Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ALLENE CYCLOOLIGOMERIZATION AND POLYMERIZATION CATALYZED BY A NICKEL(0) COMPLEX

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(Received April 30th, 1971)

SUMMARY

The complex bis(triphenylphosphine)nickel(0) catalytically converts allene into a mixture of isomeric trimers, a tetramer, a pentamer, isomeric hexamers, waxes and polymer. The complex initially formed in the reaction, $(Ph_3P)_2NiC_3H_4$, was isolated and characterized. The structures of products trapped in competitive experiments with ethylene and methyl acrylate indicate the intervention of subsequent complexes in the oligomer-forming reactions. Mechanistic routes are considered in the light of these data.

INTRODUCTION

It has been shown that allene can be oligomerized both thermally and catalytically. The thermal reactions[1] in either the liquid (140°) or the gas (400°) phase afford the expected dimers as well as higher cyclic spiro-oligomers. On the other hand the compositions of the catalytic reaction products are dependent on the choice of transition metal; dimers are predominant with Pd[2] complexes, cyclotrimers and cyclotetramers with nickel[3] and rhodium[4] complexes, and polymers with various Ziegler–Natta type catalysts[5].

The present investigation deals with allene transformations catalyzed by the coordinatively unsaturated zerovalent nickel complex $(Ph_3P)_2Ni$. A new 1/1 nickel-allene complex and allene tetramer were isolated and characterized. Several products observed in allene substrate co-reactions will be discussed in the light of mechanistic considerations.

RESULTS AND DISCUSSION

The catalyst

The Na(Hg) reduction of $(Ph_3P)_2NiBr_2$ in either CH_3CN or C_6H_6 affords a red-brown, crystalline, air-sensitive material. The spectroscopic (see Experimental) and chemical data accumulated to date indicate that this complex may be formulated

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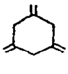
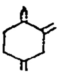
as $(Ph_3P)_2Ni$*. The complex forms 1/1 adducts with hexafluoropropene[7] or SO_2, $(Ph_3P)_2Ni(CO)_2$ on treatment with CO, $(Ph_3P)_2NiX_2$ and $(Ph_3P)_2Ni(CO)_2$ by reactions with CH_3COX ($X=Cl$, Br) (disproportionation of L_2NiCOX formed via oxidative addition of the acid chloride followed by loss of a methyl radical). The preparation and the properties of this complex which initially was prepared electrochemically[8] will be reported in greater detail elsewhere.

Homo-allene reaction.

The zerovalent nickel catalyst dissolved in various solvents catalyzes the complete conversion of allene (75°) to a mixture of volatile products, waxes, and polymer. The volatile components consist of two trimers, one tetramer, one pentamer, and 3 hexamers. No dimers were detected in the crude reaction mixture. The major hexamer was isolated by GLC and tentatively characterized spectroscopically. The structures of these volatile oligomers were related as evidenced by the basic features of their spectra (see Experimental).


(I)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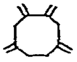
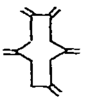

(III)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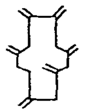
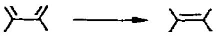

(V) (major)

The trimers are the same as those proposed by Benson and Lindsey[3]; however, the tetramer differs from the structure (1,3,5,7-tetramethylenecyclooctane) favored by these authors. The structure of the tetramer was confirmed by ^{13}C NMR spectroscopy (see Table 3). After we had isolated and characterized the pentamer, two papers appeared[9] reporting its isolation from similar reactions.

The waxes and polymer isolated from the reaction displayed infrared bands characteristic of vinylidene (major) and vinyl and *cis*-olefin (minor) groups. Spectroscopic examination suggested a head–head and head–tail random structure, similar to the material previously reported by Baker[10].

Reactions of the cyclooligomers

The tetramer and pentamer formed 1/1 adducts with dimethylacetylenedicarboxylate in high yields; the adducts were unreactive to excess reagent. As expected, the trimer mixture afforded an unreactive component as well as a 1/1 adduct with this reagent. On hydrogenation over Pd/C or Ni/Cr, the tetramer and pentamer took up ca. one mole less of hydrogen than expected. It is suspected that during hydrogenation isomerization occurs, affording a difficult-to-hydrogenate tetra-substituted double bond[11], *i.e.*:



Acid catalyzed hydrogenation, however, gave the totally hydrogenated cycloalkanes. The tetramer and pentamer reacted with the amount of bromine expected for the proposed structures.

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* The preparation of $(Ph_3P)_2Ni$ is briefly described in the patent literature; see Ref. 6.

TABLE 1

REACTIONS BETWEEN $(Ph_3P)_2Ni$ AND ALLENE

Catalyst/ allene (g)	Temp. (°C)	Solvent (ml)	Conv. (%)	$t_{1/2}$,[a] (h)	Ratio[b] $C_9/C_{12}/C_{15}/C_{18}$	Yield[c] C_9–C_{18} (%)	Added ligand (g)
0.25/10	75	C_6H_6(15)	100	10	3.5/5.9/10/1	46	
0.25/10	75	C_6H_6(15)	25		1.9/3.1/10/0.7	48	
0.08/10	75	C_6H_6(15)	78	24	1.9/1.9/10/0.6	48	
0.08/10	75	THF(15)	74	25	1.3/1.0/10/0.6	45	
0.25/10	75	Py[d](15)	25	>100	0.6/1.4/10/0.3	52	
0.25/10	75	DMF(15)	100	10	4.2/6/10/0.7	42	
0.25/10	75	C_6H_6(15)	100	25	12/32/10/0.4	47	1.0 (5 eq.) Ph_3P
0.25/10	75	C_6H_6(15)	100	24	6/7.3/10/2.3	46	1.0 $(C_6H_{11})_3P$
0.25/10	75	C_6H_6(15)	100	24	1.7/1/10/0.7	44	$[(C_6H_{11})_3P]_2Ni$
0.25/10	75	C_6H_6(15)	100	24	4.8/9.4/10/2.2	44	0.34 $[Ph_2PCH_2]_2$
0.25/10	75	C_6H_6(15)	100	15	4.3/7.6/10/0.9	42	0.15 g Bipy[e]
0.25/10	60	C_6H_6(15)	78	70	3/7.5/10/0.6	38	
0.25/10	100	C_6H_6(15)	100	1.5	6.8/6.5/10/1.7	60	

[a] Time to observe 50% pressure decrease. [b] GLC with a thermal conductivity detector. [c] Isolated, ca. 5–10% lower than actual. [d] Decomposition to metal was observed during this run; Py, pyridine. [e] Bipy, 2,2'-bipyridine.

Reaction conditions

Table 1 indicates the effect of catalyst/allene ratio, added ligand, temperature, and solvent on the qualitative rate and product distribution of the *homo*-allene reaction. Greater selectivity to form lower cyclooligomers (trimers and tetramer) was observed as either the catalyst/allene ratio or the % conversion of allene decreased. Since further evidence (*vide infra*) indicates that Ph_3P dissociates from $(Ph_3P)_2NiC_3H_4$, the initial complex formed in the reaction, it is plausible that both of these facts reflect on the variation in the free phosphine/allene ratio. Along similar lines, added tertiary phosphine increased selectivity to lower oligomers. The addition of two or more equivalents of tertiary phosphine to $(Ph_3P)_2Ni$ solutions rapidly afforded a coordinatively saturated zerovalent nickel complex $(Ph_3P)_4Ni$. The fact that the presence of excess (even bidentate) ligand reduces the reaction rate but not the allene conversion suggests (*a*), dissociation of a tertiary phosphine from a coordinatively saturated zero valent nickel complex is appreciable; (*b*), tertiary phosphine effectively competes at low concentrations with allene for vacant metal coordination sites. It is not surprising that the relatively hard[12] bipyridyl ligand (see Table 1) has the smallest effect on the product distribution and retards the rate of reaction.

A non-ionic reaction mechanism is consistent with the insensitivity of the product distribution and rates to the dielectric constant of the solvent (C_6H_6, THF, DMF). The slow reaction rate in pyridine can be rationalized by the decomposition of the nickel(0) complex in the presence of a large excess of the aromatic nitrogen donor ligand; *i.e.*, displacement of phosphorus by nitrogen ligand followed by decomposition.

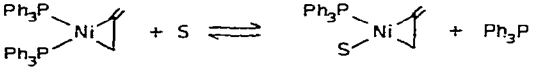
At 75°, the yield ratio of the volatile cyclooligomers (C_9–C_{18}) to waxes/polymer was ca. 1/1. This ratio is not affected by the variables (*e.g.*, catalyst/allene ratio and added ligand) that change the ratios of the volatile cyclooligomers. This suggests that the cyclooligomers are derived from different intermediates than the waxes/polymer. Higher temperatures favor the process affording the cyclooligomers (C_9–C_{18}).

Separate control reactions demonstrated that the trimers, tetramer, and pentamer are stable in the presence of $(Ph_3P)_2Ni$* under the reaction conditions. Since methylacetylene afforded different products at faster (explosive) rates under simulated reaction conditions, allene–methylacetylene interconversion must not be catalyzed by $(Ph_3P)_2Ni$.

Allene–nickel complex

A red-orange $(Ph_3P)_2NiC_3H_4$ complex can be prepared by the reduction of $(Ph_3P)_2NiBr_2$ in the presence of allene, or simply by the reaction between $(Ph_3P)_2Ni$ and allene. Similar complexes of rhodium[13] and platinum[14] have been reported, while a nickel–allene complex of indefinite composition[5] has been mentioned in the literature. The $(Ph_3P)_2NiC_3H_4$ complex can be used in place of $(Ph_3P)_2Ni$ to catalyze allene homooligomerizations.

Interestingly, various spectroscopic data (see Experimental) suggest the dissociation of one of the phosphine ligands in solution.



The complex decomposes in solution at 80° affording a mixture of cyclooligomers and $(Ph_3P)_2Ni$. Attempts to isolate higher** allene-containing nickel complexes were unsuccessful. The fact that a nickel–allene 1/1 complex is formed rapidly at room temperature suggests that subsequent reaction of this complex with allene is rate determining.

*Allene–substrate co-reactions****

In the nickel-catalyzed reaction of allene in the presence of hydrogen, only the usual cyclooligomers, waxes, and polymer are detected; there was no conversion to hydrogenated cyclooligomers. The presence of propylene (not propane) in a gas sample from the reaction mixture indicates that hydrogenation of allene stops at the olefin stage. Apparently $(Ph_3P)_2Ni$ is not a hydrogenation catalyst for weakly bound 1,4-dienes (as the cyclooligomers) or mono-olefin ligands under these reaction conditions.

Reactions between allene and ethylene or methyl acrylate**** are presented schematically below:

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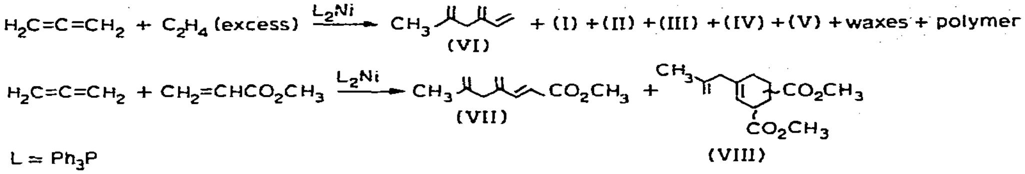
* We have noted that $(Ph_3P)_2Ni$ is not an olefin or 1,4-diene isomerization catalyst at moderate (< 100°) temperatures.

** Recrystallization mother liquors of the allene nickel 1/1 complex indicate the presence of a higher complex whose gross features fit structure (XI) (*vide infra*).

*** Control reactions demonstrated that products are not observed in the absence of the Ni^0 complex.

**** The complex $(Ph_3P)_2Ni$ is catalytically unreactive towards ethylene or methyl acrylate at moderate temperatures (< 100°).

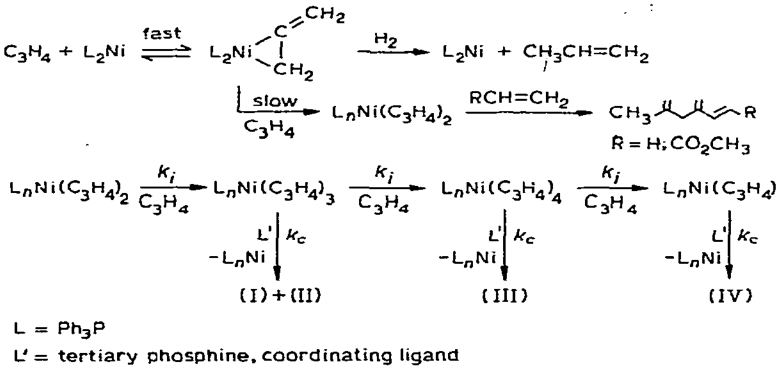


In the allene–ethylene reaction a co-product (VI) is isolable and is accompanied by the usual allene products. No other co-products were detected under a variety of conditions. When methyl acrylate is substituted for ethylene in the reaction, (VII) and (VIII) (2 isomers) were the major products; the usual allene *homo*-oligomers and polymer were present in only trace amounts. An attempt to enhance the yield of (VII) by reducing the methyl acrylate/allene ratio afforded a reduced yield of (VII) and (VIII) (same ratio), as well as allene-derived waxes and polymer. Presumably (VIII) is derived from (VII) and methyl acrylate via a thermal or catalytic cyclo-addition reaction.

It is worthy to note that in the presence of phenol, $(Ph_3P)_2Ni$ specifically catalyzes polyallene formation with a notably enhanced rate of allene comsumption. The polymer had virtually identical spectroscopic properties with the polyallene prepared in the absence of phenol.

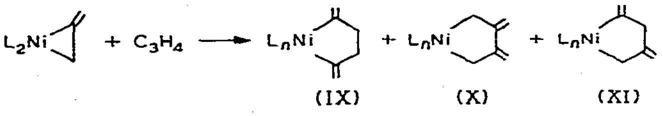
Mechanistic considerations

The data presented indicate several features of this reaction of mechanistic significance. A general scheme which leads to the volatile products observed in these reactions is presented below:

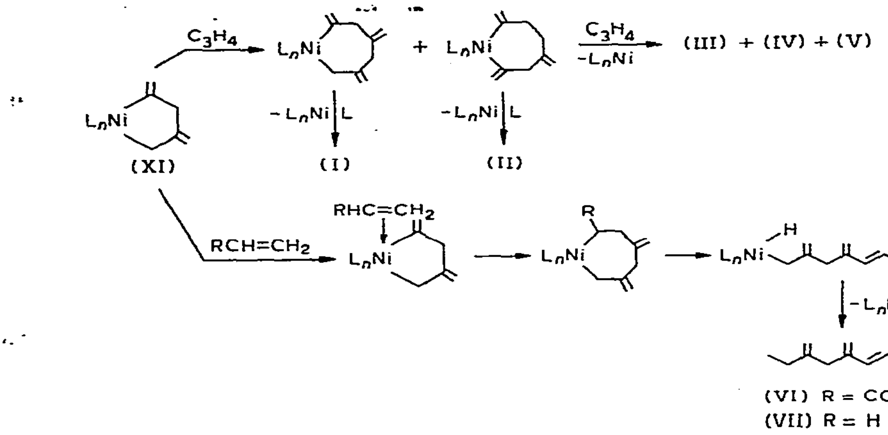


The fact that added tertiary phosphine ligand shifts the product distribution to lower cyclooligomers can be explained by the intermediacy of $L_nNi(C_3H_4)_x$ $(x > 1)$ complexes. This is represented in the scheme as a competition between the relative rate of allene insertion to cyclization (k_i/k_c); *i.e.*, k_i/k_c decreases with added ligand. In the sequence that affords the cyclooligomers, k_i/k_c must fall sharply after the pentamer stage.

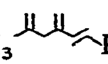
The products trapped in the co-reactions between allene and ethylene or methyl acrylate shed light on the nature of the reactive $L_nNi(C_3H_4)_2$ intermediate(s). Reaction between $L_2NiC_3H_4$ and allene via allene insertion into the nickel carbon bonds may lead to three intermediates (IX), (X) and (XI). If formed, these complexes may be bi- or polymetallic; however, in the absence of further data the monometallic species are shown for simplicity.



Allene–olefin 2/1 adducts isolated [(VI) and (VII)] can be derived from (XI). In the *homo*-allene reaction or the cross-reaction with ethylene, the allene trimer (I) can arise only from (XI), while the allene trimer (II) can arise from (IX), (X) or (XI). The fact that the (I)/(II) ratio is the same in both of these reactions strongly suggests that (I), (II) and (VI) arise from a common intermediate, *i.e.*, (XI). Intermediate (XI) is trapped in the allene/methyl acrylate reaction; higher allene oligomers or polymer are not observed in any appreciable amounts. These data suggest that the major $L_nNi(C_3H_4)_2$ complex formed is (XI). More detailed schemes leading to the allene cyclooligomers and the allene–olefin 2/1 adducts via (XI) are presented below.



In the allene/ethylene reaction, the isolation of higher cyclooligomers indicates the intervention of $L_nNi(C_3H_4)_x$ ($x > 2$) complexes according to the general scheme. It is conceivable that the failure to trap these intermediates with ethylene implies internal coordination of the olefinic groups of the organic ligand. This would provide a less effective ethylene/allene competition. Further studies involving co-reactions between allene and a series of substituted olefins intermediate in complexing strength (*i.e.*, between allene and ethylene) may be instructive in this sense. From the presented data, the ability to trap (XI) with different substrates decreases in the order $CH_2{=}CH{-}CO_2CH_3 > CH_2{=}C{=}CH_2 > CH_2{=}CH_2 \gg H_2$.

Surprising selectivity is noticed throughout these schemes; for example, the formation of CH_3  R* from (XI) involves olefin insertion in a specific orientation

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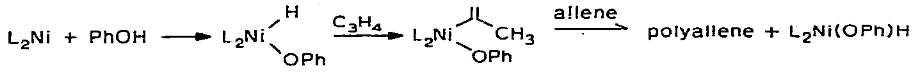
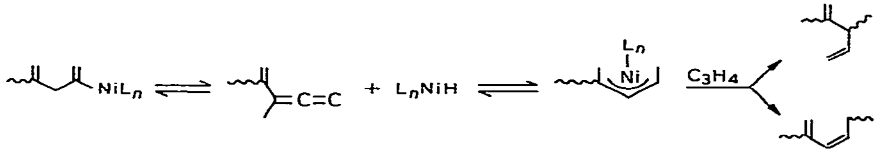
* It is possible that other isomeric products derived from allene/olefin coreactions were formed as minor products and escaped detection due to a subsequent secondary reaction.

into a vinyl–nickel rather than an allyl–nickel bond. In addition, four tetramers and five pentamers could be formed from a random allene insertion into (XI). No attempt was made to determine the nature of the effects that gave rise to the observed selection.

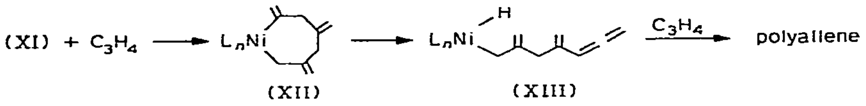
With regard to the type of intermediates responsible for polymer formation, it is notable that the presence of phenol changes the course of the allene reaction and leads specifically to polyallene. It has been documented[15] hat reactions between weak acids and low-valent nickel complexes afford stable nickel hydride species. By analogy, it is felt that polyallene is formed from a growth reaction of a nickel hydride intermediate.



A nickel hydride intermediate also may be responsible for the incorporation of vinyl and *cis*-olefin groups in the polymer and waxes.



The mode of formation of a nickel hydride intermediate is not obvious in the absence of phenol; perhaps as a side reaction a $L_nNi(C_3H_4)_x$ ($x \geqslant 2$) moiety [*e.g.*, (XII)] undergoes an internal hydride elimination similar to the scheme yielding (VI) and (VII).



This complex (XIII) would be expected to lead to linear oligomers of allene (polyallene) rather than the volatile cyclooligomers.

EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR5A instrument, while ^1H NMR spectra ($CDCl_3$ solvent, TMS internal standard) were obtained using either a Varian Associates A-60 or HA-100 spectrometer. The ^{13}C NMR spectra (neat in 10 mm tubes, C_6F_6 as lock, TMS as internal standard) were recorded on a Bruker HFX 90 spectrometer. A Cary 14 recording spectrophotometer was used to obtain ultraviolet spectra. High resolution mass spectra were recorded on a consolidated Electrodynamics Corporation Model 21-110B spectrometer. Melting and boiling points are uncorrected. All reactions were carried out in an atmosphere of argon in anhydrous, degassed solvents. Matheson allene (97% minimum) was used throughout.

Preparation of bis(triphenylphosphine)nickel(0)

Bis(triphenylphosphine)nickel dibromide (II) (22.3 g, 0.0300 mole) was added to a mechanically stirred mixture of sodium amalgam (1.73 g Na, 0.0750 g-atom, in 300 ml Hg) and acetonitrile (500 ml) over a period of 0.5 h. During the addition the color of solution changed from green to yellow to brown and then deposited the red brown $(Ph_3P)_2Ni$. At the completion of the Ni^{II} salt addition, the mixture was stirred for 0.5 h. The Hg was then removed through a stopcock at the bottom of the flask. The acetonitrile was carefully decanted from the precipitate. The remaining precipitate was dissolved with C_6H_6 (4–25 ml portions) and the solution was filtered, leaving Hg-occluded NaBr. Concentration of the dark brown C_6H_6 solution *in vacuo* gave 13–15 g (74–84%) of air sensitive $(Ph_3P)_2Ni$. The material was dried in high vacuum, m.p. 155–157° (dec.). Bis(triphenylphosphine)nickel(0) can be recrystallized from C_6H_6 (or C_6H_5Me)/hexane, but with appreciable loss due to solubility. For this reason, the uncrystallized material was used for the catalytic reactions described. (Found: C, 74.3; H, 5.3; P, 11.1. $C_{36}H_{30}P_2Ni$ calcd.: C, 74.1; H, 5.2; P. 10.6%.) Mol. wt. (cryoscopic, C_6H_6), found: 480 ± 20; calcd.: 583. The infrared spectrum of the complex was virtually identical to that of Ph_3P. The 60 MHz NMR spectrum (C_6D_6) showed two aromatic regions centered at 7.13 and 7.67 ppm (3/2). The upfield region sharpened on phosphorus irradiation [δ(P) −22 ppm from $(MeO)_3PO$].

Bis(triphenylphosphine)allene nickel(0)

(*A*). Allene was bubbled into a stirred mixture (25°) of acetonitrile (150 ml) sodium-amalgam (1.6 g Na, 0.0700 g-atom, in 120 ml Hg) for 0.25 h. With continued allene bubbling, $(Ph_3P)_2NiBr_2$ (10.0 g, 0.0135 mole) was gradually added during 0.5 h. The solution rapidly turned orange-red and remained that color throughout. After 0.25 h additional stirring, the solution was filtered and concentrated *in vacuo* leaving an oily residue; the oil was dried in high vacuum until it crystallized (ca. 24 h). Crude product (6.3 g, 74%) m.p. 51–54° (dec.) was obtained; a batch of this material was recrystallized from hexane/toluene (cold), leaving red-orange, air sensitive crystals, m.p. 60–61° (dec.). (Found: C, 74.9; H, 5.7; P, 10.4. $C_{39}H_{34}P_2Ni$ calcd.: C, 74.9; H, 5.7; P, 9.95%.) Mol. wt., found: 350 (by cryoscopy in C_6H_6), 290 (by VPO* in CH_3CN); calculated: 623. The infrared spectrum showed the usual Ph_3P bands as well as a vinylidene deformation band at 885 cm^{-1}. The 60 MHz NMR spectrum (C_6D_6) displays an aromatic region at 6.8–7.5 ppm (30), two vinylidene singlets at 2.8 and 3.04 ppm (2), and a methylene region consisting of a doublet of doublets at 1.48 and 1.57 ppm (2) J(P–H) 10.5 Hz. The 100 MHz NMR spectrum showed that the regions at 1.48 and 1.57 ppm were due to two distinct proton environments (δ not J) both coupled to one phosphorus atom [δ(P) −37 ppm from $(MeO)_3PO$]; on phosphorus decoupling two singlets remained. All other H–H and P–H coupling constants in the allene part of the molecule were < 0.5 Hz. Consistent with the molecular weight determination, it seems that only one phosphorus atom is permanently bound to the metal in solution. If the proposed structure is correct, the ligand that dissociates is probably *trans* to the vinylidene group, as shown by comparison of J(P–H) to the reported $(Ph_3P)_2Pt$–1,3-diphenylallene spectrum[14]. At elevated temperature (80°) fluctionality-coalescence of the complexed allene absorptions was not observed but rather complex decomposition to $(Ph_3P)_2Ni$ and the usual allene cyclooligomers.

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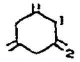
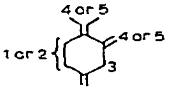
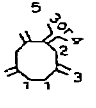
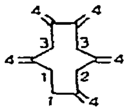
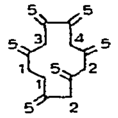
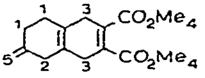
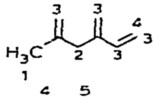
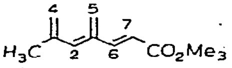
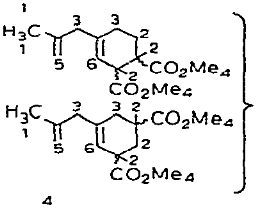
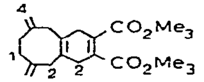
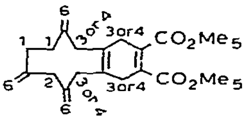
* Vapor pressure osmometry.

TABLE 2

^1H NMR DATA[a]

Compound	Assignments (area)						
	1	2	3	4	5	6	7
	2.87(1)	4.55(1) $J_{12}\sim$ 1.5 Hz					
	2.22(2)	2.22(2)	4.6(2)	4.6(4)	4.95 (1/2AB. 2) $J\sim3$ Hz		
	2.32(4)	3.1(4)	4.84(6)	~4.9 (1/2AB) (2) $J\sim3$ Hz			
 [b]	2.30(4)	2.85(2)	3.05(4)	4.75–5.3(10)			
 [c]	2.17(4)	2.6(4)	2.9(2)	3.0(2)	4.6–5.1(12)		
	2.24(4)	2.64(2)	2.83(4)	3.7(6)	4.7(2)		
	1.68(3) $J_{13}\sim1$ Hz	2.9(2) $J_{23}\sim$ 1 Hz	4.7–5.4(6)	6.1–6.6(1)			
	1.69(3) $J_{14}\sim1$ Hz	3.0(2) $J_{24}\sim J_{25}\sim$ 1 Hz	3.6(3)	4.74(2)	5.1–5.4(2)	6.38(1) $J_{67}\sim$ 13 Hz (*trans*)	6.72(1) $J_{57}\sim$ 1 Hz
	1.55(3)	1.7–2.0(4)	2.6(4)	3.55(6)	4.65(2)	5.4(1)	
	2.28(4)	3.0(8)	3.8(6)	4.78(4)			
	2.2(4)	2.69(2)	2.88(4)	3.02–3.1(4)	3.8(6)	4.7–5.1(6)	

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[a] ppm from tetramethylsilane: $CDCl_3$ solvent: J in Hz. [b] An alternate structure would place the $=CH_2$ group at the 8 rather than the 9 carbon atom in the cyclodecane ring. [c] An alternate structure would place the $=CH_2$ group at the 10 rather than the 11 carbon atom in the cyclododecane ring.

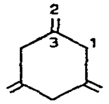
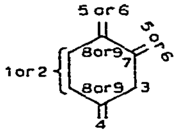
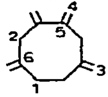
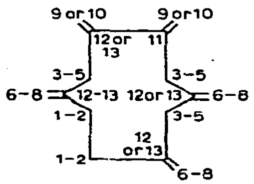
General oligomerization procedure

The catalyst was placed in a 80 ml stainless-steel autoclave in a dry box. Then the appropriate solvent and in some cases extra ligand were added (see Table 1). The bomb was cooled to ca. –30° under argon while the desired amount of allene was condensed into the vessel. The contents then were allowed to react for various times at various temperatures. Rough orders of activity ($t_{1/2}$) were recorded for the time taken to half the initial pressure at a given temperature.

At the completion of a run, the contents were cooled to room temperature, exposed to air, and filtered. GLC analysis of the filtrate (A) gave the product ratio. The crude polymer (residue) was dissolved in hot benzene, filtered through glass wool to remove metal and insoluble polymer, then cooled to precipitate the material. The polymer was collected by filtration and dried. The softening point of the polymer varied from run to run, 105–125°. Then the filtrate (A) was carefully distilled to remove the solvent. Monitoring the distillation by GLC showed that ca. 95 % of the solvent and ca. 30–50 % of the C_9 fraction (in benzene runs) were removed. The residue was distilled in high vacuum. The isolated yields are based on the weight of volatile components (C_9–C_{18}) obtained in the latter distillation. The residue is referred to in the text as "waxes".

Scale-up of this procedure afforded working amounts of the cyclooligomers: C_9, boiling point 73–75°/70 mm (4/6 ratio of I/II); C_{12}, boiling point 78–80°/10 mm; C_{15}, boiling point 74–76°/0.5 mm. GLC (150′ × 0.01″ DC 710/polyphenyl ether

TABLE 3
^{13}C NMR DATA[a]

Compound	Assignments (area)												
	1	2	3	4	5	6	7	8	9	10	11	12	13
	43.7	107.8	146.1										
	35.1	35.7	43.8	108.2	108.3	109.0	146.8	148.2	148.5				
	37.5	44.3	112.6	113.0	149.3	150.8							
	34.5	35.4	42.1	42.7	43.4	113.6	113.7	114.3	115.1	115.3	146.1	147.5	147.6 (3)

[a] Ppm from TMS, neat, C_6F_6 lock.

column) showed that the C_9 fraction was composed of two components (ca. 6/4 ratio), and that C_{12} and the C_{15} fractions each contained essentially one component. The C_{18} fraction in the crude reaction mixture consisted of $\geqslant 3$ isomers; the major component was isolated by GLC and characterized spectroscopically. The 60 MHz NMR spectra of the cyclooligomers are recorded in Table 2, while ^{13}C NMR spectra of the cyclooligomers are presented in Table 3; assignments were substantiated by decoupling techniques. A detailed analysis of these spectra will be published elsewhere. The ultraviolet spectra of the tetramer, pentamer, and major hexamer exhibited λ max (cyclohexane) 212 log ε 3.98, λ_{max} (isooctane) 230 log ε 3.75, λ_{max} (241) log ε 3.36, respectively. The high resolution mass spectra (70 eV) of the cyclooligomers all exhibited parent ions as well as major fragment ions at $M-CH_3$, $M-C_2H_4$, $M-C_3H_7$ and $M-C_4H_7$ while their IR spectra exhibited strong vinylidene bands at ca. 890 cm^{-1}.

Reaction between the cyclooligomers and acetylene-dicarboxylate

C_9H_{12}. The C_9H_{12} mixture (1.3 g, 0.011 mole) was stirred with dimethylacetylene-dicarboxylate (1.6 g, 0.011 mole) for three days at 25°. GLC analysis of the crude reaction mixture indicated the presence of unreacted C_9H_{12}, acetylene diester, and a new high boiling component. The unreacted C_9H_{12} was collected by GLC and shown to be (I), m.p. 35° (lit.[3] 33.5–35°). The higher boiling adduct was trapped by GLC, empirical formula $C_{15}H_{18}O_4$ (high resolution mass spectrometry; m/e 262.12). Its ^1H NMR spectrum (Table 3) and infrared spectrum (C=O at 1722, conjugated C=C stretch at 1650, $C=CH_2$ deformation at 885 cm^{-1}) were consistent with the Diels–Alder adduct of (II).

$C_{12}H_{16}$. The tetramer (0.4 g, 2.5 mmoles) was treated with dimethyl acetylene-dicarboxylate (0.36 g, 2.5 mmoles) in 0.5 ml of MeOH at 25° overnight. The adduct crystals were filtered, affording 0.53 g (70%) m.p. 109–112°. Recrystallization from MeOH afforded an analytical sample, m.p. 116°, characterized by NMR (Table 3), high resolution mass spectroscopy (m/e 302.15), and infrared (C=O and conjugated C=C stretch at 1740, 1705 and 1640 cm^{-1}, respectively).

$C_{15}H_{20}$. The pentamer (1.0 g, 5.0 mmoles) and dimethyl acetylene-dicarboxylate (0.7 g, 5.0 mmoles) were allowed to stand for 16 h. At this time the reaction mixture solidified. Recrystallization from MeOH afforded a 1.5 g (88%) sample with the empirical formula $C_{21}H_{26}O_4$ (m/e 342.18), m.p. 103–104°. The NMR (Table 3) and infrared spectra (C=O and conjugated C=C at 1750, 1725 and 1650 cm^{-1}, respectively) were consistent with the Diels–Alder adduct.

Saturation of the allene tetramer and pentamer

The tetramer (1.0 g, 6.3 mmoles) was dissolved in 15 ml of EtOH and the resulting solution hydrogenated at 25° (500 psi H_2) with 0.1 g 5% Pd/C for 18 h. The vessel was depressurized and a drop of 12 N HCl added. Further hydrogenation (500 psi H_2, 70°, 18 h) afforded an isomeric mixture ($\geqslant 5$ isomers) of saturated products containing $C_{12}H_{24}$ (high resolution mass spectrometry) as the major component. There was no spectroscopic evidence of unsaturation. Titration of a dioxane solution of the tetramer with bromine indicated an uptake of 2.65 moles Br_2/100 g of olefin (calcd.: 2.5 moles/100 g).

Analogous reaction with the pentamer afforded an isomer mixture ($\geqslant 7$ isomers) of C_{15} saturates; pentamer bromine number: 2.5 moles Br_2/100 g olefin (calcd.: 2.5 g Br_2/100 g olefin).

Reaction of allene in the presence of hydrogen

$(Ph_3P)_2Ni$ (0.25 g, 0.43 mmole), C_6H_6 (15 ml), allene (10 g), and hydrogen (250 psi) were charged into an autoclave and heated to 75° for 23 h. The reaction mixture was cooled and worked up as usual. GLC analysis indicated the ratio of the $C_9/C_{12}/C_{15}/C_{18}$ oligomers (9.5/12/25/3). Other volatile products were not observed. A distilled fraction of the C_9–C_{18} cyclooligomers weighed 4.3 g. The individual components were isolated by GLC and were shown to be identical spectroscopically with those components isolated in the presence of hydrogen. Futher spectroscopic data indicated that the isolated polymer (0.5 g) and gums (3.8 g) were typical. The major components of the reaction mixture gas sample were H_2, 79.5%; propene, 10.3%; allene, 0.3%; the deficit was argon and nitrogen.

Reaction of allene in the presence of ethylene

$(Ph_3P)_2Ni$ (0.25 g, 0.43 mmole), Et_2O (15 ml), allene (4.0 g, 0.10 mole), ethylene (20 g, 0.70 mole) were heated in an autoclave at 75° for 18 h, then 100° for 4 h. GLC analysis of the crude reaction mixture showed a new product which was collected by GLC. High resolution mass spectrometry confirmed the empirical formula C_8H_{12} (*m/e* 108.93). GLC (150 ft by 0.01 in. DC710 PPE) showed that the C_8 fraction was >94% one component. The NMR spectrum is presented in Table 2; the ultraviolet spectrum displayed λ_{max} (CH_3CN) 225, $\log\varepsilon = 4.16$. Structure (VI) was proposed. The $C_8/C_9/C_{12}/C_{15}$ ratio (GLC) was 2/1/3/1.5 in the crude reaction mixture. Distillation afforded 2.3 g of the C_8–C_{15} mixture; this corresponds to a 15% yield of the C_8 fraction based on allene. A GLC-mass spectrum of the crude reaction mixture gave the empirical formulas of two low-boiling products (ca. 1%), C_5H_8 (isoprene) and C_6H_8 (allene dimer). The ratio of (I)/(II) (4/6) was the same as found in the reaction run in the absence of ethylene. Waxes/polymer (1.7 g) were isolated in addition to the volatile products.

Reaction of allene in the presence of methyl acrylate

$(Ph_3P)_2Ni$ (0.25 g, 0.43 mmole), allene (4.0 g, 0.10 mole), and methyl acrylate (20 ml) were heated at 90° for 0.5 h, then at 70° for 3 h. GLC analysis of the crude reaction mixture showed the presence of 3 new major components in the ratio 7/18/9; traces (< 1%) of the usual cyclooligomers were observed. Concentration of the reaction mixture left 9.5 g of a viscous oil. This material distilled completely in high vacuum without leaving an appreciable residue. The minor component was collected by GLC (a trace of another component with a slightly greater retention time than the minor product was observed; no attempt was made to isolate this material). The mass spectrum (*m/e* 166.09) confirmed the empirical formula $C_{10}H_{14}O_2$. The ultraviolet spectrum showed λ_{max} (CH_3CN) 246, $\log\varepsilon$ 3.8. Structure (VII) was proposed on the basis of these data and the NMR (Table 2) and infrared spectra (C=O, conjugated C=C, vinylidene CH_2 deformation at 1730, 1620, and 893 cm^{-1}, respectively).

The two major higher boiling components were isolated in an analogous manner. Mass spectral data indicated that they were isomers, $C_{14}H_{20}O_4$ (*m/e* 252.13). The ultraviolet spectra did not show the presence of a conjugated chromophore, while the infrared and NMR spectra (Table 2) of the isomers were similar. The structures of the isomers (VIII) were then assigned. Our data do not allow an unambiguous assignment to the major and minor components.

Reaction of allene in the presence of phenol

$(Ph_3P)_2Ni$ (0.25 g), allene (10 g, 0.25 mole), phenol (5.6 g, 0.06 mole) and C_6H_6 (20 ml) were heated at 75° for 5 h. A rapid pressure drop was noticed ($t_{1/2} < 1$ h). Work-up only afforded a crude polymer which was washed with hot MeOH until free of residual phenol to leave 8.3 g of polymer, softening point 72°. Its infrared spectrum was similar to that of the allene polymer prepared in the absence of phenol, but with smaller amounts of *cis* and vinyl bands. There were no phenoxy groups incorporated in the polymer chain.

Methylacetylene/$(Ph_3P)_2Ni$ reaction

$(Ph_3P)_2Ni$ (0.25 g) was dissolved in 50 ml C_6H_6; then methylacetylene was bubbled into the reaction mixture (exotherm to 29°). The solution was heated to 75° with continued bubbling of methylacetylene. After 5 h, the mixture was cooled. GLC indicated the presence of 5 high-boiling components in the ratio 7/9/14/12/2 (in order of increasing retention time, 8′ × 0.25″ SE 30). The last three were identified as 1,3,5-1,3,4- and 1,2,3-trimethylbenzene. Smaller amounts (~5%) of tetramers were observed. The allene cyclooligomers were detected as minor products (~2% total) in the crude reaction mixture. These probably result from allene impurities in the methylacetylene. Work-up afforded 1.3 g of a mixture of the major components. Under analogous conditions, allene afforded the usual product distribution at a reduced rate.

ACKNOWLEDGMENT

The author wishes to thank M. Dean for technical assistance, C. A. Reilly for obtaining and interpreting the ^{13}C and the 100 MHz ^1H NMR spectra, and P. A. Wadsworth for the mass spectral data.

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