

averaged, giving an agreement factor of 0.024 on F_o for the averaged observed reflections.

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques.⁵¹ The positions of the iridium and bromine atoms were determined from a Patterson synthesis. All other non-hydrogen atoms were located from difference Fourier maps following full-matrix least-squares refinement of previously located atoms. Atomic scattering factors were taken from the usual tabulations and the effects of anomalous dispersion were included.⁵² After anisotropic refinement of the non-hydrogen atoms, the dppe hydrogen atom positions were calculated (C-H distance 0.95 Å) and included in structure factor calculations but were not refined (fixed isotropic thermal parameters were 5.0 Å² for CH₂ hydrogens and 6.5 Å² for phenyl hydrogens). Final least-squares refinements established the correct enantiomer for the structure in P2₁2₁2₁ and led to the *R* values and esd in an observation of unit weight given in Table VI. The final difference Fourier showed only one peak with electron density greater than 25% of the height of a typical C atom. This peak was located ca. 2.3 Å from Ir with a height of 60% of a typical C atom. The location of this peak which

(52) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Cromer, D. T. *Ibid.*, Table 2.3.I.

did not refine successfully suggests that if it is not an artifact, it may be due to co-crystallization of <1% of the kinetic isomer **5b** with crystal packing determined by the Ir(dppe) part of the complex.

Tables III and IV in the text contain final positional parameters and selected bond distances and angles. Calculated hydrogen atom positions, refined anisotropic thermal parameters, and a listing of observed and calculated structure factor amplitudes are available as supplementary material.

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Supplementary Material Available: Listings of anisotropic thermal parameters (Table VII), bond lengths and angles within phenyl groups (Table VIII), calculated hydrogen atom positions (Table IX), and observed and calculated structure factors (Table X (34 pages). Ordering information is given on any current masthead page.

Study of the Reactions of Substituted Allenes with Tris(triphenylphosphine)nickel(0). An Analysis of the Factors Affecting the Regio- and Stereochemistry of π -Complex Formation and Coupling To Form Nickelacyclopentane Complexes

Daniel J. Pasto,* Nai-Zhong Huang, and Charles W. Eigenbrot

Contribution from the Department of Chemistry and the Molecular Structure Facility, University of Notre Dame, Notre Dame, Indiana 46556. Received December 5, 1984

Abstract: The reactions of ethylallene (ETA), *tert*-butylallene (TBA), phenylallene (PHA), cyanoallene (CYA), and methoxyallene (MEA) with tris(triphenylphosphine)nickel(0) [(TPP)₃Ni] have been investigated and compared with the reaction of dimethylallene (DMA) with (TPP)₃Ni reported earlier. At low temperatures (<-70 °C) ETA, TBA, and DMA reversibly form mono- and bis-allene π -complexes which can be detected by NMR. π -Complex formation involves predominantly the least substituted double bond. DMA displaces ETA and TBA, while MEA in turn displaces DMA from the π -complexes. PHA and CYA undergo immediate coupling at low temperatures (<-70 °C), and the relative stabilities and structures of their π -complexes could not be determined. The relative stabilities and structures of the π -complexes are discussed in terms of steric and electronic effects. The cis bis- π -complexes undergo coupling to form nickelacyclopentane σ -complexes: the relative reactivity sequence being CYA > PHA > MEA ≫ DMA > ETA > TBA. Evidence for a competitive electron-transfer process with CYA is presented. The structures of the intermediate substituted nickelacyclopentane complexes are inferred from the structures of the hydrocarbon products formed in reductive-elimination and hydrogen-migration, reductive-elimination reactions and from the structures of the ketonic products formed on reaction with carbon monoxide. Specific π - π , π - σ , and σ - σ modes of coupling in syn and anti conformations of the bis- π -complexes have been identified. The regio- and stereochemistry of formation of the nickelacyclopentane σ -complexes are discussed in terms of steric and electronic (orbital energy and AO coefficients) effects in the rate-determining transition state for σ -complex formation.

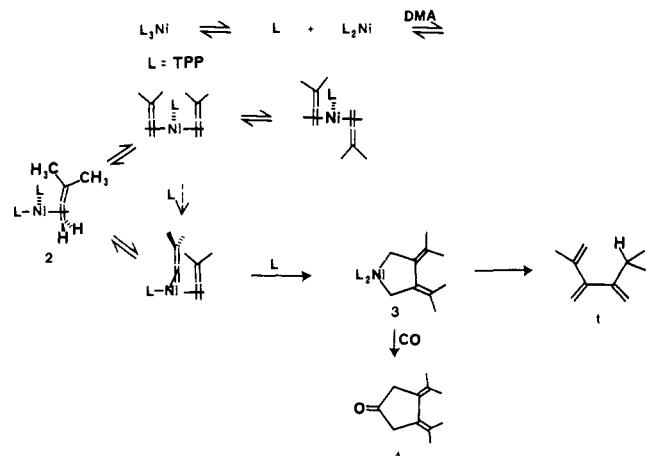
Our discovery that the formation of substituted allenes in the reactions of Grignard reagents with propargyl halides is catalyzed by salts of iron, cobalt, nickel and copper¹ and the reductive cyclization of propargyl chlorides with tris(triphenylphosphine)-nickel(0) [(TPP)₃Ni] to form 3,4-bis(alkylidene)cyclobutenes² has led us to study in detail the reactions of allenyl and propargyl systems with low valence state transition metal complexes. Recent studies have focused on the reactions of substituted allenes with

Ni(0) complexes. Although several reports had appeared describing the reactions of allene with Ni(0) complexes,³ relatively few investigations had been carried out with substituted allenes. It had been observed that dimethylallene (DMA) was converted to the dimeric-triene **1** in the presence of [(*o*-CH₃C₆H₄O)₃P]₃Ni and that 1,2-cyclooctadiene forms a π -complex with the same

(1) Pasto, D. J.; Chou, S.-K.; Waterhouse, A.; Shultz, R. H.; Hennion, G. F. *J. Org. Chem.* 1978, 43, 1385.
(2) Pasto, D. J.; Mitra, D. K. *J. Org. Chem.* 1982, 47, 1381.

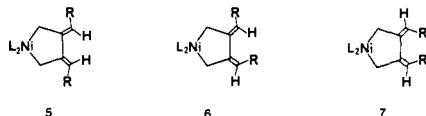
(3) Otsuka, S.; Mori, K.; Imaizumi, F. *J. Am. Chem. Soc.* 1965, 87, 3017. Otsuka, S.; Mori, K.; Suminoe, T.; Imaizumi, F. *Eur. Polym. J.* 1967, 3, 73. Hoover, F. W.; Lindsey, R. V., Jr. *J. Org. Chem.* 1969, 34, 3051. Otsuka, S.; Nakamura, A.; Tani, K.; Ueda, S. *Tetrahedron Lett.* 1969, 297. DePasquale, R. J. *J. Organomet. Chem.* 1971, 32, 381. Otsuka, S.; Tani, K.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* 1973, 2491.

Scheme I



complex, but it does not react further.⁴ We have recently investigated in detail the reactions of DMA with several Ni(0) complexes⁵ and have found that in addition to the formation of **1** four other dimeric hydrocarbon products are also formed in low yield. Carbonylation of the reaction mixture produced a major (**4**) and a minor ketone. Low-temperature NMR studies resulted in the characterization of a mono-DMA π -complex (**2**) and a σ -complex (**3**). The results of this study led to the proposed mechanism for formation of the major hydrocarbon **1** and ketone **4** shown in Scheme I.⁵ The minor hydrocarbon products and ketone are derived from a different mode of coupling of the DMA's in a bis-DMA π -complex.⁵

It was of interest to then investigate the reactions of other substituted allenes with $(TPP)_3Ni$ in an effort to determine the relative stabilities of the π -complexes, to determine the relative rates of coupling to form σ -complexes, and to evaluate the factors that determine the regiochemistry of the coupling process and the stereochemistry present in the σ -complexes (i.e., **5**, **6**, or **7**). Finally, it was of interest to determine what reactions the σ -complexes might undergo.



In this article we describe the results derived from the studies on the reactions of phenyllallene (PMA), ethyllallene (ETA), *tert*-butylallene (TBA), and cyanoallene (CYA) with $(TPP)_3Ni$.

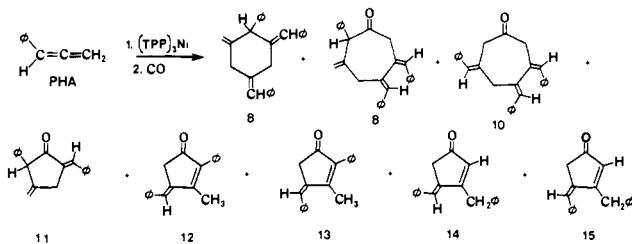
Results

Reaction of Phenyllallene (PHA) with $(TPP)_3Ni$. Preliminary low-temperature studies (<-70 °C) in THF- d_8 indicated that the reaction of 2 molar equiv of PHA with $(TPP)_3Ni$ occurs very rapidly to produce an apparent mixture of σ -complexes. No evidence was obtained for the formation of observable mono- or bis-PHA π -complexes. In toluene- d_8 , however, the NMR spectra at low temperatures showed broad vinyl resonances at reasonably normal positions for the PHA, suggesting rapid reversible formation of π -complexes. At ca. -20 °C the resonances of PHA disappear, and a complex NMR spectrum is obtained of what is presumed to be a mixture of σ -complexes. No free hydrocarbon products are formed at 20 °C, indicating that reductive elimination of the σ -complexes occurs only very slowly, if at all.

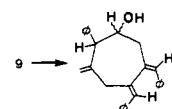
Carbonylation of the σ -complex mixture produces a complex mixture of mostly carbonyl compounds which was partially separated by chromatography. The structures of the products have been assigned on the basis of their IR, MS, an NMR spectral properties, and, in one case, by X-ray diffraction.

(4) Englert, M.; Jolly, P. W.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* 1972, 11, 136.

(5) Pasto, D. J.; Huang, N.-Z. *Organometallics*, in press.



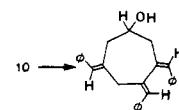
The first fraction contained ketone **9**. The IR spectrum contained a carbonyl band at 1710 cm⁻¹ suggestive of a saturated six or larger membered ring ketone. The MS showed a parent ion at *m/e* 376, indicating that **9** was composed of three molecules of PHA plus CO. The NMR spectrum contained two AB doublets with *J*'s of 16.21 and 14.56 Hz representing isolated methylene units having diastereotopic hydrogens, thus requiring the presence of a chiral center in the structure. The NMR spectrum also contained peaks for methylene vinyl hydrogens and two benzylidene vinyl hydrogens. The benzyl hydrogen attached to the chiral carbon atom appeared as a singlet. Reduction of **9** produced an essentially equimolar mixture of two diastereomeric



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alcohols whose NMR spectrum showed two doublets at δ 2.27 and 2.58. Irradiation of the carbinol hydrogen resonance resulted in the collapse of the δ 2.27 and 2.58 doublets to singlets, thus requiring that the chiral center be at an α -position to the carbonyl group. The stereochemistry about the two benzylidene groups is based on analogy with that observed in the isomeric ketone **10** whose structure was determined by X-ray diffraction.

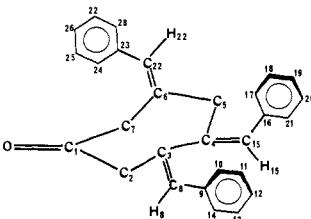
Fraction 2 contained two stereoisomers in an ca. 95:5 ratio. The IR spectrum contained a band in the carbonyl region at 1705 cm⁻¹ suggestive of a six or medium sized membered ring ketone. The MS indicated a structure consisting of three PHA molecules plus CO. The NMR spectrum contained three saturated methylene singlets and three benzylidene vinyl hydrogen singlets. These data suggested that the ketone possessed a 2,4,6- or a 3,4,6-tribenzylidenecycloheptanone structure. Reduction of the ketone produced a single hydroxyl-containing compound, whose NMR



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spectrum indicated the presence of a -CH₂-CH(OH)-CH₂- part structure, eliminating the possibility of a 2,4,6-tribenzylidenecycloheptanone structure. The stereochemistry about the benzylidene groups, however, could not be determined from the spectral data. The major ketonic component formed excellent crystals suitable for X-ray crystallographic studies.

An X-ray crystallographic structure determination was carried out to determine the stereochemistry about the three benzylidene groups. The stereochemistry about the double bonds was shown to be that illustrated below. The structural parameters show that



several severe sterically induced distortions are present.⁶ Bond

Table I. Bond Distances (\AA) in **10**

atom 1	atom 2	distance	atom 1	atom 2	distance
O1	C1	1.203 (2)	C1	C2	1.504 (3)
C2	C3	1.515 (3)	C3	C4	1.480 (3)
C3	C8	1.341 (3)	C4	C5	1.515 (3)
C4	C15	1.331 (3)	C5	C6	1.508 (3)
C6	C7	1.507 (3)	C6	C22	1.330 (3)
C7	C1	1.511 (3)	C8	C9	1.463 (3)
C9	C10	1.390 (3)	C10	C11	1.378 (3)
C11	C12	1.375 (3)	C12	C13	1.365 (4)
C13	C14	1.374 (3)	C14	C9	1.389 (3)
C15	C16	1.474 (3)	C16	C17	1.390 (3)
C17	C18	1.374 (3)	C18	C19	1.366 (3)
C19	C20	1.368 (3)	C20	C21	1.379 (3)
C21	C16	1.393 (3)	C22	C23	1.466 (3)
C23	C24	1.386 (3)	C24	C25	1.383 (3)
C25	C26	1.375 (3)	C26	C27	1.377 (4)
C27	C28	1.372 (3)	C28	C23	1.391 (3)
C8	H8	1.00 (2)	C15	H15	0.97 (2)
C22	H22	0.94 (2)			

Table II. Bond Angles (deg) in **10**

atoms	angle	atoms	angle
O1-C1-C2	121.3 (2)	C8-C9-C10	124.1 (2)
O1-C1-C7	121.1 (2)	C8-C9-C14	118.6 (2)
C7-C1-C2	117.5 (2)	C10-C9-C14	117.3 (2)
C1-C2-C3	111.7 (2)	C9-C10-C11	120.8 (2)
C2-C3-C4	114.6 (2)	C10-C11-C12	120.6 (2)
C2-C3-C8	118.8 (2)	C11-C12-C13	119.4 (2)
C8-C3-C4	126.6 (2)	C12-C13-C14	120.4 (2)
C3-C4-C5	115.8 (2)	C13-C14-C9	121.5 (2)
C3-C4-C15	119.8 (2)	C15-C16-C17	119.4 (2)
C15-C4-C5	124.3 (2)	C15-C16-C21	123.6 (2)
C4-C5-C6	112.6 (2)	C17-C16-C21	117.0 (2)
C4-C6-C7	115.8 (2)	C16-C17-C18	121.6 (2)
C5-C6-C22	120.8 (2)	C17-C18-C19	120.5 (2)
C22-C6-C7	123.3 (2)	C18-C19-C20	119.3 (2)
C6-C7-C1	114.4 (2)	C19-C20-C21	120.8 (2)
C22-C23-C24	123.0 (2)	C20-C21-C16	120.9 (2)
C22-C23-C28	119.3 (2)	C25-C26-C27	119.4 (2)
C24-C23-C28	117.7 (2)	C26-C27-C28	120.3 (2)
C23-C24-C25	120.9 (2)	C27-C28-C23	121.4 (2)
C23-C25-C26	120.0 (2)	H22-C22-C23	115 (1)
C3-C8-H8	112 (1)	C4-C15-H15	118 (1)
C3-C8-C9	130.4 (2)	C4-C15-C16	129.7 (2)
H8-C8-C9	118 (1)	H15-C15-C16	113 (1)
C6-C22-H22	115 (1)	C6-C22-C23	129.5 (2)

Table III. Dihedral Angles about the Benzylidene Groups in **10**

plane 1	plane 2	angle, deg	type of distortion
C2,C3,C4	C9,C8,H8	4.7	C=C twist
C3,C8,H8	C10,C9,C14	31.8	phenyl rotation
C3,C4,C5	C16,C15,H15	5.1	C=C twist
C4,C15,H15	C17,C16,C21	34.2	phenyl rotation
C5,C6,C7	C23,C22,H22	5.4	C=C twist
C6,C22,H22	C23,C22,C27	38.2	phenyl rotation
C8,C3,C4	C3,C4,C16	53.1	diene skew

lengths are given in Table I, bond angles in Table II, and selected interplanar dihedral angles in Table III. All of the bond lengths are of reasonably normal magnitude. However, several bond angles and dihedral angles are unusual, revealing structural distortions induced by the highly congested environment about the benzylidene groups. Severe bond angle distortions include 4,3,8 (126.6°), 3,8,9 (130.4°), and 3,8,H8 (112°) about the 3-benzylidene group; 5,4,15 (124.3°) and 4,15,16 (129.7°) about the 4-benzylidene group; and 7,6,22 (123.3°) and 6,22,23 (129.5°) about the 6-benzylidene group. Each double bond is twisted out of planarity by 4.7–5.4°, while the phenyl groups are twisted out of coplanarity with the double bonds by 31.8–38.2° (see Table

(6) Severely distorted, or skewed, diene systems have been reported previously (see: Pasto, D. J.; Scheidt, W. R. *J. Org. Chem.* 1975, 40, 1444 and references contained therein).

III). The skew about the 8,3,4,15 diene system is 53.1°. These distortions from coplanarity severely interrupt conjugation and result in the unusually short wavelength absorption of **10** in the UV (end absorption with an inflection at 220 nm and shoulder at 246 nm).

The minor component in fraction 2 is believed to be stereoisomeric about the 6-benzylidene group, although no conclusive evidence is available to support this assumption (see later discussion).

Fraction 3 was a trimeric hydrocarbon whose NMR spectrum contained two sets of AB doublets (J 's = 13.6 and 16.4 Hz) for two sets of isolated diastereotopic methylene hydrogens, two methylene vinyl hydrogens, and two benzylidene vinyl hydrogens. These NMR data are consistent only with structure **8**.

Fraction 4 consisted of a single carbonyl compound with $\nu_{\text{C=O}}$ 1700 cm⁻¹ and λ_{\max} 288 nm. The spectral data are consistent with the presence of a five-membered, α,β -unsaturated, carbonyl system. The NMR spectrum contained two methylene hydrogen and one benzylidene vinyl hydrogen resonances. In addition, two singlets for one and two hydrogens were also present. These data are consistent with structure **11**. The data do not allow for an unambiguous assignment of the stereochemistry about the exocyclic benzylidene double bond.

Fraction 5 consisted of a mixture of two stereoisomeric, α,β,δ -unsaturated cyclopentanones ($\nu_{\text{C=O}}$ 1690 cm⁻¹ and λ_{\max} 290 nm). The NMR spectrum showed the presence of an allylic methyl group and a benzylidene vinyl hydrogen. The assignment of the positions of the substituents on the cyclopentenone ring is based on NMR chemical shift comparisons, and Eu(fod)₃ induced shifts. In the major isomer **12** the allylic methyl appears at δ 2.29, while in the minor isomer the methyl resonance appears at δ 1.60. This shielding effect is caused by the phenyl group in **13** which must reside essentially perpendicular to the plane of the C=C. In this conformation the methyl group resides over the face of the phenyl ring in a highly shielding environment. The α -methylene group in the major isomer **12** appears at lower field than in **13**. Molecular models indicate that the phenyl ring in **12** can exist in a conformation coplanar with the C=C. In this conformation the α -methylene group lies in a deshielding region of the phenyl group. That the methylene group is α to the carbonyl group is indicated by the results of chemical shift studies: the chemical shift of the methylene hydrogens being more strongly affected by the addition of Eu(fod)₃ (see Table IV, Experimental) than are any of the other resonances. Additional evidence that one phenyl group is attached to an α -position is also derived from the chemical shift studies. One of the sets of *ortho* aromatic hydrogens appears as a very distinct doublet. The addition of the shift reagent results in a large deshielding effect which can only result if that aromatic ring is attached to an α -position. Collectively, the data are only consistent with structures **12** and **13**.

Fraction 6 consisted of a mixture of the $\alpha,\beta,\sigma,\delta$ -unsaturated cyclopentenones **14** and **15** ($\nu_{\text{C=O}}$ 1690 cm⁻¹ and λ_{\max} 292 nm). The position of the benzyl group in **14** and **15** is assigned on the basis of its substantially different chemical shift in **14** and **15**, being shielded in **15** by $\Delta\delta$ 0.54 ppm relative to **14**. This shielding is due to the required perpendicular conformation of the phenyl group in **14** (see above discussion on the stereochemical assignments of **12** and **13**). In **15** the α -methylene group appears at higher field than in **14** which is also consistent with the structural assignments. The addition of shift reagent results in substantial deshielding effects only on the methylene and one vinyl hydrogen resonance, requiring these groups to be α to the carbonyl group. The data are consistent only with structures **14** and **15**.

Ethylallene. The results of low-temperature NMR studies indicate that ETA forms loosely bound π -complexes with (TPP)₃Ni. On addition of ETA to (TPP)₃Ni in either THF-*d*₈ or toluene-*d*₈ at -70 °C, the reaction solution turns from dark red to dark green. In THF-*d*₈ the vinyl resonances of ETA are not present; instead a very broad resonance appears in the δ 4.55 region, along with broadened methylene and methyl peaks. In toluene-*d*₈ broad vinyl hydrogen resonances appear at δ 4.85 and 5.32, along with a very broad resonance in the δ 3.4–3.8 region.

Scheme II

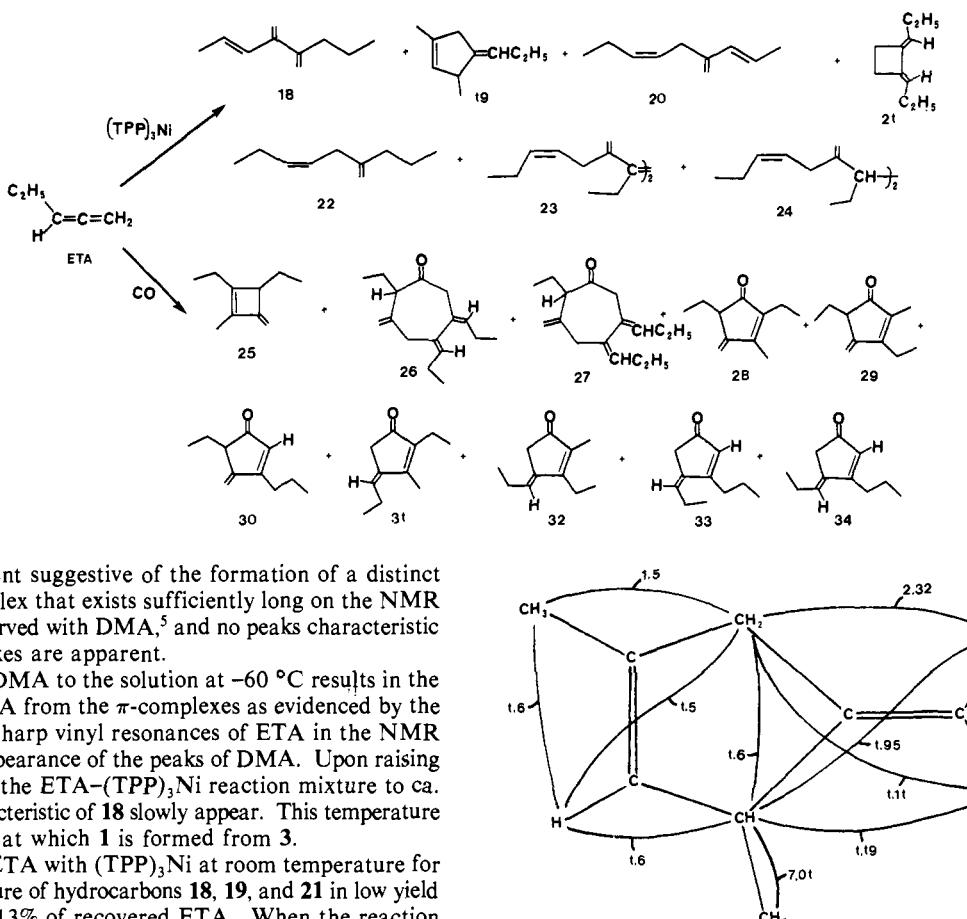


Figure 1. Vicinal and long-range couplings in structure **19**

The structure of **18** was readily assigned on the basis of its

NMR spectrum. The trans spectrochemistry about the disubstituted double bond is assigned on the basis of the J of 16.06 Hz which is typical of *trans*-dialkyl-substituted double bonds.

The NMR spectrum of **19** showed extensive long-range coupling interactions which were fully identified by double resonance studies (see Experimental Section). All of the vicinal and long-range coupling interactions are shown in Figure 1. The NMR data are consistent only with the structure shown for **19** as a dimer of ETA.

The presence of one terminal and two internal double bonds in **20** was clearly evident in the NMR spectrum. The trans stereochemistry of the C2–C3 double bond was indicated by the large vinyl hydrogen coupling constant of 15.51 Hz, while the cis stereochemistry of the C6–C7 double bond was indicated by a smaller coupling constant of 11.86 Hz. The value of the trans coupling constant is similar to that in **18** (16.06 Hz), while the cis coupling constant is similar to those in **22**, **23**, and **24** (10.62, 10.58, and 10.73 Hz).

The NMR spectrum of **21** is very simple, indicating a symmetrical dimeric structure. The presence of a conjugated diene chromophore was indicated by the absorption maxima at 254 and 263 nm, which compares well with those reported for 1,2-dimethylenecyclobutane at 240, 247, and 256 nm.⁷ The long-range, allylic coupling constant between the vinyl and ring methylene hydrogens of <0.7 Hz indicated an *E* configuration about the double bonds.

The structure of **22** was readily assigned on the basis of its NMR spectrum. The cis stereochemistry about the double bond was indicated by the J value of 10.62 Hz.

The tetrameric nature of the next to the last fraction **23** was indicated by its mass spectrum. The NMR spectrum of the compound was very simple, and integrated for a total of 16 hydrogen atoms, consistent only with a symmetrical structure formed from two identical dimeric units. The assignment of the cis stereochemistry is based on the *J* value of 10.58 Hz. The stereochemistry about the tetrasubstituted double bond could not be determined.

The mass spectrum of the last fraction also indicated a tetrameric structure *plus* two hydrogen atoms. The NMR spectrum was relatively simple, indicating a symmetrical structure. The presence of a chiral center in the molecule was indicated by the diastereotopic nature of the hydrogen atoms of the methylene group between the two double bonds and the complexity of the pattern of the methylene hydrogens of the ethyl group. The NMR data are consistent with those of structure 24. It should be noted that although *dl* and *meso* structures are possible, only a single stereoisomer was indicated to be present by the NMR spectrum.

The carbonylation of the ETA-(TPP)₃Ni reaction mixture produces a complex mixture of hydrocarbons and ketones which could be partially separated by chromatographic techniques. The only hydrocarbon compound identified was assigned structure 25. The NMR spectrum showed resonances for two sets of diastereotopic methylene hydrogens, one set of which was coupled to an additional hydrogen. Precluding a gross structural rearrangement, the NMR spectrum is consistent with 25 or its regiosomer. Available data do not allow for a distinction between the two regiosomeric structures. The regiochemistry assigned is the same as that in 21.

A mixture of trimeric noncrystalline ketones **26** and **27** (6:4 ratio) was isolated, which was further separated by HPLC. The NMR spectra of the two ketones were very similar, with only small differences in chemical shifts and coupling constants. Each spectrum showed the presence of two isolated sets of diastereotopic

(7) Weinstein, B.; Fenselau, A. H. *J. Chem. Soc., C* 1967, 368.

methylene hydrogens, a set of diastereotopic methylene hydrogens coupled to methyl hydrogens, and a single methine hydrogen. Also present in each spectrum were two terminal methylene vinyl hydrogens and two propylidene vinyl hydrogens. The spectral data are consistent with two stereoisomers of 2-ethyl-3-methylenecyclohexanone. Extensive decoupling experiments were carried out, but a completely unambiguous assignment of stereochemistry was not possible on the basis of the observed long-range allylic coupling constants. This is probably due to the extensively twisted conformation of the ring system. The assignment of **26** as one of the stereoisomers is based on analogy with structure **9** derived from PHA. The stereochemistry of the other isomer **27** is not known.

The cyclopentenones **28** and **29** were isolated as an inseparable mixture (7:3 ratio). The IR ($\nu_{C=O}$ 1695 cm⁻¹) and UV (272.5 nm) spectra indicated the presence of an extended conjugated system. The NMR spectra of the two components were clearly distinguishable. Both spectra indicated the presence of two sets of diastereotopic methylene hydrogens of the ethyl groups, one set further coupled to a single hydrogen atom. The regiochemistry in **28** and **29** of the vinyl ethyl and methyl groups has been assigned on the basis of the following chemical shift correlations. β -Vinyl hydrogens resonate at lower field than do α -hydrogen atoms in cyclopentenone and cyclohexenone,^{8a} a trend that appears to also hold true for methyl and methylene groups. For example, the methyl resonance of 3-methylcyclohexenone appears at δ 1.98,^{8b} whereas that of the 2-methyl group in carvone appears at δ 1.78.^{8c} Similar trends are apparent in acyclic aldehydes and ketones. In the NMR spectrum of the compound assigned structure **28** the vinyl methyl resonance appears at δ 2.08, while that of **29** appears at δ 1.41. The methylene hydrogens of the 2-ethyl group of **28** (δ 2.11) appear at higher field than the β -methylene hydrogens in **29**, **30**, **33**, and **34** (δ 2.41–2.47). Of importance for later stereochemical arguments is the fact that the two low-field vinyl hydrogens of **28** and **29** appear as well-resolved doublets with J 's of 1.73 and 1.90 Hz, whereas the higher field hydrogen resonances are coupled both geminally and allylically with much smaller J 's, resulting in their appearing only as broad singlets. The lower field hydrogens must be cis to the α -hydrogen of the chiral center, and the higher field hydrogen trans.

The second ketonic fraction is assigned structure **30**. The IR ($\nu_{C=O}$ 1695 cm⁻¹) indicates the presence of an extended conjugated system. The UV absorption at 264 nm indicates a lesser degree of substitution on the conjugated system than in **28** and **29**. The NMR spectrum indicates the presence of a chiral center, and a propyl group. The only question to be resolved is what is the regiochemistry about the 2,3 double bond. The 2-vinyl hydrogen appears at δ 6.07 which is only consistent with an α -vinyl hydrogen.⁹

The third ketonic fraction was a mixture of inseparable stereoisomeric ketones **31** and **32**. The IR and UV spectra indicated the presence of more highly substituted, extended, conjugated systems ($\nu_{C=O}$ 1690 cm⁻¹ and 285 nm, respectively). The assignment of the regiochemistry about the 2,3 double bond is based on the relative chemical shifts of the vinyl methyl and methylene hydrogens. The methyl of **31** appears at δ 2.06 typical of a β -methyl, while that of **32** appears at δ 1.41 typical of an α -methyl. The allylic methylene hydrogens of **31** appear at δ 2.26 (α -position) while those of **32** appear at lower field at δ 2.46 (β -position). The stereochemistry about the propylidene groups is assigned on the basis of their low-field chemical shift and the magnitude of the long-range coupling with the tertiary α -hydrogen, being 1.63 Hz in **31** and not resolvable (<0.7 Hz) in **32**.

The final ketonic fraction was a mixture of **33** and **34**. The presence of an extended conjugated system was indicated by the

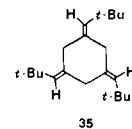
(8) Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co., 1974; Vol. II, (a) spectra 139 A and 139 C, (b) spectrum 139 D, (c) spectrum 141 A.

(9) The α -vinyl hydrogens of 2-cyclohexenone and 2-cyclopentenone appear at δ 6.05 and 6.25, respectively, while the β -vinyl hydrogens appear at much lower field at δ 7.05 and 7.85, respectively (see spectra 139 A and 139 C, ref 8).

IR absorption at 1685 cm⁻¹, and the absorption in the UV at 280 nm (at shorter wavelength than with **31** and **32**). The vinyl hydrogen resonances at δ 6.02 in **33** and δ 6.09 in **34** indicate the regiochemistry about the 2,3 double bond as shown. The stereochemistry about the propylidene groups is indicated by the relative chemical shifts and the magnitude of the long-range coupling constants between the vinyl and α -hydrogens, being ~1.5 Hz in **33** and nonresolvable (<0.7 Hz) in **34**.

tert-Butylallene (TBA). The addition of TBA to (TPP)₃Ni at low temperature produces a dark green solution. The NMR spectrum of this solution does not contain peaks for free TBA. Instead, three broad resonances were observed whose positions were temperature dependent (see Table VI, Experimental). The addition of DMA resulted in the immediate appearance of the peaks of free TBA. At temperatures above 10 °C the broad resonances of the vinyl hydrogens of TBA in the π -complexes slowly disappeared; however, the resulting NMR spectrum was very complex and contained only rather broad resonances.

The removal of the volatiles from a reaction mixture of TBA and (TPP)₃Ni (2:1 molar ratio) under high vacuum resulted in the recovery of TBA (13%) and the isolation of the cyclic trimer **35**. (No dimeric or other hydrocarbon products could be isolated.)

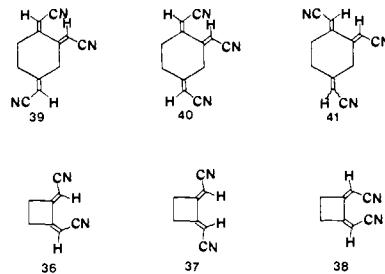


Extraction of the residue remaining after pumping off the volatiles produced a residue which contained **35** (13%) and an apparent TBA oligomer or polymer (very complex NMR spectrum).

Attempted carbonylation of a TBA-(TPP)₃Ni reaction mixture produced only **35**; no carbonyl-containing products were formed.

Cyanoallene (CYA). CYA reacts with (TPP)₃Ni very rapidly, even at temperatures <-70 °C. The NMR spectrum of the reaction mixture recorded immediately at -70 °C contained only broad resonances, which remained broad even at room temperature. No characterizable peaks could be discerned. No CYA-containing products were found in the volatile fraction, or in the hexane extract of the residue.

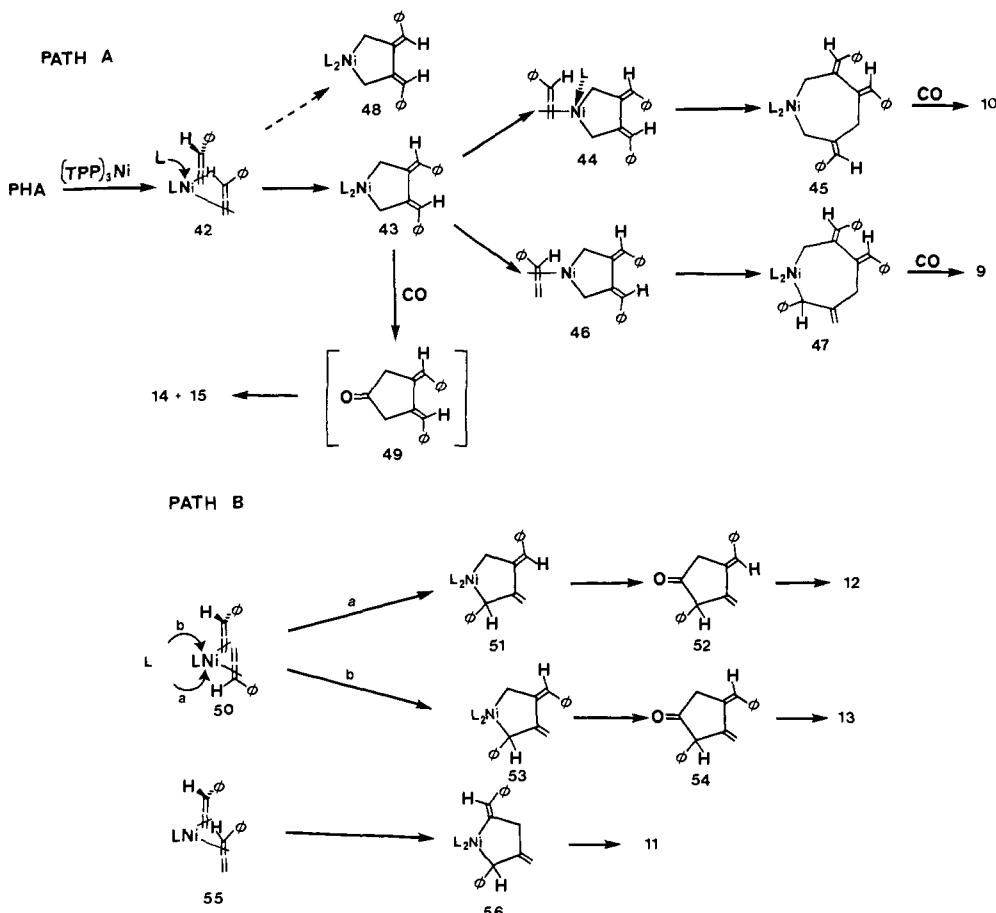
Carbonylation of the reaction mixture did not produce any carbonyl-containing products. Two dimeric and two trimeric products were isolated. The dimers have been assigned structures **36** and **37** on the basis of UV and NMR spectral data. Both



dimers absorbed in the UV (281 and 280 nm), indicating the presence of conjugated diene chromophores. The NMR spectrum of **36** showed two vinyl resonances which are long-range coupled to methylene groups consistent with the unsymmetrical structure. The high-field vinyl hydrogen (δ 5.33) is long-range coupled with a J of 2.12 Hz, while the low-field vinyl hydrogen (δ 6.19) shows a J of 2.65 Hz. These coupling constants indicate that the high-field resonance is that of the inner hydrogen, and the low-field resonance is that of the outer hydrogen. The NMR spectrum of the second dimer showed single vinyl hydrogen and single methylene resonances with a long-range J of 1.0 Hz. The stereochemistry of this dimer is assigned as that in **37** by comparison of the long-range J with that of the other symmetrical, conjugated dimer **38** (J = 1.37 Hz) isolated from the thermal cyclo-dimerization of CYA.¹⁰ The stereochemical assignment of **37**

(10) Pasto, D. J.; Yang, S.-H.; Huang, N.-Z., unpublished results.

Scheme III



has been confirmed by X-ray diffraction studies.¹¹

The NMR spectra of both of the trimers contained three vinyl hydrogen resonances, a broadened isolated methylene singlet, and a broadened AA'BB' multiplet. Both trimers absorbed in the UV at 300 nm. These data are consistent only with unsymmetrical cyclic trimers containing a conjugated diene system. Of the many stereoisomers possible, structure **39** is assigned as one of the trimers based on analogy with the stereochemistry exhibited in the cyclic ketone **10** derived from PHA. The structure of the other trimer is tentatively assigned as either **40**, differing only in the stereochemistry about the isolated exocyclic double bond, or one of the stereoisomers of **41** which possesses the same stereochemistry about the conjugated diene chromophore as that in **37**. Unfortunately, there is no obvious trend in the vinyl hydrogen chemical shift data of the dimers and trimers which would allow for an unambiguous assignment of the stereochemistry of the trimers. The long-range, allylic coupling in the trimers could not be resolved, again precluding assignment of stereochemistry. Crystals suitable for X-ray analysis have not been obtained due to the small amounts of material available.

Also isolated from the carbonylation reaction mixture was material whose NMR spectrum was very complex, suggesting a mixture of complex polymeric compounds.

Discussion

The reactions of PHA, ETA, TBA, and CYA with $(TPP)_3Ni$ are considerably more complex than that with DMA, involving a greater number of reaction pathways and π - and σ -complexes. In order to simplify the following discussion and mechanistic schemes, mono- and trans bis- π -complexes will not be included, even though they must be present.

Reasonable pathways for the formation of the products in the reaction of PHA with $(TPP)_3Ni$ are shown in Scheme III. Path

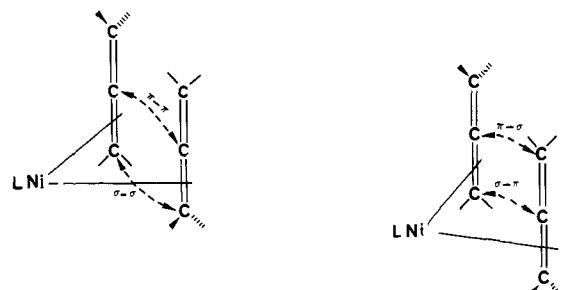


Figure 2. Illustrations of the $\pi-\pi$, $\pi-\sigma$, $\sigma-\pi$, and $\sigma-\sigma$ modes of coupling in bis(allene) π -complexes.

A involves formation of a bis- π -complex in which π -bond formation involves the unsubstituted double bond of the PHA's. Coupling in **42** occurs to produce apparently only **43**. (We shall refer to this mode of coupling as a $\pi-\pi$ coupling. Other modes of coupling discussed in this article are $\pi-\sigma$, or $\sigma-\pi$, and $\sigma-\sigma$ couplings. These are illustrated in Figure 2 and will be discussed in more detail later in this article). Although **48**, also formed by $\pi-\pi$ coupling, is less sterically congested than **43**, no products were isolated possessing that stereochemistry about the diene chromophore, and this mode of coupling is considered not to occur. A σ -complex having the stereochemistry shown in **7** also is not formed.

The stereochemistry of the σ -complex is controlled by steric effects generated in the ligand-induced coupling process. During the coupling process the benzylidene groups must undergo rotation into the plane of the nickelacyclopentane ring. During attack by TPP (*L*) on the nickel atom, rotation of the adjacent benzylidene phenyl away from the approaching TPP (to form **43**) will develop far less steric congestion than in a rotation toward the approaching TPP (to form **48**). The direction of rotation of the second benzylidene phenyl group is controlled by the direction of rotation

(11) The results of the CYA cyclodimerization and X-ray structural studies will be published separately.

of the first benzylidene function, the rotation away from the inwardly rotating first benzylidene function involving far less steric congestion than a rotation toward the first benzylidene group (to form a σ -complex having the stereochemistry shown in 7).

Carbonylation of 43 produces 49 which undergoes prototropic rearrangement to produce the two stereoisomeric ketones 14 and 15. All attempts to detect the presence of 49 were without success, the rearrangement having occurred before extraction of the mixture of carbonyl compounds. It is doubtful that the prototropic rearrangement occurred with 43 prior to carbonylation in that no product was isolated which would have resulted from further reaction of such a complex. It is believed that the prototropic rearrangement is catalyzed by some Lewis acidic or basic species present in the reaction mixture after carbonylation. The drive for isomerization of 49 to 14 and 15 is the relief of strain in the twisted diene chromophore.

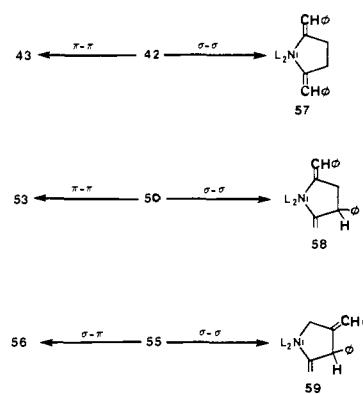
The formation of the trimeric ketones 9 and 10 involves further reaction of 43 with PHA to form the π -complexes 44 and 46: the former involving π -complex formation with the least-substituted double bond, the latter with the phenyl-substituted double bond. The regio- and stereochemistry involved in the insertion reaction with 44 to form 45 must be controlled by several steric factors, the dominant factor appearing to involve the direction of attack by TPP on the nickel atom. Attack from the direction shown in 44 forces the insertion to occur into the Ni-C bond trans to the approaching TPP. The approach by TPP from this direction is less sterically inhibited than is approach from the opposite direction (by the phenyl group of the benzylidene function). The stereochemistry about the newly formed benzylidene function must be controlled by steric interactions generated between the phenyl group and the organic portion of the nickelacyclopentane ring system. (Also present with 10 was a very small amount of a stereoisomeric ketone which may be stereoisomeric about the 6-benzylidene group in 45 formed by rotation in the more sterically hindered manner.) The regiochemistry observed in the formation of 47 from 46 can be attributed to the same steric factors as present in the formation of 45.

Mechanisms for the formation of the minor ketones 11–13 are illustrated in path B in Scheme III. The bis-PHA π -complexes involved in path B have one PHA π -bonded with the least-substituted double bond, the other with the phenyl-substituted double bond. $\pi-\pi$ coupling in 50 results in the formation of 51 and 53, depending on the direction of approach of the TPP. $\pi-\sigma$ coupling in the complex 55, which is a rotational conformer of 50, results in the formation of 56. The ketones 52 and 54 derived from 51 and 53 undergo subsequent prototropic rearrangement to form 12 and 13. The ketone 11 derived from 56, being less sterically strained, does not undergo rearrangement.

The majority (90%) of the reaction of PHA with $(TPP)_3Ni$ occurs via path A. The reasons for this preference will be discussed in a latter section of this paper.

The dominant mode of coupling in the PHA π -complexes occurs via the $\pi-\pi$ mode. $\pi-\sigma$ coupling occurs only with complex 55, and it represents a very minor pathway. The $\sigma-\sigma$ mode of coupling in 42, 50, and 55 to form 57, 58, and 59, respectively, apparently does not occur, no products having been isolated which would be derived from these σ -complexes. The reasons for this will also be considered later when the details of the mechanism of the coupling reaction are discussed.

Ethylallene. The reaction of ETA with $(TPP)_3Ni$ is considerably more complex than that of PHA with $(TPP)_3Ni$. This greater complexity, however, provides greater insight on the mechanism of the coupling process to form the σ -complexes. The careful analysis of the structures of the hydrocarbon and ketone products reveals six different pathways of coupling in the bis- π -complexes. (Only three were observed with PHA.) This is the maximum possible number of pathways for coupling in the bis- π -complexes. Scheme IV shows the overall mechanism for the formation of the bis- π - and σ -complexes in the reaction of ETA with $(TPP)_3Ni$. The six modes of coupling are designated A–F. The intermediate 3,4-bis(alkylidene)cyclopentanones are not illustrated in the scheme; only the final structures are indicated.



The first two modes of coupling (A and B) involve bis- π -complexes in which complex formation involves the least substituted double bond of ETA. The two modes differ only in rotational conformation within the π -complexes 60 and 64. In 60, $\pi-\pi$ coupling results in the formation of 61 and 62. On the basis of the steric arguments that govern the direction of rotation of the alkylidene functions presented above, 61 is expected to be preferred. As ethyl is smaller than phenyl, some non-least sterically hindered rotation occurs, producing the stereochemistry shown in 62. Reductive elimination within 62 forms the simple ETA cyclodimer 21.

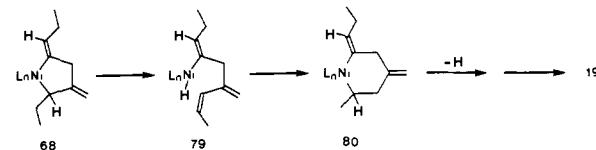
It is important to note that no simple cyclodimer is derived from 61. This complex undergoes hydrogen migration-reductive elimination to produce 18, and further insertion of ETA to ultimately produce 26 (and/or 27). These processes occur more rapidly than does simple reductive elimination. This supports our earlier conclusion that the hydrogen migration occurs intramolecularly and requires an inward orientation of the alkyl group from which the hydrogen migrates.⁵

In the B pathway of coupling, $\pi-\sigma$ modes of coupling occur, both modes of coupling producing the same σ -complex 65 (=66). In this mode of coupling the stereochemistry about the propylidene group, as reflected in the cis configuration about one of the double bonds in 20 and 22–24, is controlled by the preference for the least sterically congested exo orientation of the ethyl groups in 64.

It is important to note that 20 and 22–24 are not formed under mild conditions as are 18, 19, and 21. When the reaction is carried out at 20 °C for 2 h, only ETA (13%) is recovered, and 18, 19, and 21 are formed (20% yield). The majority of the original ETA is tied up in less reactive σ -complexes which require more vigorous reaction conditions to proceed on to 20 and 22–24. Under more vigorous conditions 75% of the ETA is recovered in the products, mostly in 20 and 22–24. σ -Complex 65 (66) does not undergo carbonylation. This reduced reactivity toward reductive elimination and carbonylation must be due to the presence of the stronger Ni-C_{sp²} bond present in 65 (66).

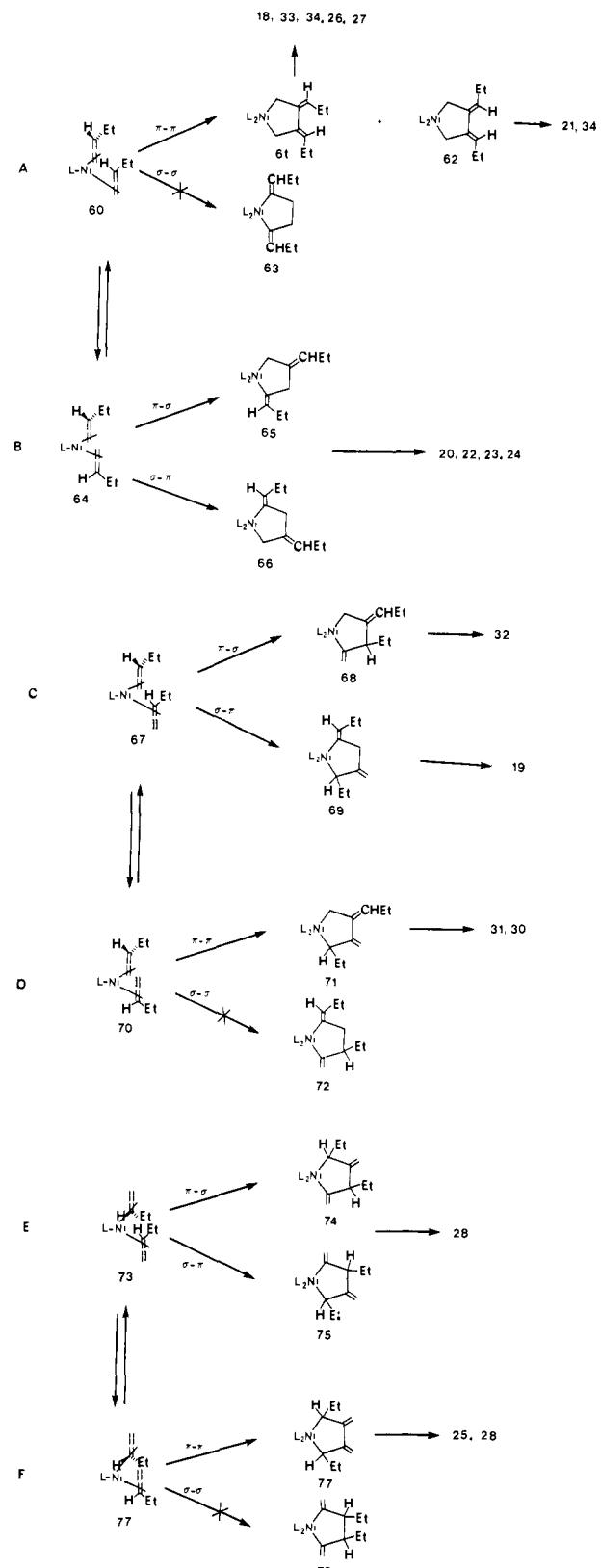
The second two pathways of coupling, C and D, occur within π -complexes in which one ETA is π -bonded to the least substituted double bond and the other ETA is π -bonded to the ethyl-substituted double bond, the two π -complexes 67 and 70 differing only in the orientation of the ETA's. In 67, $\pi-\sigma$ coupling produces 68 which is the precursor of 32. Although carbonylation of 68 occurs, it occurs to only a very minor extent (0.4%).

The alternative $\sigma-\pi$ mode of coupling produces 69 which appears to be a likely precursor for the unusual product 19. In contrast to the rather unreactive 65 (66), 69 can undergo β -hydride elimination to form 79 which can undergo intramolecular addition to produce 80. Hydrogen migration followed by reductive elimination produces 19.



The final two pathways of coupling, E and F, occur within

Scheme IV



bis- π -complexes in which both ETA's are π -complexed with the ethyl-substituted double bond. In pathway E coupling in 73 can occur in either π - σ or σ - π processes which produce the same σ -complex 74, or 75, which are the precursors to 29. Coupling via the F pathway in a π - π process produces 77 which is the precursor to 25 and 28. σ - σ coupling in 77 apparently does not occur.

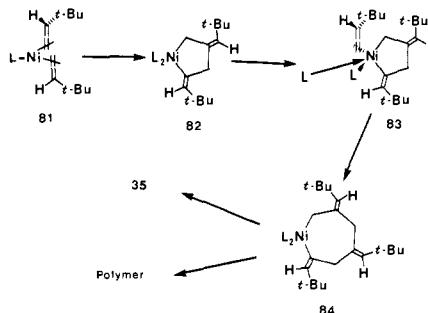
Several interesting trends are apparent in the product distri-

bution data. Of the six pathways for coupling, the pathway B is dominant (48.1%), followed by A (16.2%), F (7.7%), D (4.8%), C (4.4%), and E (3.1%). The σ - π coupling processes occur to a greater extent (50.6%) than does the π - π process (27.7%). The σ - σ mode of coupling does not occur. Of the two types of rotational conformations possible for each combination of π -complexation, the anti conformations 64, 70, and 73 couple to a greater extent (59.1%) than do the syn conformations 60, 67, and 77 (19.7%). Finally, product formation occurs to a much greater extent through the π -complexes in which both ETA's are π -bonded to the least substituted double bond pathways A and B (64.3%), compared to those in which one ETA is π -bonded to the least substituted double bond and one to the ethyl-substituted double bond (modes C and D, 7.4%), and in which both ETA's are π -bonded to the ethyl-substituted double bond (modes E and F, 9.8%). These preferences appear to be controlled by steric and electronic properties that will be discussed later.

The low-temperature NMR spectrum of a reaction mixture of ETA with $(TPP)_3Ni$ suggests that there is a rapid equilibrium exchange between the various π -complexes and their rotational conformations.

tert-Butylallene. The reaction of TBA with $(TPP)_3Ni$ appears to be much simpler, but in fact it reveals yet even more of the subtleties of the relative reactivities of the π - and σ -allene complexes. Low-temperature NMR studies indicate that a complex equilibrium of π -complexes exists. Like the ETA π -complexes, the TBA is quantitatively displaced from the π -complexes by DMA.

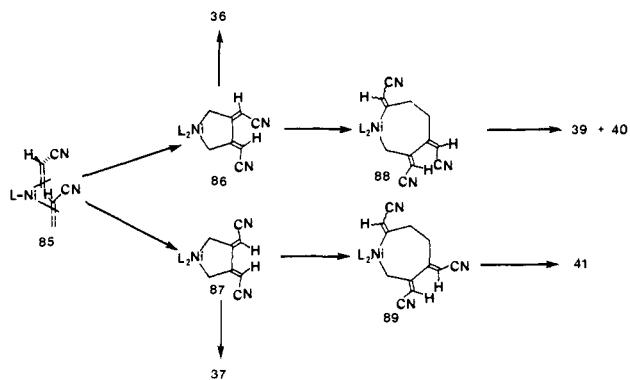
Only a single symmetric, cyclic trimeric hydrocarbon is formed (13%), along with apparent polymeric material. No carbon monoxide insertion products are formed. On the basis of these observations TBA must react with $(TPP)_3Ni$ only via a B-type, π , σ -type coupling process in the π -complex 81 to form the σ -complex 82. The π -complex 81 is strongly favored over the π -complexes involving π -complexation with the *tert*-butyl-substituted double bond for steric reasons, while the very bulky *tert*-butyl group favors the anti conformation over the syn con-



formation. This results in the predominant, if not the sole, formation of 82. By analogy with 65 this complex does not undergo reductive elimination or carbon monoxide insertion; and it cannot undergo β -hydride elimination as proposed for 69. Therefore, its only mode of reaction is the further insertion of TBA via 83. The structure of the insertion product is expected to be 84 on the basis of steric arguments presented earlier which dictate the approach of the TPP (L) and the direction of rotation of the π -complexed TBA during the insertion process. Reductive elimination with 84 produces 35. The further reaction of 84 with TBA ultimately produces polymeric products.

Cyanoallene. The reaction of CYA with $(TPP)_3Ni$ produced only low yields of the cyclic dimers 36 (0.5%) and 37 (6.5%) and trimers 39 (1.2%) and 40 or 41 (0.8%), along with an extensive amount of polymeric material. The dimers and trimers are formed only via an A-type, π - π mode of coupling in 85 to form the σ -complexes 86 and 87, both of which may undergo further insertion of CYA, leading to the trimeric and possibly polymeric products.

Low-temperature NMR studies gave results substantially different from those obtained with DMA, ETA, TBA, and PHA in which π -complexes were detected. In the case of CYA the



low-temperature NMR spectrum contained only very broad resonances (including those of the solvent), suggesting the formation and presence of paramagnetic species. The paramagnetic species could be formed by electron transfer from the $(TPP)_3Ni$ to CYA followed by coupling and polymerization. Such a process has been observed in the reaction of DMA with $(COD)_2Ni^5$. CYA apparently reacts both via π -complex formation and electron transfer, whereas DMA, ETA, TBA, and PHA react only via π -complex formation. This is undoubtedly due to the much lower lying LUMO of CYA (+6.32 eV, STO-3G)¹² relative to the other substituted alenes (~+8.8 eV, STO-3G).

Summary

Factors Affecting the Structures of and Equilibria between Substituted Allene π -Complexes. At low temperatures DMA, ETA, and TBA form equilibrium mixtures of π -complexes in which the least substituted π -bond is involved in π -complex formation. In displacement studies, DMA displaces both ETA and TBA from their π -complexes, while DMA is displaced by methoxyallene (MEA).¹³ The relative stability sequence of the substituted allene π -complexes is TBA \sim ETA $<$ DMA $<$ MEA.

It is assumed that in simple alkene-Ni π-complexes the π^* MO of the alkene lies above the nickel valence orbitals while the π MO lies below the nickel valence orbitals.¹⁴ The first interaction energy will increase as the energy of the π^* MO of the alkene is lowered, while the second interaction energy will increase as the energy of the π MO is elevated. In the π -complexes formed from substituted alenes both effects play a role, as do also steric effects. Unfortunately it is not possible to determine which electronic interaction is dominant as one does not know the energies of the nickel valance orbitals relative to those of the substituted allene π and π^* MO's.

The preference for formation of the π -bond with the least substituted double bonds of the monoalkyl allenes TBA and ETA and DMA must be due to steric effects. The energies of the $\pi_{1,2}^*$ and $\pi_{2,3}^*$ MO's in each case are nearly identical (see Figure 3). The energies of the $\pi_{1,2}$ MO's, however, are higher than those of the $\pi_{2,3}$ MO's which would favor π -complex formation with the substituted double bond. The increased stability of the DMA π -complex over those formed from ETA and TBA must arise from an increase in the interaction energy of the π MO with the vacant nickel hybrid orbital; the π -HOMO - Ni-LUMO energy difference decreasing, while the π^* -LUMO - Ni-HOMO energy difference increases very slightly. With methoxyallene (MEA) both the π -HOMO - Ni-LUMO and π^* -LUMO - Ni-HOMO energy gaps decrease relative to those with DMA. These effects should increase in interaction energies in the MEA π -complex, which is consistent with the experimental observation.

$\text{RCH}=\text{C}=\text{CH}_2$ <u>8.8</u> <u>8.8</u>	$\text{R}_2\text{C}=\text{C}=\text{CH}_2$ <u>8.9</u> <u>8.8</u>	$\text{ROCH}=\text{C}=\text{CH}_2$ <u>8.7</u> <u>8.1</u>	$\phi\text{CH}=\text{C}=\text{CH}_2$ <u>8.6</u> <u>6.8</u>
			<u>7.4</u> <u>6.3</u>



Figure 3. STO-3G energies of $\pi_{1,2}$ and $\pi^*_{1,2}$ (left energy levels) and $\pi_{2,1}$ and $\pi^*_{2,3}$ (right energy levels) of substituted allenes.¹² In the calculations R in $\text{RCH}=\text{CH}=\text{CH}_2$ is methyl, and in $\text{ROCH}=\text{C}=\text{CH}_2$ it is hydrogen. The phenyl group has been approximated by the use of a vinyl group. The valence level orbitals of Ni have been approximated by the crossed-level energy region¹⁴

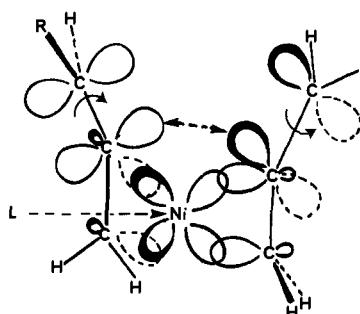


Figure 4. Orbital interactions and rotational motions in the $\pi-\pi$ mode of coupling.

The reactions of PHA and CYA with $(TPP)_3Ni$ resulted in immediate coupling, even at very low temperatures. Intermediate π -complexes were not observed, and thus the relative stabilities of the π -complexes and their structures could not be determined. Although the major coupling pathways occur via π -complexes involving the least substituted double bond, this does not necessarily mean that these π -complexes were the most thermodynamically stable, the rate-determining step for σ -complex formation being the coupling process. In these cases, however, one might expect π -complex formation to involve the least substituted double bond for steric reasons, and due to the fact that the energetically more favorable interaction with the $\pi_{1,2}$ -bond would disrupt the resonance of the conjugated π -systems which remain intact when the least substituted double bond is involved in π -complex formation. Further studies with other metal complexes should resolve this point.

The dominant coupling processes involve the syn conformations of the bis(allene) π -complexes. Only the TBA π -complex couples via the anti conformation. The preference for coupling in the more sterically congested syn conformations is apparently due to the preferred π - π mode of coupling. In the anti conformations only π - σ modes of coupling are possible. In the bis(TBA) π -complex steric effects in the π -complex, or in the transition state for coupling, must force the coupling to occur only in the anti conformation.

Factors Affecting the Mode and Rate of Coupling. As outlined earlier in this article there are three orbital combinations that can be involved in the C-C bond-forming process: $\pi-\pi$, $\pi-\sigma$, and $\sigma-\sigma$. In the $\pi-\pi$ process the 2 p AO's of the noncomplexed double bond on the carbon atom involved in the π -complex interact to form the C₃-C₄ bond of the nickelacyclopentane ring. The exocyclic double bonds are formed from the remaining 2 p AO's of the π -bonds and the hydrid orbital on the carbon involved in the π -complex bonding. This requires a 90° rotation in order to achieve π -bond formation, the direction of rotation being controlled by steric effects as discussed earlier. The Ni-C σ -bonds form from the remaining Ni and C hybrid orbitals involved in bonding in

the π -complex. These bonding processes are illustrated in Figure 4 in which the π -complex bonds are illustrated as the nickelacyclopropane resonance hybrid. The C-C bond being formed is between the 2 p AO's connected by the double-headed, dashed arrow. The direction of approach of the TPP (L) and the directions of rotation are indicated in the figure.

The reactivity toward $\pi-\pi$ coupling will be directly related to the magnitude of the coefficients of the AO's involved in the bond-forming process. The magnitude of these coefficients will follow the general trend for substituted alkenes, increasing with increasing alkyl substitution and increasing with increasing electronegativity of a π -substituent.¹⁵ The rate of the coupling process is rate determining, π -complex formation being fast and reversible. The observed reactivity toward coupling appears to be directly related to the magnitude of the coefficients of the interacting p AO's.

The $\pi-\sigma$ coupling process involves interaction between one of the p AO's and a hybrid orbital on carbon which is involved in bonding to the nickel in the nickelacyclopropane ring. As the hybrid orbital will be more contracted than the p AO, the overlap achieved in the coupling process will be less, and the rate of coupling will be slower. In the case of ETA, however, the $\pi-\sigma$ coupling processes are slightly dominant over the $\pi-\pi$ processes; whereas the DMA the $\pi-\pi$ processes are dominant. In the ETA π -complex the c_p (the coefficient of the p AO) is less than in the DMA π -complex, and the $c_p c_p$ product must be comparable to the $c_p c_{sp}$ product (c_{sp} is the coefficient of the hybrid orbital). In the DMA π -complex $c_p c_p \gg c_p c_{sp}$.

In the $\sigma-\sigma$ coupling process the C-C bond-forming process occurs between the σ -hybrid orbitals of the two nickelacyclopropane units. This process is least favorable on the basis of orbital overlap generated during the coupling process. This mode of coupling was not observed in this study. It is interesting to note that the $\sigma-\sigma$ mode of coupling is the only mode available for coupling of two simple π -bonded alkenes in a Ni complex. The coupling of simple alkenes in bis- π -alkene Ni(0) complexes has not been observed,¹⁶ although coupling between highly strained π systems has been observed.¹⁷

Factors Affecting Reductive Elimination and Carbon Monoxide Insertion. Reductive elimination and the insertion of carbon monoxide within nickelacyclopentane complexes having an exocyclic double bond in the α -position was not observed in this study. Reductive elimination, but not carbon monoxide insertion, was observed with nickelacycloheptane complexes **84**, **88**, and **89** which contain α -exocyclic double bonds. It is not obvious why reductive elimination occurs with the nickelacycloheptane complexes and not the nickelacyclopentane complexes. Perhaps the more flexible nature of the seven-membered ring provides for a decrease in strain energy in the transition state for reductive elimination in the nickelacycloheptane complexes, but yet has little or no effect in the transition states for carbon monoxide insertion. The stronger $Ni-C_{sp^2}$ bond, relative to a $Ni-C_{sp^3}$ bond, should retard any process which involves cleavage of the $Ni-C$ bond.

Experimental Section

General. Previously published procedures were used for the synthesis of ETA,¹⁸ TBA,¹⁸ PHA,¹⁹ CYA,²⁰ and MEA.²¹ NMR spectra were recorded on a Nicolet NB-300 spectrometer using FT techniques. Deuterated solvents were obtained from Aldrich Chemical Co., and were freeze-degassed prior to use.

Reaction of Phenylallene (PHA) with $(TPP)_3Ni$. In a 100-mL round-bottom flask containing a magnetic stirring bar and filled with

Table IV. Chemical Shifts of **12** and **13** in the Presence of Added Eu(fod)₃

	vol (μL) of Eu(fod) ₃ solution added			
	0	5	10	15
12				
2.29	2.72	3.15	3.55	
3.38	4.51	5.73	6.72	
6.72	6.98	7.24	^a	
7.3 ^b	8.17	9.05	9.78	
13				
1.60	2.19	2.63	3.00	
3.25	4.36	5.62	6.66	
6.83	7.36	^a	^a	
7.24 ^b	8.01	8.90	9.60	

^a Obscured by the aromatic peaks. ^b An ortho aromatic hydrogen doublet.

Table V. Chemical Shifts of **14** and **15** in the Presence of Added Eu(fod)₃

	vol (μL) of Eu(fod) ₃ solution added				
	0	2.5	5.0	7.5	10.0
15					
3.25	3.87	4.63	5.38	6.06	
3.43	3.60	3.82	4.01	4.21	
5.89	6.47	6.90	^a	^a	
6.85	6.98	7.11	7.23	^a	
14					
3.35	4.18	4.79	5.50	6.22	
3.97	4.00	4.47	4.58	4.77	
5.95	6.54	7.03	^a	^a	
6.80	6.92	7.08	7.23	7.37	

^a Obscured by the aromatic peaks.

argon and stoppered with a rubber septum was placed 4.5 mmol of $(TPP)_3Ni$ in 40 mL of THF. The solution was cooled to -70 °C with a dry ice-acetone bath, and 1.04 g (9.0 mmol) of phenyllallene was added. The solution immediately turned from red to purple in color. The reaction mixture was slowly brought up to 20 °C and was stirred for 0.5 h. The THF was removed under reduced pressure, and the residue was extracted with 60 mL of hexane. Evaporation of the hexane left no residue.

Carbonylation. Carbon monoxide was bubbled through a reaction solution, prepared as described above, for 2.5 h. The THF was removed under reduced pressure, and the residue was extracted with 50 mL of pentane followed by 50 mL of ether. The extracts were combined and the solvents removed under reduced pressure, giving a viscous residue. The residue was separated by chromatography on a Chromatron with a 4 mm thick silica gel plate and hexane-methylene chloride gradient elution. Six fractions were collected.

Fraction 1 (9, 8.5%), a viscous oil: NMR ($CDCl_3$) δ 3.17 (d, $J = 16.21$ Hz, 1 H), 3.38 (d, $J = 16.21$ Hz, 1 H), 3.43 (d, $J = 14.56$ Hz, 1 H), 3.47 (d, $J = 14.56$ Hz, 1 H), 4.75 (s, 1 H), 5.07 (s, 1 H), 5.37 (d, $J = 1.8$ Hz, 1 H), 6.72 (s, 1 H), 6.80 (s, 1 H), and 7.2-7.5 (m, 15 H); IR ($CDCl_3$) 1710 cm^{-1} ; UV (95% ethanol) end absorption with an inflection at 220 nm and shoulder at 248 nm; MS, M^+ *m/e* 376.

Fraction 2 (10, 6.1%), yellow crystals, mp 148-150 °C (from ether-methylene chloride): NMR ($CDCl_3$) δ 3.38 (s, 2 H), 3.44 (s, 2 H), 3.53 (br s, 1 H), 6.38 (overlapping s, 2 H), 6.45 (s, 1 H), and 7.2-7.5 (m, 15 H). Also present in the NMR spectrum were weak peaks at δ 4.68, 4.98, 5.21, 6.73, and 6.83, suggesting the presence of a stereoisomer of D (~5% of total); IR ($CDCl_3$) 1705 cm^{-1} ; UV (95% ethanol) end absorption with an inflection at 220 nm and shoulder at 246 nm; MS, exact mass calcd for $C_{28}H_{24}O$ 376.183, found 376.183.

Fraction 3 (8, 0.7%), viscous oil: NMR ($CDCl_3$) 3.42 (d, $J = 16.4$ Hz, 1 H), 3.62 (d, $J = 13.6$ Hz, 1 H), 3.66 (d, $J = 16.4$ Hz, 1 H), 3.75 (d, $J = 13.6$ Hz, 1 H), 4.65 (s, 1 H), 5.32 (s, 1 H), 5.36 (s, 1 H), 5.87 (s, 1 H), 6.39 (s, 1 H), and 7.2-7.5 (m, 15 H); IR ($CDCl_3$) transparent in the carbonyl region; MS, M^+ *m/e* 348.

Fraction 4 (11, 0.5%), pale yellow oil: NMR ($CDCl_3$) δ 3.86 (s, 2 H), 4.02 (s, 1 H), 5.11 (s, 1 H), 5.55 (s, 1 H), 5.91 (s, 1 H), 7.2-7.6 (m, 10 H); IR ($CDCl_3$) 1700 cm^{-1} ; UV (95% ethanol) λ_{max} 288 nm; MS, M^+ *m/e* 260.

Fraction 5 (mixture of **12**, 0.8%, and **13**, 0.2%), pale yellow oil. **12**: NMR ($CDCl_3$) 2.29 (s, 3 H), 3.38 (s, 2 H), 6.72 (s, 1 H), and 7.2-7.6 (m, 10 H); IR ($CDCl_3$) 1690 cm^{-1} ; UV (95% ethanol), of

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mixture) λ_{max} 290 nm; MS (of mixture), M^+ *m/e* 260. **13:** NMR (CDCl_3) δ 1.60 (s, 3 H), 3.25 (s, 2 H), 6.83 (s, 1 H).

The addition of incremental amounts of a solution of $\text{Eu}(\text{fod})_3$ resulted in the changes in chemical shifts shown in Table IV.

Fraction 6 (mixture of **14**, 1.2% and **15**, 4.8%), pale yellow oil. **14:** NMR (CDCl_3) δ 3.35 (s, 2 H), 3.97 (s, 2 H), 5.95 (s, 1 H), 6.80 (s, 1 H), and 7.2–7.6 (m, 10 H); IR (CDCl_3 , of mixture) 1690 cm^{-1} ; UV (95% ethanol, of mixture) λ_{max} 292 nm; MS (of mixture), M^+ *m/e* 260. **15:** NMR (CDCl_3) δ 3.25 (s, 2 H), 3.43 (s, 2 H), 5.89 (s, 1 H), 6.85 (s, 1 H), and 7.2–7.6 (m).

The addition of incremental amounts of a solution of $\text{Eu}(\text{fod})_3$ resulted in the changes in chemical shifts shown in Table V.

Reduction of Ketone 9. In a 25-mL, three-necked, round-bottom flask equipped with an addition funnel and a condenser was placed 100 mg of lithium aluminum hydride in 5 mL of ether. To this solution was added 20 mg of **9** dissolved in 5 mL of ether. The reaction mixture was stirred at 20 °C for 1 h and hydrolyzed by the addition of 5 mL of ice water. The ether layer was separated, and the aqueous layer was extracted with two 10-mL portions of ether. The ether extracts were combined and dried (MgSO_4), and the ether was removed under reduced pressure, leaving a colorless, viscous oil. The NMR spectrum of the material indicated that two diastereomerically related alcohols were present in approximately equal quantities, showing four benzylidene hydrogen resonances at δ 6.58, 6.88, 6.77, and 6.88, four methylene hydrogen resonances at δ 5.46, 5.42, 4.98, and 4.87, two AB doublets at δ 4.70 and 4.75 and δ 3.42 and 3.68 for two isolated $-\text{CH}_2-$ groups, two carbinol hydrogen multiplets at δ 3.91 and 4.06, two doublets at δ 2.27 and 2.58 ($-\text{CH}-(\text{C}_6\text{H}_5)-$), and multiplets at δ 2.2–2.3 and 3.0. Irradiation of the multiplets at δ 3.91 and 4.06 resulted in the collapse of the δ 2.27 and 2.58 doublets to singlets.

Reduction of Ketone 10. Following the procedure described above, 20 mg of **10** was reduced. NMR (CDCl_3) δ 2.05 (m, 1 H), 2.56 (dd, $J = 12.66, 7.37 \text{ Hz}$, 1 H), 2.60 (dd, $J = 13.40, 3.84 \text{ Hz}$, 1 H), 2.67 (dd, $J = 13.40, 7.38 \text{ Hz}$, 1 H), 2.76 (dd, $J = 12.66, 3.52 \text{ Hz}$, 1 H), 3.45 (d, $J = 15.27 \text{ Hz}$, 1 H), 3.50 (d, $J = 15.27 \text{ Hz}$, 1 H), 4.04 (br m, 1 H), 6.29 (br s, 1 H), 6.31 (br s, 1 H), 6.42 (br s, 1 H), and 7.1–7.4 (m, 15 H). Irradiation of the δ 4.04 region resulted in the simplification of the high-field region which then displayed peaks at δ 2.56 (d, $J = 12.66 \text{ Hz}$), 2.60 (d, $J = 13.40 \text{ Hz}$), 2.67 (d, $J = 13.40 \text{ Hz}$), and 2.76 (d, $J = 12.66 \text{ Hz}$); MS, M^+ *m/e* 378.

X-ray Structure Determination of 10. Crystal data: $\text{C}_{28}\text{H}_{24}\text{O}$, monoclinic, space group $C2/c$, $a = 23.785$ (7) Å, $b = 14.216$ (2) Å, $c = 12.659$ (4) Å, $B = 98.64$ (2). Calculated density 1.183 and found 1.180, for 8 molecules per unit cell. Intensity data were collected on an Enraf-Nonius CAD4 automatic diffractometer equipped with a Cu X-ray tube ($m\mu = 5.043 \text{ cm}^{-1}$) and graphite monochromator. Lattice constants were determined from a least-squares refinement on the setting angles of reflections between 15.2 and 21.5° in θ . There were 1671 unique reflections with $F_o > 3\sigma(F_o)$ between 2.0 and 62.5° in θ . The final unweighted and weighted *R* factors were 0.039 and 0.050. The bond lengths are given in Table I, bond angles in Table II, and selected dihedral angles in Table III.

NMR Studies of the Reaction of PHA with (TPP)₃Ni. To 0.05 mmol of (TPP)₃Ni in 0.7 mL of THF-*d*₈ in an NMR tube equipped with a screw cap and septum was added 0.10 mmol of PHA. The reaction solution immediately turned from red to purple in color. The NMR spectrum of the resulting solution displayed numerous, reasonably well resolved peaks.

The addition of 0.10 mmol of PHA to 0.05 mmol of (TPP)₃Ni in 0.7 mL of toluene-*d*₈ at <-70 °C in an NMR tube resulted in an NMR spectrum that showed slightly broadened resonances for PHA, along with many weak peaks. On raising the temperature to -20 °C the peaks of PHA decreased in intensity, and the other peaks increased in intensity.

Reaction of Ethylallene (ETA) with (TPP)₃Ni. In a septum stopped flask filled with argon was placed 2.0 mmol of (TPP)₃Ni in 10 mL of THF. ETA (27 mg, 4.0 mmol) was added. The reaction solution immediately turned dark green in color. The reaction mixture was stirred at 20 °C for 2 h, during which time the reaction mixture turned brown in color. The volatiles were removed on a vacuum line and analyzed by GLC, showing the presence of ETA (13%). The THF was carefully removed under reduced pressure, leaving 32 mg (12%) of a mixture of **18** (7.6% yield), **19** (3.8%), and **21** (0.6%). The residue was extracted with 50 mL of refluxing hexane. The extract was filtered, and the hexane was removed under reduced pressure. NMR analysis of the residue (mostly TPP) showed the presence of additional small amounts of **18**, **19**, and **21**.

A reaction of 3.0 mmol of (TPP)₃Ni and 6.0 mmol of ETA was heated at 40 °C for 3 days and worked up as described above. The hydrocarbon fraction from the volatile fraction and that extracted from the residue were combined (0.30 g, 75%) and analyzed by GLC. In addition to the

presence of **18**, **19**, and **21**, five additional peaks appeared in the GC. The mixture was separated by preparative GLC with a 10 ft by $3/8$ in. SE-30 on Chromasorb P column at 140 °C. Eight fractions were collected.

Fraction 1 (**18**, 16.1% of 75% recovered yield): NMR (CDCl_3) δ 0.87 (t, $J = 7.26 \text{ Hz}$, 3 H), 1.41 (sept, $J = 7.49 \text{ Hz}$, 2 H), 1.74 (dd, $J = 6.60, 1.46 \text{ Hz}$, 3 H), 2.15 (t, $J = 7.57 \text{ Hz}$, 2 H), 4.87 (d, $J = 1.82 \text{ Hz}$, 1 H), 4.90 (br s, 2 H), 4.95 (d, $J = 1.82 \text{ Hz}$, 1 H), 5.74 (dq, $J = 16.06, 6.60 \text{ Hz}$, 1 H), and 6.07 (dq, $J = 16.06, 1.46 \text{ Hz}$, 1 H); UV (95% ethanol) λ_{max} 220 nm ($\log \epsilon 4.13$); MS, exact mass calcd for $\text{C}_{10}\text{H}_{16}$ 136.125, found 136.123.

Fraction 2 (**19**, 4.0%): NMR (CDCl_3) δ 0.87 (t, $J = 7.36 \text{ Hz}$, 3 H), 0.96 (d, $J = 7.01 \text{ Hz}$, 3 H), 1.65 (dt, $J = 1.6, 1.5 \text{ Hz}$, 3 H), 1.89 (qdd, $J = 7.36, 6.88, 1.19 \text{ Hz}$, 2 H), 2.81 (m, 2 H), 3.06 (br m, 1 H), 5.20 (tt, $J = 6.88, 2.32, 1.90 \text{ Hz}$, 1 H), 5.26 (m, 1 H). Irradiation of the 5.2 resonance resulted in the appearance of the δ 3.06 resonance as a quartet ($J = 6.44 \text{ Hz}$) and the δ 2.81 resonance as a doublet ($J = 3.04 \text{ Hz}$). Irradiation of the δ 3.01 region resulted in changes to the following patterns: δ 0.95 (tt, $J = 7.02, 2.32 \text{ Hz}$); 5.26 (br q, $J = 1.53 \text{ Hz}$). Irradiation of the δ 2.81 region resulted in collapse to the following patterns: δ 1.89 (broadened doublet, $J = 7.25, 6.88$), 5.20 (td, $J = 7.21, 1.95 \text{ Hz}$), and 5.26 (pent, $J = 1.6 \text{ Hz}$). Irradiation of the δ 1.89 region resulted in collapse to the following patterns: δ 0.87 (s) and 5.20 (q, $J \approx 2.3 \text{ Hz}$). UV (95% ethanol) λ_{max} 237 nm ($\log \epsilon 3.13$); MS, exact mass calcd for $\text{C}_{10}\text{H}_{16}$ 136.125, found 135.123.

Fraction 3 [20 (10.7%) and an Unidentified Component (5.4%)]**: 20:** NMR (CDCl_3) δ 0.96 (t, $J = 7.54 \text{ Hz}$, 3 H), 1.75 (dd, $J = 6.59, 1.38 \text{ Hz}$, 3 H), 2.05 (br q, apparent $J = 7.2 \text{ Hz}$, 2 H), 2.90 (d, $J = 5.88 \text{ Hz}$, 2 H), 4.86 (br s, 2 H), 4.86 (br s, 2 H), 5.42 (dt, $J = 11.86, 5.88, 1 \text{ Hz}$, 1 H), 5.47 (dt, $J = 11.86, 5.88, 1 \text{ Hz}$, 1 H), 5.73 (dq, $J = 15.51, 6.59 \text{ Hz}$, 1 H), 6.11 (dq, $J = 15.51, 1.38 \text{ Hz}$, 1 H); UV (95% ethanol, of mixture) λ_{max} 222 nm; MS, M^+ *m/e* 136, with major fragment ions at 121 and 107. Unidentified component: partial NMR (CDCl_3) δ 0.87 (t, $J = 7.38 \text{ Hz}$), 1.96 (br s), 2.77 (br s), 5.68 (dq, $J = 13.78 \sim 6.6 \text{ Hz}$), 5.89 (br d, $J = 13.78$), plus unidentified resonance patterns in the δ 5.3–5.5 region.

Fraction 4 (**21**, 2.5%): NMR (CDCl_3) δ 0.95 (t, $J = 7.61 \text{ Hz}$, 3 H), 1.96 (~pent, $J \sim 7.32 \text{ Hz}$, 2 H), 2.51 (br s, 2 H), 5.47 (br t, $J = 7.08, 1 \text{ Hz}$); UV (95% ethanol) λ_{max} 247 (sh), 254, and 263 nm; MS, exact mass calcd for $\text{C}_{10}\text{H}_{16}$ 136.125, found 136.125.

Fraction 5 (3.6%). The NMR spectrum was very complex, suggesting the presence of several components. No structural assignments were possible.

Fraction 6 [22 (14.6% Plus an Unidentified Minor Component (4.8%)). (22 is not present in the pumped-off volatile fraction.) **22:** NMR (CDCl_3) δ 0.97 (t, $J = 7.50 \text{ Hz}$, 3 H), 1.10 (t, $J = 7.54 \text{ Hz}$, 3 H), 1.62 (m, 2 H), 2.13 (br t, $J = 6.54 \text{ Hz}$, 2 H), 2.37 (pent, $J \sim 7.47 \text{ Hz}$, 2 H), 2.99 (br d, $J = 7.05 \text{ Hz}$, 2 H), 4.87 (apparent q, $J \sim 1.54 \text{ Hz}$, 1 H), 5.00 (br s, 1 H), 5.16 (dt, $J = 10.62, 7.05, 1.85 \text{ Hz}$, 1 H), 5.35 (dt, $J = 10.62, 7.05, 1.90 \text{ Hz}$, 1 H); MS (on mixture), M^+ *m/e* 138. The NMR spectrum also showed the following resonances for the unidentified minor component: δ 0.89 (t, $J = 7.47 \text{ Hz}$), 0.95 (t, $J = 7.36 \text{ Hz}$), 2.04 (m), 2.7–2.9 (complex multiplet), 4.01 (d, $J = 7.16 \text{ Hz}$), 5.45 (complex multiplet).

Fraction 7 (**23**, 25.7%): NMR (CDCl_3) δ 0.94 (t, $J = 7.44 \text{ Hz}$, 3 H), 1.09 (t, $J = 7.31 \text{ Hz}$, 3 H), 2.01 (br q, apparent $J \sim 6.9 \text{ Hz}$, 2 H), 2.70 (q, $J = 7.31 \text{ Hz}$, 2 H), 2.97 (br d, $J = 7.34 \text{ Hz}$, 2 H), 5.33 (br dt, $J = 10.58, 7.34 \text{ Hz}$, 1 H), 5.50 (br dt, $J = 10.58, 6.49 \text{ Hz}$, 1 H), 5.71 (br s, 1 H), 5.98 (br s, 1 H). Irradiation of the δ 5.4 region caused the collapse of the δ 2.01 resonance to a quartet. Irradiation of the δ 2.97 region resulted in the collapse of the δ 5.33 pattern to a dt ($J = 10.58, 1.1 \text{ Hz}$) and the δ 5.50 pattern to a sharp dt ($J = 10.58, 6.49 \text{ Hz}$). Irradiation of the δ 2.01 region resulted in the collapse of the δ 5.33 pattern to a sharp dt ($J = 10.58, 7.34 \text{ Hz}$) and the δ 5.50 region to a sharp dt ($J = 10.58, 1.5 \text{ Hz}$). UV (95% ethanol) 280 ($\log \epsilon 3.42$) and 220 nm ($\log \epsilon 3.98$); MS, M^+ *m/e* 272.

Fraction 8 (**24**, 12.5%): NMR (CDCl_3) δ 0.90 (t, $J = 7.47 \text{ Hz}$, 3 H), 0.93 (t, $J = 7.48 \text{ Hz}$, 3 H), 1.6 (m, 2 H), 2.03 (pent, $J \approx 7.40 \text{ Hz}$, 2 H), 2.74 (dd, $J = 16.29, 7.42 \text{ Hz}$, 1 H), 2.79 (dd, $J = 16.29, 7.02 \text{ Hz}$, 1 H), 4.00 (t, $J = 6.28 \text{ Hz}$, 1 H), 4.86 (q, $\sim 1.4 \text{ Hz}$, 1 H), 5.01 (br s, 1 H), 5.39 (dt, $J = 10.73, \sim 7.26, 2.78 \text{ Hz}$, 1 H), 5.50 (dt, $J = 10.73, 6.25, 3.33 \text{ Hz}$, 1 H). Irradiation of the δ 5.3–5.5 region resulted in the collapse of the δ 2.03 pattern to a quartet ($J = 7.48 \text{ Hz}$) and the 2.79 pattern to AB doublets ($J = 16.29 \text{ Hz}$). Irradiation of the δ 2.74 region caused the collapse of the δ 5.39 pattern to a doublet ($J = 10.73 \text{ Hz}$), the δ 4.86 pattern to a doublet ($J_{\text{gem}} = 1.4 \text{ Hz}$), and the δ 5.01 pattern to an apparent doublet. Irradiation of the δ 2.03 region caused collapse of the δ 0.93 triplet to a singlet and the δ 5.50 pattern to a doublet triplet ($J = 10.73, 3.33 \text{ Hz}$). Irradiation of the δ 1.6 region caused collapse of the δ 4.00 triplet to a singlet and the δ 0.93 triplet to a singlet. UV (95% ethanol) λ_{max} 220 nm ($\log \epsilon 3.45$) with end absorption at 200 nm ($\log \epsilon 3.91$); MS, M^+ *m/e* 274.

Carbonylation of the Ethylallene- $(TPP)_3Ni$ Reaction Mixture. To 3.0 mmol of $(TPP)_3Ni$ in 25 mL of THF in a septum stoppered flask under an argon atmosphere at $-60^\circ C$ was added 408 mg (6.0 mmol) of ethylallene. The reaction solution immediately turned green in color. The reaction mixture was stirred for 1 h and brought up to $-20^\circ C$. Carbon monoxide was bubbled through the solution for 1 h at $-20^\circ C$ and then for 0.5 h at $20^\circ C$. The volatiles were removed on a vacuum line. Analysis of the volatile fraction by GLC showed the presence of ETA (13%). The THF was removed from the volatile fraction by fractional distillation, leaving 45 mg (11%) of material which was comprised of **18** (98%) and **20** (2%) (by GLC).

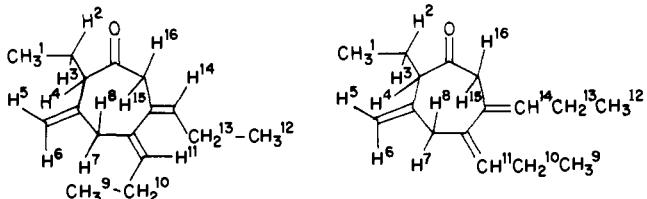
The residue remaining after removal of the volatile material was extracted with four 25-mL portions of refluxing hexane. The extract was filtered, and the hexane was removed under reduced pressure. The residue was separated by chromatography on a Chromatron with 4 and 2 mm thick silica gel plates, eluting with a gradient mixture of hexane and methylene chloride. Seven fractions were collected.

Fraction 1 (25, 0.3%). NMR ($CDCl_3$) δ 0.75 (t, $J = 7.41$ Hz, 3 H), 1.00 (t, $J = 7.58$ Hz, 3 H), 1.72 (ddq, $J = 12.95, 6.64, 7.29$ Hz, 1 H), 1.85 (ddq, $J = 12.95, 7.29, 5.30$ Hz, 1 H), 2.13 (s, 3 H), 2.27 (q, $J = 7.58$ Hz, 2 H), 2.76 (br t, $J = 5.41$ Hz, 1 H), 5.11 (d, $J = 1.27$ Hz, 1 H), 5.30 (d, $J = 1.27$ Hz, 1 H); MS, M^+ m/e 136, with fragment ions at m/e 121 and 107.

Fraction 2 (0.5%). The NMR spectrum was very complex, suggesting the presence of several components. No structures could be assigned. The IR was transparent in the $\nu_{C=O}$ region.

Fraction 3 (60:40 Mixture of 26 and 27, 3.7%). This fraction was further separated by HPLC with a 25 cm by 4.6 mm, 5 μ m silica gel, analytical column, eluting with hexane-methylene chloride mixtures.

26: NMR ($CDCl_3$) δ 0.82 (t, $J = 7.36$ Hz, CH^1_3), 0.92 (t, $J = 7.54$ Hz, 3 H), 0.99 (t, $J = 7.54$ Hz, 3 H), 1.47 (ddq, $J(2,3) = 13.24, J(3,1) = 7.36, J(3,4) = 7.16$ Hz, H^3), 1.85 (dq, $J(2,3) = 13.24, J(2,1) = 7.36, J(2,4) = 5.80$ Hz, H^2), 1.97 (p, $J \sim 7.5$ Hz, 2 H), 2.09 (p, $J \sim 7.5$ Hz, 2 H), 2.98 (d, $J(7,8) = 16.07$ Hz, H^7), 3.02 (d, $J(7,8) = 16.07$ Hz, H^8), 2.97 (dd, $J(3,4) = 7.16, J(2,4) = 5.80$ Hz, H^4), 3.17 (d, $J(15,16) = 15.10$ Hz, H^{15}), 3.27 (d, $J(15,16) = 15.10$ Hz, H^{16}), 4.80 (dd, $J(5,6) = 2.05$ Hz, H^5), 5.34 (br t, $J = 6.90$ Hz with long-range coupling <0.8 Hz, H^{11}), 5.37 (tt, $J = 7.31, 1.55$ Hz, H^{14}).



27: NMR ($CDCl_3$) δ 0.83 (t, $J = 7.37$ Hz, CH^1_3), 0.93 (t, $J(9,10) = 7.50$ Hz, CH^9_3), 1.01 (t, $J(12,13) = 7.58$ Hz, CH^{12}_3), 1.51 (dq, $J(2,3) = 13.45, J(1,2) = 7.37, J(2,4) = 5.03$ Hz, H^2), 1.91 (dq, $J(2,3) = 13.45, J(1,3) = 7.37, J(3,4) = 7.11$ Hz, H^3), 2.02 (dq, $J(12,13) = 7.58, J(13,14) = 7.13$ Hz, H^{13}), 2.12 (dq, $J(9,10) = 7.50, J(10,11) = 7.67$ Hz, H^{10}), 3.08 and 3.15 (d's, $J(7,8) = 16.55$ Hz, $H^{7,8}$), ~ 3.09 ($H^{15,16}$), 3.09 (dd, $J(4,3) = 7.11, J(4,2) = 5.03$ Hz, H^4), 4.78 (dd, $J(5,6) = 1.70, J(6,?) \sim 0.9$ Hz, H^6), 5.02 (d, $J(5,6) = 1.70$ Hz, H^5), 5.31 (br t, $J(10,11) = 7.67$ Hz, H^{11}), 5.43 (tt, $J(13,14) = 7.13, J[14,15(16)] = 1.43$ Hz, H^{14}).

Fraction 4 [Mixture of 28 (7.4%) and 29 (3.1%)]. **28:** NMR ($CDCl_3$) δ 0.75 (t, $J = 7.40$ Hz, 3 H), 0.99 (t, $J = 7.62$ Hz, 3 H), 1.73 (ddq, $J = 13.84, 5.68, 7.40$ Hz, 1 H), 1.84 (ddq, $J = 13.84, 5.62, 7.40$ Hz, 1 H), 2.08 (s, 3 H), 2.27 (q, $J = 7.62$ Hz, 2 H), 3.10 (br t, 1 H), 5.11 (d, $J = 0.62$ Hz, 1 H), 5.30 (d, $J = 1.73$ Hz, 1 H); IR ($CDCl_3$) 1695 cm^{-1} ; UV (95% ethanol, of mixture) λ_{max} 272.5 nm; MS (of mixture), M^+ m/e 164.

29: NMR ($CDCl_3$) δ 0.83 (t, $J = 7.45$ Hz, 3 H), 1.01 (t, $J = 7.53$ Hz, 3 H), 1.41 (s, 3 H), 1.87 (m, partially obscured by the $\delta 1.84$ pattern of **28**), 2.03 (m, 1 H), 2.11 (q, $J = 7.53$ Hz, 2 H), 2.76 (br t, $J \sim 5.5$ Hz, 1 H), 4.78 (br d, $J = 1.90$ Hz, 1 H).

Fraction 5 (30, 3.0%). NMR ($CDCl_3$) δ 0.78 (t, $J = 7.39$ Hz, 3 H), 0.99 (t, $J = 7.39$ Hz, 3 H), 1.64 (septet, $J \sim 7.4$ Hz, 2 H), 1.74 (ddq, $J = 14.20, 5.64, 7.39$ Hz, 1 H), 1.87 (ddq, $J = 14.20, 5.38, 7.39$ Hz, 1 H), 2.47 (t, $J = 7.60$ Hz, 2 H), 2.82 (br t, $J \sim 5.5$ Hz, 1 H), 5.20 (dd, $J = 1.56, 1.15$ Hz, 1 H), 5.42 (br d, $J = 1.67$ Hz, 1 H), 6.07 (br s, 1 H); IR ($CDCl_3$) 1695 cm^{-1} ; UV (95% ethanol) λ_{max} 264 nm; MS, M^+ m/e 164.

Fraction 6 [Mixture of 31 (1.8%) and 32 (0.4%)]. **31:** NMR ($CDCl_3$) δ 0.99 (t, $J = 7.53$ Hz, 3 H), 1.04 (t, $J = 7.53$ Hz, 3 H), 2.06 (s, 3 H), 2.15 (pent, $J \sim 7.5$ Hz, 2 H), 2.26 (q, $J = 7.53$ Hz, 2 H), 2.86 (s, 2 H), 5.69 (tt, $J = 7.49, 1.63$ Hz, 1 H); IR ($CDCl_3$) 1690 cm^{-1} ; UV (95%, on

Table VI. Temperature Dependence of the Vinyl Hydrogen Chemical Shifts of TBA-($TPP)_3Ni$ Complexes

temp, $^\circ C$	δ 's		
-84	6.81	4.65	2.88
-68	6.53	4.65	2.99
-55	6.23	4.52	3.17
-47	6.03	4.50	4.36
-37	5.77	4.4	a
-24	5.48	4.38	a
-8	5.14	4.37	a
+10	4.71	4.41	a

^a Merged with δ 4.3 region peak.

mixture) λ_{max} 285 nm; MS, M^+ m/e 164.

32: NMR ($CDCl_3$) δ 0.98 (t, $J = 7.45$ Hz, 3 H), 1.07 (t, $J = 7.53$ Hz, 3 H), 1.41 (s, 3 H), 2.05 (pent, $J = 7.5$ Hz, 2 H), 2.46 (q, $J = 7.53$ Hz, 2 H), 2.91 (s, 2 H), 5.50 (br t, $J = 7.49$ Hz, 1 H).

Fraction 7 [Mixture of 33 (1.0%) and 34 (0.5%)]. **33:** NMR ($CDCl_3$) δ 0.98 (t, $J = 7.57$ Hz, 3 H), 1.04 (t, $J = 7.57$ Hz, 3 H), 1.62 (septet, $J \sim 7.5$ Hz, 2 H), 2.16 (pent, $J = 7.49$ Hz, 2 H), 2.41 (t, $J = 7.50$ Hz, 2 H), 2.90 (s, 2 H), 5.79 (tt, $J = 7.26, 1.5$ Hz, 1 H), 6.02 (br s, 1 H); IR ($CDCl_3$, of mixture) 1685 cm^{-1} ; UV (95% ethanol, of mixture) λ_{max} 280 nm; MS (of mixture), M^+ m/e 164.

34: NMR ($CDCl_3$) δ 1.01 (t, $J = 7.64$ Hz, 3 H), 1.07 (t, $J = 7.69$ Hz, 3 H), 1.61 (m, partially obscured by the $\delta 1.63$ resonance of **33**), 2.41 (t, $J = 7.49$ Hz, 2 H), 2.61 (pent, $J = 7.69$ Hz, 2 H), 2.98 (s, 2 H), 5.56 (br t, $J = 7.80$ Hz, 1 H), 6.09 (s, 1 H).

Low-Temperature NMR Studies of the Reaction of ETA with $(TPP)_3Ni$ in $THF-d_8$. To an NMR tube equipped with a septum and screw cap containing 0.05 mmol of $(TPP)_3Ni$ in 0.7 mL of $THF-d_8$ at $-70^\circ C$ was added 0.05 mmol of ETA. The solution immediately turned from red to dark green in color. The NMR spectrum did not show the typical vinyl resonances of ETA at $\delta 4.75$ and 5.22. An extremely broad peak was present at $\delta 4.55$, along with broad ethyl resonances at $\delta 0.90$ and 2.04, and splitting due to coupling between the CH_2 and CH_3 protons was not observable. The positions of the peaks were not temperature dependent. No other peaks were apparent in the NMR spectrum. The addition of 0.10 mmol of DMA at $-60^\circ C$ resulted in the appearance of the vinyl hydrogen resonances of free ETA and appearance of the resonances characteristic of the DMA σ -complex 3.

Low-Temperature NMR Studies of the Reaction of ETA with $(TPP)_3Ni$ in Toluene- d_8 . To 0.05 mmol of $(TPP)_3Ni$ in 0.7 mL of toluene- d_8 in an NMR tube (as described above) at $-70^\circ C$ was added 0.10 mmol of ETA. The solution immediately turned green in color. The NMR spectrum showed extremely broad peaks at $\delta 4.85$ and 5.32 superimposed on an extremely broad resonance centered near $\delta 3.4-3.8$. As the temperature of the sample was raised, the broad underlying resonance moved to lower field. At ca. $-15^\circ C$ additional sharp peaks slowly formed and increased intensity which corresponded to those of **18**. Several other unidentified peaks were also present.

Reaction of tert-Butylallene (TBA) with $(TPP)_3Ni$. In a 100-mL, round-bottom flask filled with argon containing a magnetic stirring bar and stoppered with a rubber septum was placed 0.2 mmol of $(TPP)_3Ni$ in 15 mL of THF. To this solution at $20^\circ C$ was added 0.38 g (0.4 mmol) of TBA, resulting in a red-orange colored solution. The reaction mixture was stirred at $20^\circ C$ for 3 h. The volatiles were pumped off on a vacuum line. Analysis of the volatile fraction by GLC showed the presence of TBA (15%). The THF and TBA were removed by distillation under reduced pressure, giving 50 mg (13%) of a viscous residue (**35**). NMR ($CDCl_3$) δ 1.01 (s, 9 H), 3.41 (t, $J = 2.35$ Hz, 2 H), and 5.14 (pent, $J = 2.35$ Hz, 2 H); MS, Exact mass calcd for C_2H_{36} 288.282, found 288.281.

The residue remaining after removal of the volatiles was extracted with 50 mL of refluxing hexane. The hexane was removed under reduced pressure, giving 0.28 g of a semisolid. This material was chromatographed on a 2 mm thick silica gel plate with a Chromatron. Elution with hexane gave 0.25 g (13%) of additional **35**. Elution with methanol gave 0.10 g of a semisolid material whose NMR spectrum contained a broad resonance at $\delta 0.9-1.0$ and weak broad resonances in the $\delta 2.5$ and 4.5 region.

Low-Temperature NMR Study of the Reaction of tert-Butylallene (TBA) with $(TPP)_3Ni$. To a solution of 0.05 mmol of $(TPP)_3Ni$ in 0.7 mL of $THF-d_8$ at $-80^\circ C$ under an argon atmosphere in an NMR tube equipped with a septum and screw cap was added 0.1 mmol of TBA, producing a dark green solution. The NMR spectrum was recorded over the temperature range of -84 to $10^\circ C$. The NMR spectrum contained three broad, temperature-dependent vinyl resonances (see Table VI). The temperature dependence of the chemical shifts was completely re-

versible. At temperatures above 10 °C the broad resonances slowly disappeared, giving rise to a complex NMR spectrum containing several broad resonances.

Reaction of DMA with the (TBA)Ni(TPP)₂ Complexes. DMA (0.1 mmol) was added to a solution containing 0.05 mmol of tris(triphenylphosphine)nickel(0) and 0.1 mmol of TBA at <-60 °C (see preceding experimental). The NMR spectrum of the resulting solution showed the presence of free TBA (>95%) and the absence of free DMA. At temperatures above -20 °C the peaks of 1 appeared.

Reaction of Cyanoallene (CYA) with (TPP)₃Ni. In a rubber septum stoppered, 100-mL, round-bottom flask filled with argon was placed 3.0 mmol of (TPP)₃Ni in 25 mL of THF. The solution was cooled to -30 °C, and 0.39 g (6.0 mmol) of CYA was slowly added. The reaction mixture initially turned green in color and then rapidly turned red-orange in color. The reaction mixture was brought to 20 °C and stirred for 0.5 h. The volatiles were removed on a vacuum line, and the THF was removed by fractional distillation. No residue derived from CYA was present (by NMR).

The residue remaining after the removal of the volatiles was extracted with refluxing hexane. The hexane extract was filtered, and the hexane was removed under reduced pressure. The NMR spectrum of the residue showed only the presence of 37 in very low yield along with an extensive amount of TPP.

Carbonylation of the Cyanoallene-(TPP)₃Ni Reaction Mixture. In a rubber septum stoppered, 100-mL, round-bottom flask filled with argon was placed 3.0 mmol of (TPP)₃Ni in 25 mL of THF. The contents of the flask were cooled to -30 °C, and 0.39 g (6 mmol) of CYA was added. The reaction mixture was stirred for 0.5 h and brought to 20 °C. Carbon monoxide was bubbled through the solution (via a syringe needle) for 3 h. The volatiles were then removed on a vacuum line. Analysis of the volatile fraction by NMR showed no CYA-derived product. The residue was extracted with five 50-mL portions of refluxing ether. The extract was filtered and the ether was removed under reduced pressure, giving 0.7 g of a viscous residue. The residue was triturated with 3 mL of ether, and the white insoluble material [(TPP)₂Ni(CO)₂] was removed by filtration. The ether was evaporated, leaving 0.20 g of material which was chromatographed on a Chromatron with a 2 mm thick silica gel plate by

eluting with hexane-methylene chloride mixtures.

Fraction 1 (Mixture of Two Trimers 39 and 40 or 41, 1.2% and 0.8%). 39: NMR (CDCl₃) δ 2.91 (AA'BB' m, 4 H), 3.41 (br s, 2 H), 5.36 (br s, 1 H), 5.48 (s, 1 H), and 6.75 (s, 1 H); UV (of mixture, in 95% ethanol) λ_{max} 300 nm with shoulders at 288 and 313 nm; MS (of mixture), M⁺ exact mass calcd for C₁₂H₉N₃ 195.079, found 195.080. 40 or 41: NMR (CDCl₃) δ 2.85 (m, 4 H), 3.45 (br s, 2 H), 5.46 (br s, 1 H), 5.50 (br s, 1 H), and 7.08 (br s, 1 H).

Fractions 2 and 3 contained only TPP.

Fraction 4 (36, 0.5%): NMR (CDCl₃) δ 3.05 (AA'BB' m, 4 H), 5.33 (br t, J = 2.12 Hz, 1 H), and 6.19 (br t, J = 2.65 Hz, 1 H); UV (95% ethanol) λ_{max} 280 nm with shoulders at 270 and 294 nm; MS, M⁺ m/e 130.

Fraction 5 (37, 6.5%): NMR (CDCl₃) 3.03 (t, J = 1.12 Hz, 4 H) and 5.62 (pent, 2 H); UV (95% ethanol) λ_{max} 283 nm with shoulders at 273 and 296 nm; MS, exact mass calcd for C₈H₆N₂ 130.053, found 130.053.

After elution with methylene chloride the silica gel plate was washed with methanol, giving material whose NMR spectrum was extremely complex showing many peaks in the δ 1.0–4.5 region.

Low-Temperature NMR Studies of the Reaction of CYA with (TPP)₃Ni. To 0.05 mmol of (TPP)₃Ni in 0.7 mL of THF-d₈ at -70 °C contained in an NMR tube equipped with a screw cap and septum was added 0.10 mmol of CYA. The NMR spectrum recorded immediately showed only extremely broad resonances (including those of THF-d₈). On slowly raising the temperature to 20 °C the peaks still remained quite broad. No peaks were evident in the vinyl hydrogen region.

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Supplementary Material Available: Tables of positional parameters, calculated hydrogen atom positions, and temperature factor positions (3 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of a Cyclopentadienylidene Ketene Complex

Charles P. Casey,* Joseph M. O'Connor, and Kenneth J. Haller

Contribution from the Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received October 3, 1984

Abstract: ($\eta^1\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(CO)(PMe₃)₂ (**5**) reacts with high concentrations of PMe₃ at 72 °C to give the cyclopentadienylidene ketene complex (PMe₃)₃(NO)ReC(C₅H₄)O (**8**) and methane. **8** reacts with acetone to give (PMe₃)₃(NO)ReC(C₅H₄)OC(CH₃)₂O (**9**). **8** also reacts with HCl to give the enol complex (PMe₃)₃(NO)(Cl)ReC(C₅H₄)OH (**11**). Reaction of **5** with carbon monoxide gives the cyclopentadienylidene-ester bridged bimetallic complex **13**. ($\eta^1\text{-C}_5\text{H}_5$)Re(NO)(CO)(H)(PMe₃)₂ (**15**) reacts with PMe₃ to give the very electron-rich complex (PMe₃)₃Re(NO)(CO) and cyclopentadiene.

The accessibility of open coordination sites at a metal is of prime importance in the design of catalytic systems. Exploitation of cyclopentadienyl ring slippage reactions ($\eta^5\text{-C}_5\text{H}_5 \rightleftharpoons \eta^3\text{-C}_5\text{H}_5 \rightleftharpoons \eta^1\text{-C}_5\text{H}_5$) as a method of obtaining open coordination sites on a metal catalyst will depend on the chemical reactivity of the $\eta^1\text{-C}_5\text{H}_5$ ligand. To date, the only well-characterized reactions of the $\eta^1\text{-C}_5\text{H}_5$ ligand are the formation of Diels-Alder adducts with dienophiles,¹ the conversion of $\eta^1\text{-C}_5\text{H}_5$ complexes to $\eta^5\text{-C}_5\text{H}_5$ complexes,² and our recently discovered ionization of an $\eta^1\text{-C}_5\text{H}_5$

ligand.⁹ Monohaptocyclopentadienyl complexes have been postulated as intermediates in a number of other reactions, such

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