated by column chromatography on silica gel. These components were formed in about 45% and 40% yields, respectively. Compound **17** melted at 202.5–203.5 °C (from ethanol): MS (70 eV), *m/e* (relative intensity) selected peaks at 333 (25), 332 (98), 331 (31), 315 (11), 305 (17), 304 (48), 303 (100), 302 (66), 301 (11), 300(25), 226(19), 151 (27), 150 (31), 104 (30), 76 (34); NMR (C_6D_6) δ 6.2–6.8 (m, 16 H), 6.9–7.2 (m, 2 H); IR (KBr, cm^{-1}) 1640 (s), 1590 (m), 765 (s), 750 (s). These data permit **17** to be identified as tetrabenzo-2,4,6,8-cyclononatetraenone. Anal. Calcd for $C_{25}H_{16}O$: C, 90.33; H, 4.85. Found: C, 90.16; H, 4.88.

Table I. Crystallographic Data for Tetrabenzo-1,2-dinickelecin–1,2-Bis(triethylphosphine) (13)

Crystal Data	
formula	$C_{36}H_{46}P_2Ni_2$
M_r	658.14
cryst system	monoclinic
space group	*Pa* (No. 7)
a, Å	17.188 (1)
b, Å	11.890 (1)
c, Å	17.226 (1)
β, deg	102.111 (7)
V, Å^3	3442.04
Z	4
D_{calcd}, g cm^{-3}	1.27
Measurement of Data	
X-radiation	λ = 1.541 79 Å
reflctns measd	202 217
μ(Cu Kα)	23.9 cm^{-1}
θ limits, deg	$1.8 < \theta < 70$
θ–2θ scan technique (48 steps)	
horizontal detector aperture, mm	$(5.0 + 1.25 \tan\theta)$
vertical aperture, mm	4.0
Ω scan range	$0.8 + 0.35 \tan\theta$
$\sigma(F)$	$(\sigma(I)\text{ Poisson}^2 + (Ik)^2)^{1/2}$ $2F$, $k = 0.2$
no. of variables	361
unique reflctns	6527
obsd reflctns	3118 ($I > 2.0\sigma(I)$)
R	0.078
R_w ($w = I/\sigma^2(F_o)$)	0.086

(d) Lithium Aluminum Hydride. A solution of 5.5 mmol of **13** in 25 mL of THF was heated at reflux with an excess of $LiAlH_4$ for 2 h. Cautious addition of D_2O in ethyl ether, followed by 25% aqueous DCl, gave upon the usual isolation steps 82% of largely undeuterated 1,1′:2′,1″:2″:1‴-quaterphenyl.

Experimental Details of the Structural Analysis of Dinickelecin (13). A suitable single crystal of **13** was selected for data collection and sealed in a glass capillary under an atmosphere of argon. Intensity data were collected on a Nonius CAD-4 diffractometer using CuK *Kα* radiation. A total of 20217 reflections were collected in a range (1.8° < θ < 70°) [$\pm h,+k,+l$] by using Ω–2θ scan technique with the scan speeds varying from 1.3 to 10.0° min^{-1}, depending on the standard deviation to intensity ratio of a preliminary 10° min^{-1} scan. The intensity of the reflection and its standard deviation were calculated from INT − 2(BGL + BGR) and (INT + 4(BGL + BGR))$^{1/2}$, respectively, where INT, BGL, and BGR are the peak intensity and the left and right backgrounds. The time spent measuring the backgrounds was half taken to measure the peak. A Ni filter was inserted in front of the detector if the peak count was greater than 5000 counts s^{-1}. The intensity of the three monitor reflections remeasured after every 90 min of X-ray exposure showed no significant variation during the course of data collection. Intensities were corrected for Lorentz and polarization effects,[34] but no absorption of extinction correction was applied (μ = 23.9 cm^{-1}). Weissenberg and precession photographs showed the Laue symmetry of the diffracted intensities to be $2/m$. Possible space groups consistent with the systematic absences were *Pa* (No. 7) of *P*2/*a* (No. 13). Subsequent refinement of the structure showed the acentric space group *Pa* to be the correct choice. Equivalent reflections were averaged, $R = (\sum(F - \langle F\rangle)^2/\sum\langle F\rangle^2(m-1))^{1/2}$ = 0.031, where m is the number of equivalent reflections averaged, and yielded a total of 3118 observed intensities ($I > 2.0\sigma(I)$), which were used in the solution and refinement of the structure. Pertinent crystal data are given in Table I; the cell parameters were obtained by least-squares fit to the θ values of 75 auto-

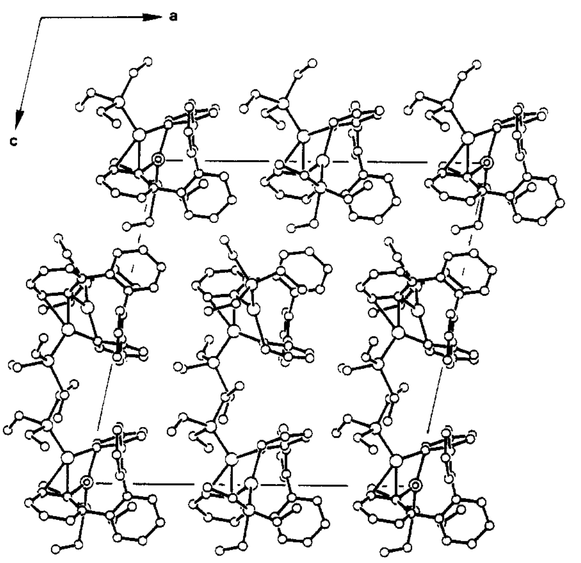

Figure 2. The atomic numbering scheme and the structure of one of the two molecules of tetrabenzo-1,2-dinickelecin-1,2-bis(triethylphosphine) (**13**) in the asymmetric cell unit.

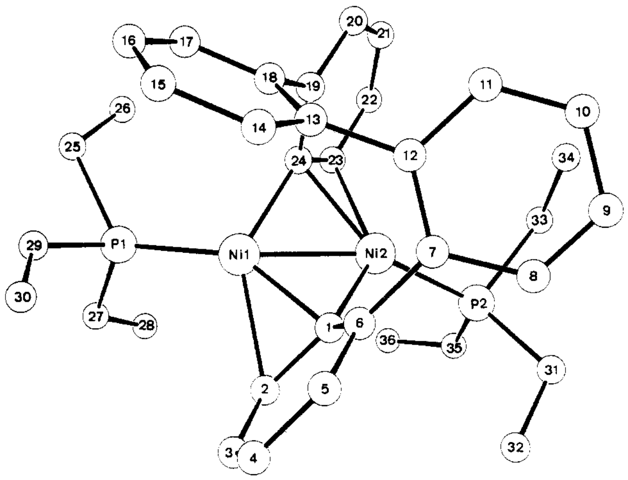

Figure 3. The packing diagram for tetrabenzo-1,2-dinickelecin-1,2-bis(triethylphosphine) (**13**) shown as a projection along the monoclinic axis.

matically centered reflections (6° < θ < 34°).

The structure was solved by heavy-atom methods. Because of the unfavorable reflection to parameter ratio only the nickel and phosphorus atoms were refined with anisotropic temperature factors. The remaining non-hydrogen atoms were given isotropic thermal motion. Refinement was done by least squares, and the function minimized was $\sum_w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Hydrogen atoms of the phenyl and methylene groups were included at calculated positions [d(C–H) = 1.0 Å, U = 0.05] for the final refinement cycles. The subsequent difference Fourier map showed no chemically relevant residual electron density (max 0.8 e/Å^3). The neutral, isolated atom scattering factors used for all non-hydrogen atoms were taken from ref 33;[34] the scattering factors of the hydrogen atoms, based on a bonded spherical atom model, were those of Stewart, Davidson, and Simpson.[35] Anomalous scattering factors for the nickel and phosphorus atoms were taken from ref 33. The atomic numbering scheme and the structure of one of the two molecules in the asymmetric unit are shown in Figure 2. The packing diagram (Figure 3) shown as a projection along the monoclinic axis illustrates the arrangement of the independent molecules within the unit cell. Bond lengths and angles, together with their standard deviations, are listed in Table II. There are no intermolecular contacts between non-hydrogen atoms in adjacent molecules less than 3.0 Å. Listings of final coordinates, final thermal parameters, and calculated and observed structure factors may be obtained as supplementary material.

Table II. Bond Lengths (Å) and Bond Angles (deg) for Tetrabenzo-1,2-dinickelecin-1,2-Bis(triethylphosphine) (13)

	mol 1	mol 2
Ni1-Ni2	2.323 (4)	2.314 (4)
Ni1-P1	2.142 (6)	2.147 (6)
Ni1-C1	1.99 (1)	1.93 (1)
Ni1-C2	2.23 (2)	2.25 (2)
Ni1-C24	1.97 (2)	1.89 (2)
Ni2-P2	2.152 (5)	2.166 (5)
Ni2-C1	1.91 (2)	1.87 (1)
Ni2-C23	2.26 (2)	2.27 (2)
Ni2-C24	2.03 (2)	2.01 (2)
C1-C6	1.42 (2)	1.46 (2)
C6-C7	1.49 (2)	1.53 (2)
C7-C12	1.38 (2)	1.38 (2)
C12-C13	1.50 (2)	1.54 (2)
C13-C18	1.37 (2)	1.41 (2)
C18-C19	1.51 (2)	1.49 (2)
C19-C24	1.44 (2)	1.47 (2)
C1-C2	1.45 (2)	1.43 (2)
C2-C3	1.42 (3)	1.39 (2)
C3-C4	1.37 (3)	1.34 (3)
C4-C5	1.39 (3)	1.39 (2)
C5-C6	1.38 (2)	1.37 (2)
C7-C8	1.44 (2)	1.40 (2)
C8-C9	1.33 (3)	1.39 (3)
C9-C10	1.39 (3)	1.39 (3)
C10-C11	1.39 (3)	1.37 (2)
C11-C12	1.41 (2)	1.38 (2)
C13-C14	1.40 (2)	1.39 (2)
C14-C15	1.44 (3)	1.42 (2)
C15-C16	1.35 (3)	1.35 (2)
C16-C17	1.38 (3)	1.41 (2)
C17-C18	1.39 (2)	1.45 (2)
C19-C20	1.38 (3)	1.32 (2)
C20-C21	1.42 (3)	1.38 (3)
C21-C22	1.36 (3)	1.33 (3)
C22-C23	1.39 (3)	1.39 (2)
C23-C24	1.37 (2)	1.47 (2)
Ni2-Ni1-P1	151.4 (2)	155.5 (2)
Ni2-Ni1-C2	82.2 (5)	82.0 (4)
Ni2-Ni1-C24	55.6 (5)	56.0 (4)
P1-Ni1-C1	147.7 (5)	145.7 (5)
P1-Ni1-C2	108.7 (5)	107.8 (4)
P1-Ni1-C24	108.6 (5)	111.3 (5)
C1-Ni1-C24	103.3 (7)	103.0 (6)
C2-Ni1-C24	137.8 (7)	138.0 (6)
Ni1-Ni2-P2	154.3 (2)	151.1 (2)
Ni1-Ni2-C1	55.1 (4)	53.5 (5)
Ni1-Ni2-C23	81.7 (5)	81.8 (4)
P2-Ni2-C1	111.5 (5)	110.2 (5)
P2-Ni2-C23	108.4 (5)	109.8 (5)
P2-Ni2-C24	144.0 (5)	148.9 (5)
C1-Ni2-C23	136.8 (6)	135.4 (6)
C1-Ni2-C24	104.4 (7)	100.4 (6)

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Registry No. **1a**, 1295-35-8; **1b**, 55425-72-4; **1c**, 51320-65-1; **1d**, 15133-82-1; **1e**, 23777-40-4; **2**, 259-79-0; **6**, 93604-90-1; **7**,

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[33] "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[34] In addition to several locally written programs, the following programs were used: TRACER by Lawton and Jacobson for cell reduction; Shelrick's SHELX-76 for Fourier calculations and initial least squares refinement; GFMLS, a highly modified version of ORFLSD, by Hirshfeld, Coppens, Leiserowitz, and Rabinovich for subsequent full-matrix least-squares refinement; Davis' DAESD for bond distance and angle calculations and best plane torsion angle calculations; Johnson's ORTEP for the molecular drawings.

[35] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J.Chem. Phys.* **1965**, *42*, 3175.

16327-75-6; **8**, 486-25-9; **9**, 602-15-3; **10**, 92-52-4; **11**, 90-43-7; **12**, 132-64-9; **13**, 93644-84-9; **14**, 93604-91-2; **15**, 641-96-3; **16**, 212-74-8; **17**, 93604-92-3; Ni, 7440-02-0; nickel(II) acetylacetonate, 3264-82-2; 2,2′-diiodobiphenyl, 2236-52-4; diphenylacetylene, 501-65-5.

Supplementary Material Available: Listings of final coordinates, final thermal parameters, and calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

Functional Trimethylphosphine Derivatives. 21.[†] (Phosphinomethyl)aluminum Compounds: Phosphinomethyl-Bridged Dimers and X-ray Structures of $[Me_2AlCH_2PMe_2]_2$ and $[ClAl(CH_2PMe_2)_2]_2$[‡]

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Phosphinomethyl-substituted organoaluminum compounds $(Me_2PCH_2)_nAlCl_{3-n}$ (n = 1–3) and $(Me_2PCH_2)_nAlMe_{3-n}$ (n = 1–3) have been prepared by various routes and characterized by analytical and spectroscopic methods. NMR measurements (^1H, ^{13}C, ^{31}P, ^{27}Al) in solution reveal an intra- and intermolecular exchange of the CH_2PMe_2-, Me-, and Cl- substituents. From these and other measurements, a dimeric structure of the molecules with a central six-membered ring moiety, $\overline{CH_2(Me_2)P(Me_2)AlCH_2(Me_2)P(Me_2)Al}$, I, is indicated. In the solid state this central unit adopts a chair conformation with crystallographically imposed centrosymmetry as shown by X-ray structure determinations of $[Me_2AlCH_2PMe_2]_2$, **7**, and $[ClAl(CH_2PMe_2)_2]_2$, **3**. Both compounds crystallize in the triclinic space group $P\bar{1}$ with one (dimeric) formula unit in the unit cell. The lattice constants are as follows. **7**: a = 6.8850 (4) Å, b = 7.8363 (4) Å, c = 9.5416 (4) Å, α = 76.039 (3)°, β = 68.191 (4)°, γ = 65.599 (4)°, V = 432.91 Å^3, d_{calcd} = 1.014 g/cm^3 for Z = 1. **3**: a = 6.511 (2) Å, b = 9.956 (3) Å, c = 10.034 (3) Å, α = 104.98 (2)°, β = 104.48 (2)°, γ = 103.06 (2)°, V = 578.27 Å^3, d_{calcd} = 1.221 g/cm^3 for Z = 1. For **7** full-matrix least-squares refinement of 64 parameters on 1450 observed reflections ($I > 2.0\sigma(I)$) converged at R = 0.090 and R_w = = 0.109 ($w = 1/\sigma^2(F_o)$). For **3** the final agreement indices were R = 0.034 and R_w = 0.038 ($w = k/\sigma^2(F_o)$; k = 1.33) for 155 refined parameters and 2001 observed reflections. In **3** the terminal phosphinomethyl groups are in the equatorial positions of the six-membered ring. The P–Al bond lengths are 2.451 (2) Å (**7**) and 2.425 (1) Å (**3**).

Introduction

The combination of an electrophilic and a nucleophilic center in one molecule is one of the most attractive prospects for synthetic chemistry. In general, self-association of such molecules, either intra- or intermolecular, may lead to ring systems, and synergetic effects may promote reactivity patterns.

For the combination of R_2Al and R_2P groups, connected by an NR linkage, i.e., $R_2AlN(R')PR''_2$, the term "amphoteric ligand" has been used to characterize the utility of these systems in transition-metal and catalytic chemistry.[1] Compounds of the type $R_2AlPR'_2$ also have been described.[2]

It is somewhat surprising in this context that the system $R_2AlCH_2PR'_2$ has not received any attention as yet.[3] We have synthesized a variety of phosphinomethyl compounds, Me_2PCH_2E (E = Cl,[4] PR_2,[5] $^+PR_3$, $P(O)R_2$, or $P(CR'_2)R_2$,[6] SiR_3 or SnR_3,[7] Li,[5] or a transition-metal center[5,8,9]). The most general route is a reaction according to eq 1. The extention of this method to E–X = Me_nAlCl_{3-n}, n = 0–2, is described in this paper.[9]

$$\underset{\textbf{1}}{LiCH_2PMe_2} + E\text{–}X \rightarrow E\text{–}CH_2PMe_2 + LiX \qquad (1)$$

Results and Discussion

Preparation and Properties. The (phosphinomethyl)aluminum compounds **2**–**4** were obtained in moderate to good yields by stepwise substitution of $AlCl_3$ with $LiCH_2PMe_2$, **1**, according to Scheme I. The reactions were carried out in ether at room temperature, and after removal of the solvent, the products **2**–**4** were sublimed in vacuo. The colorless, pyrophoric crystals (from toluene, **2** and **3**, or pentane, **4**) have melting points that increase

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[†] Part 20: see ref 12a. Part 19: see ref 8b.

[‡] Dedicated to Prof. Günther Wilke on the occasion of his 60th birthday.

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