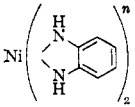
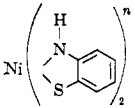


Table I. Polarographic and Electron Spin Resonance Results

Complex	$E_{1/2}^a$ for		$\langle g \rangle$	g values ^c for $n = -1$		
	$n = 0 \rightarrow n = -1$	$n = -1 \rightarrow n = -2$		g_1	g_2	g_3
Ni(tdt) ₂ ⁿ	<i>b</i>	-1.068 ^d	2.082	2.016	2.048	2.183
Ni(mnt) ₂ ⁿ	<i>b</i>	-0.218 ^d	2.063	1.996 ^e	2.043 ^e	2.140 ^e
Ni() ₂ ⁿ	-1.404	-2.075	2.034 ^f	<i>b</i>	<i>b</i>	<i>b</i>
Ni() ₂ ⁿ	-0.720	-1.573	2.055	2.006	2.030	2.123
Ni(gma) ⁿ	-0.823	-1.605	2.051	2.009	2.027	2.119

^a Potentials in volts measured in DMF using a dropping Hg electrode with a Ag-AgClO₄ reference electrode. Oscillpolarography was used to establish that all waves are due to reversible electron transfers. We thank R. Williams, B. Werden, and M. J. Baker for assistance. ^b Accurate value not available. ^c $\langle g \rangle$ normally obtained in several solvents; g_1 , g_2 , and g_3 obtained from DMF-CHCl₃ glass at 77°K. unless otherwise noted. ^d From ref. 4. ^e A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963); glass at 100°K. ^f Obtained in DMSO only.

Using precisely the same synthetic procedure, we have prepared the Ni(II) complex, Ni(gma) = V ($n = 0$). The Ni(gma) complex shows two polarographic reduction waves, indicating the existence of Ni(gma)⁻ and Ni(gma)²⁻.

The polarographic and e.s.r. data pertinent to this discussion are set out in Table I. The important point is the obvious electronic similarity of complexes IV ($n = -1$) and Ni(gma)⁻. Their polarography, $\langle g \rangle$ values, and anisotropic g -values are almost identical. The lack of axial symmetry in the g -tensor rules against the d⁹ Ni(I) formulation⁹ for Ni(gma)⁻, and the electronic similarity of IV ($n = -1$) with Ni(gma)⁻, rules out the d⁷, Ni(III) formulation for IV ($n = -1$). The $n = -1$ complexes are both consistently formulated as Ni(II)-radical-ligand complexes. In this scheme, the $n = 0$ complexes are assigned as Ni(II)-radical-ligand complexes with both spin-singlet and spin-triplet ground states as possibilities in a molecular orbital system for the planar geometry. The difference in the three possible members of each series I-V is then understood as a change in oxidation state of the ligand.

Examination of anisotropic g -values for Ni(mnt)₂⁻ and Ni(tdt)₂⁻, obtained on oxidation of the classical Ni(II) complexes Ni(mnt)₂²⁻ and Ni(tdt)₂²⁻, reveals that these complexes are electronically similar to IV ($n = -1$) and Ni(gma)⁻. Thus again the Ni(II)-radical-ligand formulation is applicable.

We wish to emphasize that although Ni(II)-radical-ligand is a more consistent formalism than Ni(II), Ni(III), or Ni(IV) for this series of related complexes, it is in no way a substitute for a complete molecular orbital description of electronic structure. The detailed MO calculations of the Ni(mnt)₂ⁿ system are fully consistent with the Ni(II)-radical-ligand formulation for the $n = -1$ and 0 complexes.²

The present results are inconsistent with the conclusion of Maki, Edelstein, Davison, and Holm¹⁰ that Ni(mnt)₂⁻ is correctly d⁷, Ni(III). Their conclusion was based on an analysis of single crystal e.s.r. results,

(9) Planar complexes in which d⁹ is an acceptable assignment have axial or near axial symmetry: see, for example, H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(10) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

using a basis set of pure 3d-functions. It seems clear, however, that not only are the highest-filled levels in these systems *not* pure d-levels, they *are* in fact much closer to pure ligand levels. These e.s.r. spectra¹⁰ must be reinterpreted in terms of a complete molecular orbital basis set.

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Received March 24, 1965

Crystalline 1,2-Polyallene

Sir:

Allene has been polymerized by Ziegler-type catalysts containing VOCl₃ and other metals,¹ but the polymer was not of regular structure. We wish to report here a successful synthesis of 1,2-polyallene by use of transition metal π -complex catalysts.

Polymerization of Allene. Typical catalysts which control the microstructure satisfactorily are π -complexes of nickel such as bis(1,5-cyclooctadiene)nickel² (I), (π -C₈H₁₂)₂Ni; bis(π -allyl)nickel³ (II), (π -C₃H₅)₂Ni; π -allylnickel bromide⁴ (III), (π -C₃H₅NiBr)₂; bis(acrylonitrile)nickel,⁵ (CH₂=CHCN)₂Ni.

Results of some polymerization runs using nickel catalysts are summarized in Table I. If one regards π -allyl ligand as a formal three-electron donor,⁶ the formal oxidation state of nickel in II and III will be zero- and univalent, respectively. As shown in Table I divalent nickel complexes were inactive. Thus it appears that low valency states of nickel are important electronic structure for the catalysis.

If, however, nickel(II) acetylacetonate was reduced by 2 moles of triethylaluminum, the allene polymer

- (1) W. P. Baker, Jr., *J. Polymer Sci.*, **A1**, 655 (1963).
- (2) G. Wilke, *Angew. Chem.*, **72**, 581 (1960).
- (3) G. Wilke and B. Bogdanovic, *ibid.*, **73**, 756 (1961).
- (4) E. O. Fischer and G. Burger, *Z. Naturforsch.*, **16b**, 77 (1961).
- (5) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); *Chem. Ber.*, **94**, 642, 650 (1961).
- (6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 654.

Table I. Polymerization of Allene by Transition Metal Catalysts^a

Expt. no.	Catalyst		Monomer concn., M	Solvent ^b	Polymn. temp., °C.	Polymn. time, hr.	Polymer yield, %	\overline{M}_n^c
	Complex	concn., mM						
A-8	$(\pi\text{-C}_8\text{H}_{12})_2\text{Ni}$	2	2	B ^d	40	24	67.5	...
A-30	$(\pi\text{-C}_8\text{H}_{12})_2\text{Ni}$	2	2	B	7	48	18.0	...
A-31	$(\pi\text{-C}_8\text{H}_{12})_2\text{Ni}$	2	2	B	0	48	0	...
A-111	$(\pi\text{-C}_3\text{H}_5\text{NiBr})_2$	2	1	B	15	24	92.5	...
A-98	$(\pi\text{-C}_3\text{H}_5\text{NiBr})_2$	8.4	2.7	T ^e	40	1	46.4	1.07×10^6
A-116	$(\pi\text{-C}_3\text{H}_5\text{NiBr})_2$	8.4	2.6	T	0	20.5	85.0	1.38×10^6
A-15	$\text{Ni}(\text{acac})_2/\text{-AlEt}_3$	2 ^g	2	B	40	24	16.2 ^h	...
A-117	$\text{Ni}(\text{acac})_2$	2	2	B	40	24	0	...
A-118	$(\text{Pph}_3)_2\text{NiBr}_2$	2	2	B	40	24	0	...

^a Polymerization was carried out under purified nitrogen and the polymer was isolated as usual. As an antioxidant for the polymer 2,2'-methylenebis(4-methyl-6-*t*-butylphenol) was used. ^b Solvents were deoxygenated and the water content was kept below 10 p.p.m. In toluene a comparable yield of the polymer having the same microstructure was obtained as in benzene, but the yield was lower in *n*-hexane and diethyl ether than in benzene. ^c The number average molecular weight was measured by a membrane osmometer (Mechrolab Inc., Model 502). ^d B = benzene. ^e T = toluene. ^f acac = acetylacetonate. ^g This is the concentration of $\text{Ni}(\text{acac})_2$ and the mole ratio of $\text{AlEt}_3/\text{Ni}(\text{acac})_2$ is 2. ^h The polymer was insoluble in benzene.

obtained with this two-component catalyst was insoluble gel. Practically no gel formation was observed in any of the cases where low-valent nickel π -complex catalysts were used.

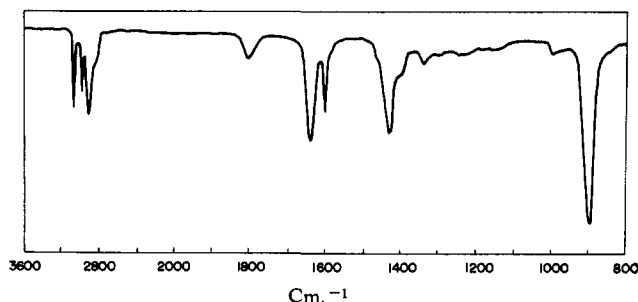


Figure 1. Infrared absorption spectrum of the 1,2-polyallene film, measured by a grating spectrophotometer (Japan Spectroscopic Co. Ltd., Model DS-402G).

Several other transition metal complexes have been tested as catalysts. Greenfield, *et al.*,⁷ described polymerization activity of dicobalt octacarbonyl for allene with no comment on structure of the polymer formed. The activity was confirmed but the polymer was insoluble in benzene. Similar results were obtained in polymerization with tris(π -allyl)cobalt,⁸ although the polymerization was carried out below 0°. Iron pentacarbonyl failed to polymerize allene at 40°. Triiron dodecacarbonyl also lacks polymerization activity; instead it forms rather stable complexes at above 80°, such as red $[\text{C}_3\text{H}_4\text{Fe}(\text{CO})_3]_2$ (m.p. 88–89°) and orange yellow $[(\text{C}_3\text{H}_4)_2\text{Fe}(\text{CO})_3]_{1-2}$ isolated by Nakamura and Hagihara.⁹ π -Cycloheptatriene-[1,3,5]iron(0)- π -cycloheptadiene[1,3]¹⁰ was too inert to initiate the polymerization.

In catalytic polymerizations coordination of a monomer to a catalyst metal is generally assumed but seldom verified. Formation of a labile allene complex was confirmed when I was dissolved in liquefied

(7) H. Greenfield, I. Wender, and J. H. Wotiz, *J. Org. Chem.*, **21**, 875 (1956).

(8) G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **2**, 110 (1961).

(9) A. Nakamura and N. Hagihara, "Symposium on Organometallic Compounds," Osaka, Japan, Oct. 1964; A. Nakamura, P. J. Kim, and N. Hagihara, *J. Organometal. Chem.*, **3**, 7 (1965).

(10) E. O. Fischer and J. Müller, *ibid.*, **1**, 89 (1963).

allene at below -20° . Reddish brown needles isolated at lower temperature were an allene-nickel complex active for allene polymerization at above 10° .

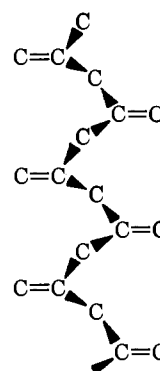


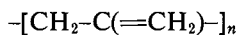
Figure 2. 2_1 Helix structure of 1,2-polyallene (all the double bonds are placed in the plane of the paper).

Polymer Structure. The polyallenes obtained with the nickel catalysts are colorless solids (m.p. 60–61°) highly soluble in benzene, toluene, carbon disulfide, carbon tetrachloride, and chloroform, soluble in cyclohexane and diethyl ether, but slightly or hardly soluble in *n*-hexane, acetone, and ethyl alcohol. The solubilities of the polymer suggest a linear structure. The infrared absorption spectrum of the polymer film is shown in Figure 1. The out of plane deformation of $:\text{CH}_2$ (vinylidene), the $-\text{CH}_2-$ bending deformation, $\text{C}=\text{C}$ stretching, and $\text{C}-\text{H}$ stretching are observed at 897, 1426, 1636, and 2900–3100 cm^{-1} , respectively. A very weak band at 990 cm^{-1} may be derived from the vinyl group possibly involved in trace amount. Hence, the predominant structural units will be vinylidene and methylene groups. A more detailed version of the infrared spectroscopic studies will be given elsewhere.¹¹

In agreement with the infrared spectrum, the nuclear magnetic resonance absorption spectrum measured in carbon tetrachloride is a quite simple one showing only two intense peaks (singlet) at τ 7.31 ($-\text{CH}_2-$) and 5.05 ($=\text{CH}_2$) with an approximately equal integral value. As a reasonable conclusion, the polymer structure, at least its major part, is believed to be quite regular and

(11) H. Tadokoro, *et al.*, to be published.

the repeating sequence is



Substantiating evidence for the correctness of the structure outlined above is available from X-ray analysis. An oriented sample showed a highly crystalline X-ray fiber diagram.¹¹ Results of the X-ray studies indicate that the molecular structure is a succession of nearly gauche conformations, *i.e.*, a 2_1 helix¹¹ as shown in Figure 2.

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The Valence Isomerization of 1,2,3,4-Tetraphenylcyclobutene and Its Anion

Sir:

As part of our program on small ring compounds accessible *via* tetraphenylcyclobutadiene, we have prepared *cis*- and *trans*-1,2,3,4-tetraphenylcyclobutene and have investigated the stereospecificity and kinetics of their valence isomerization.¹ A novel finding is that the tetraphenylcyclobutenyl anion can also undergo an extremely facile cyclobutene-butadiene valence isomerization.

Reduction of tetraphenylcyclobutadiene-nickel bromide complex² with LiAlH_4 yields (90%) a single isomer of 1,2,3,4-tetraphenylcyclobutene³ (I) whose geometry was demonstrated as *cis* by catalytic hydrogenation to 1,*trans*-2,*trans*-3,*cis*-4-tetraphenylcyclobutane.⁴ *cis*-I undergoes ring opening at 50° to yield exclusively the expected⁵ product, *cis,trans*-1,2,3,4-tetraphenylbutadiene (*cis,trans*-II), whose identity and absence of *cis,cis*- and *trans,trans*-II was demonstrated by n.m.r. characterization of all three butadiene isomers. The chemical shift of the olefinic protons (Table I) correlate well with the deshielding influence of the β -phenyl groups.⁶ The solvent-independent, first-order isomerization of *cis*-I has rate constants of $8 \times 10^{-5} \text{ sec.}^{-1}$ at 50° and 2.5×10^{-6} at 25°, with $E_a = 25 \text{ kcal./mole}$.

Addition of butyllithium to *cis*-I in THF generates the stable, deep-green tetraphenylcyclobutenyl monoanion (III), which incorporates 1 deuterium atom on

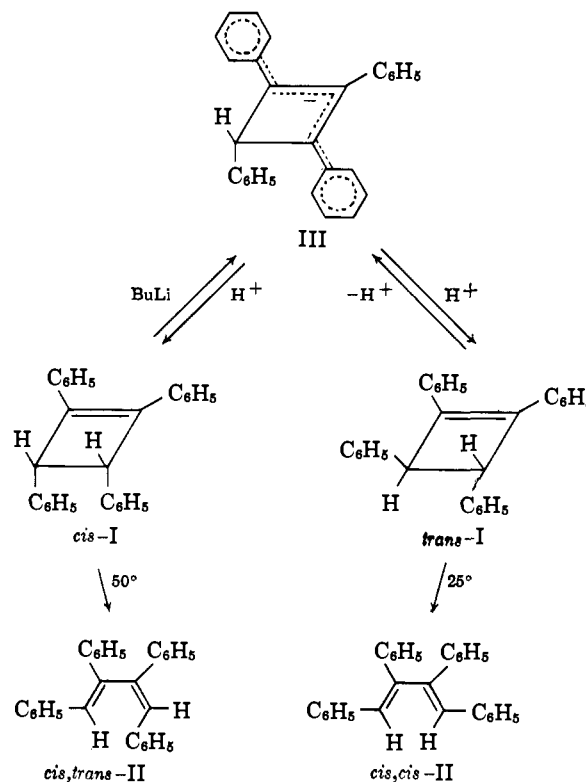
Table I. Properties of 1,2,3,4-Tetraphenylbutadiene Isomers (II)

Isomer	M.p., °C.	λ_{max} , (log ϵ) ^a	N.m.r. ^b (δ)
<i>cis,cis</i> ^c	185–186	312 ^c (4.57)	6.32 ^d
<i>cis,trans</i>	82–83	285 (4.43)	6.72, ^e 6.98 ^e
<i>trans,trans</i>	148–149	292 (4.6)	>7.0 ^f

^a In ethanol. ^b In CDCl_3 . ^c Center of doublet. ^d Two-proton singlet. ^e One-proton singlet. ^f Hidden by phenyl protons.

D_2O quenching.⁸ The assumption that the stability of III is due to charge delocalization over the planar, 1,3-diphenylallylic system is supported by its n.m.r. spectrum, which parallels that of the diphenylmethyl anion.⁹ While steric considerations predict *trans*-I to be thermodynamically favored, protonation of III by oxy acids leads entirely to the kinetically controlled product, *cis*-I.

Dramatically different results are realized when *cis*-I is equilibrated by means of lithium cyclohexylamide or potassium *t*-butoxide in THF; within minutes the 2-proton singlet of *cis*-I at δ 4.67 is replaced by a similar resonance at δ 4.02. The lability of this new product has precluded isolation in a pure state, but it is assumed to be *trans*-I from n.m.r. data¹⁰ and its chlorination to 3,4-dichlorotetraphenylcyclobutene.¹¹



trans-I isomerizes significantly faster than *cis*-I and, as expected from analogy with *trans*-tetramethylcyclo-

(1) For leading references in this active field see: R. Criegee, D. Seebach, R. Winter, B. Borretzen, and H. Brune, *Ber.*, in press. We thank Professor Criegee and Dr. Winter for a copy of the manuscript prior to publication.

(2) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961).

(3) This compound is identical with the product obtained from the hydride transfer process between cycloheptatriene and tetraphenylcyclobutenyl cation [H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962)].

(4) (a) J. D. Dunitz, *Acta Cryst.*, **2**, 1 (1949); (b) H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **85**, 1601 (1963).

(5) (a) *Cf. cis*-1,2,3,4-tetramethylcyclobutene to *cis,trans*-1,2,3,4-tetramethylbutadiene [R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959)]; (b) *cis*-3,4-dicarboxycyclobutene to *cis,trans*-muconic acid [E. Vogel, *ibid.*, **615**, 14 (1958)].

(6) D. Curtin, H. Gruen, and B. Shoulders, *Chem. Ind.* (London), 1205 (1958).

(7) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962).

(8) The potential Hückel aromatic dianion cannot be prepared by this technique. However, other approaches have proved more rewarding (to be published).

(9) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(10) The chemical shift difference of the allylic protons of *cis*- and *trans*-I parallels that for *cis*- and *trans*-1,2-diphenylbenzocyclobutene [L. A. Carpino, *ibid.*, **84**, 2196 (1962)] and *cis*- and *trans*-1,2-diphenyl-naphtho[b]cyclobutene [M. P. Cava, B. Hwang, and J. P. Van Meter, *ibid.*, **85**, 4031 (1963)].

(11) First reported in reference cited in ref. 3.