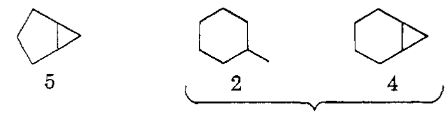
ity should be independent of the natures of the matrices of the pure materials.

Although an exact analysis was made difficult by the overlap on the gas chromatograph trace of the cyclohexane substrate and some products of the cyclopentane reaction, a comparison could be made using the peak for the bicyclo[3.1.0]hexane (which accounts for 60% of the cyclopentane reaction products, *vide supra*) and the methylcyclohexane and norcarane peaks. The relative amounts of these products are shown below. This indicates that cyclopentane and cyclohexane are of comparable reactivity under these conditions. It also supports the assertion that the reactivity of a substrate toward carbon atom addition is greatly dependent on its physical state.



5 2 4

5/0.6 = 8.3 6/0.8 = 7.5 relative rates

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research and the Army Research Office (Durham).

π-Complex Multicenter Reactions Promoted by Binuclear Catalyst Systems. "Binor-S," a New Heptacyclotetradecane *via* Stereospecific Dimerization of Bicycloheptadiene

G. N. Schrauzer,[1] B. N. Bastian, and G. A. Fosselius

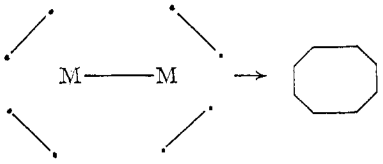
Contribution from the Shell Development Company, Emeryville, California.

Received June 17, 1966

Abstract: The principle of binuclear catalysis has been applied to the dimerization of bicyclo[2.2.1]heptadiene. In contrast to mononuclear catalysts, *e.g.*, those derived from nickel carbonyl, binuclear carbonyl catalysts such as $Zn[Co(CO)_4]_2$, and other heavy metal derivatives of $HCo(CO)_4$ dimerize bicycloheptadiene to a new dimer, *endo,-endo*-heptacyclo[$5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}$]tetradecane ("Binor-S"). In this stereospecific dimerization of norbornadiene, intermediate π complexes giving rise to only one transition state are formed. These intermediates must contain one norbornadiene molecule coordinated to each of the two cobalt atoms in a fashion allowing the formation of the new dimer *via* a "π-complex multicenter process." Factors influencing the stereocontrol of the reaction, particularly the effects of Lewis acids and bases, are discussed.

Zero-valent transition metal complexes with ligands such as phosphines, olefins, and carbon monoxide constitute some of the most versatile catalyst systems for olefin and alkyne oligomerizations. Until now most catalysts used in these reactions were mononuclear or gave mononuclear reactive catalyst fragments. For instance, many of the reactions catalyzed by Ni^0 complexes are considered to proceed *via* "bare" nickel atoms. The scope of such reactions could be increased by using catalysts having at least two metallic centers connected close to each other and which would not dissociate during the reaction. Under these circumstances it is conceivable that the substrates could interact with the catalyst in a fashion substantially different from any previously known system and lead to transition state geometries from which new products could result. A series of compounds which are in essence metal salts of carbonyl hydrides (*e.g.*, $M[Co(CO)_4]_n$, n = 2 or 3, M = Zn, Cd, Hg, In, etc.) were considered to fulfill these requirements. Some of these compounds have been described in the literature[2] but they have not been used for any catalytic reaction. It was hoped that these compounds would form reactive intermediate π complexes which could catalyze the intermolecular formation of new products by way of "π complex multicenter reactions." The anticipated differences for monodentate substrates on mononuclear (I) and binuclear (II) centers are illustrated below.

I. mononuclear center



II. binuclear center

Stereospecific Dimerization of Bicycloheptadiene with Heterometal Carbonyl Catalysts

To test the validity of this concept a study was initiated to use the above-mentioned complexes with the highly reactive bicycloheptadiene as the substrate. In contrast to other metal–carbonyl catalyzed dimerizations of this diolefin[3–7] which yielded mixtures of

---

[1] Department of Chemistry, University of California, San Diego, La Jolla, Calif.

[2] W. Hieber and U. Teller, *Z. Anorg. Allgem. Chem.*, **249**, 43 (1942).

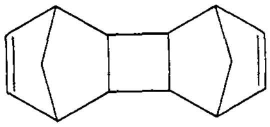
[3] D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 368 (1961).

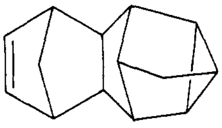
[4] (a) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *ibid.*, 373 (1961); (b) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (London), 20 (1960).

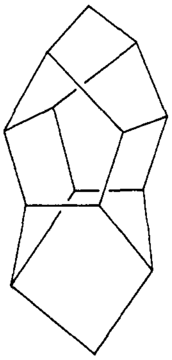
[5] G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962).

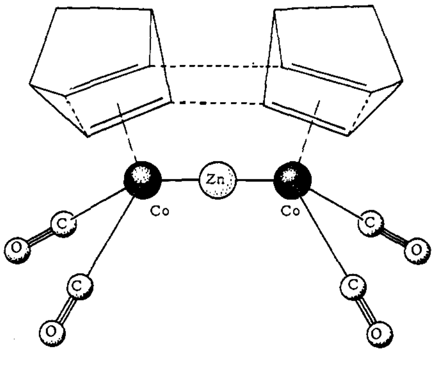
[6] P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).

ketones and dimers and their stereoisomers having structures III–V, a new dimer was obtained stereospecifically over a broad range of reaction conditions and in virtually quantitative yield with $Zn[Co(CO)_4]_2$. In substantiation of the working hypothesis, and assuming unrestricted rotation of the cobalt atoms in the Co–Zn–Co axis, the only transition state in which the substrate molecules would come sufficiently close for bond formation is VI, giving rise to the formation of "Binor-S."


III


IV

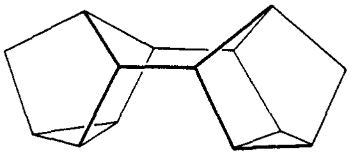

V



VI

Structure and Physical Properties of "Binor-S"

The new dimer of bicycloheptadiene, a crystalline solid of mp 65–65.6°, designated as "Binor-S," has been shown to be *endo,cis,endo*-heptacyclo$[5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}]$tetradecane (VII). The structure is proven unequivocally by elemental analysis and infrared, nuclear magnetic resonance, and mass spectroscopy. The structure proof can be summarized as follows: (a) elemental analysis corresponds to $C_{14}H_{16}$; (b) parent peak in the mass spectrum is at 184 as required; (c) the nuclear magnetic resonance spectrum shows no olefinic protons and is characterized by four peaks at δ 1.05, 1.28, 1.60, and 1.88, with relative intensities of 6:4:2:4; (d) the infrared spectrum shows the characteristic substituted nortricyclene bands at 12.53–12.69 μ and does not contain olefinic absorptions. The *cis* rather than *trans* structure is supported by the fact that eleven absorption bands are found in the C–H region. The C_{2h} symmetry of the *trans* structure predicts eight infrared active bands in this region while the C_{2v} *cis* structure predicts 13, providing none are accidentally degenerate.[8]


VII

Effect of Catalyst Concentration

"Binor-S" is obtained exclusively and quantitatively using a high catalyst to monomer ratio (*e.g.*, 1:28) with $Zn[Co(CO)_4]_2$. As the catalyst concentration is reduced two isomers each of dimers having structures III and IV appear, and at a monomer to catalyst ratio of more than 1000:1 very little "Binor-S" is formed. This suggests that the catalytically active species responsible for the formation of "Binor-S" is destroyed at high conversion. It is conceivable that intermediates containing more than two molecules of norbornadiene per Co–Zn–Co unit are formed under these less favorable conditions (Table I), which has the effect of changing the binuclear catalyst to a normal "mononuclear" action.

Table I. Effect of Catalyst Concentration on Product Distribution[a]

Monomer/catalyst, moles	Unreacted BCH, g	Dimers, wt %[b]				
		IIIa	IIIb	IVa	IVb	"Binor-S"
238	0.0	60.3	13.6	16.7	7.4	1.9
98	4.3	30.5	9.2	26.8	14.6	14.6
56	4.0	15.2	6.3	14.0	8.9	52.5
37	0.8	5.7	0	0	0	93.5
28	0.0	0	0	0	0	100

[a] Catalyst, $Zn[Co(CO)_4]_2$; solvent, toluene 10 ml, bicycloheptadiene 5 ml (4.53 g). [b] Dimer IIIa is the *exo-trans-exo* isomer of mp 67.5°. Dimer IIIb is the *exo-trans-endo* diene (see D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965)). The isomers IVa and IVb are probably identical with the dimers IVa and IVb obtained by J. J. Mrowca and T. J. Katz, *ibid.*, **88**, 4012 (1966); IVa is regarded to be one of the *exo* isomers, whereas IVb is probably an *endo* isomer of the four possible dimers of type IV.

Effect of Lewis Acids

It was found that Lewis acids greatly activate the dimerization and greatly enhance the formation of "Binor-S." Table II illustrates the increase in the conversion of monomer to "Binor-S" with increasing amounts of Lewis acids. In those reactions where the molar ratio of $BF_3O(C_2H_5)_2/Zn[Co(CO)_4]_2$ exceeded 4, the reaction essentially stopped at the conversion shown in Table II. At the lower cocatalyst/catalyst ratio (1:2) reaction proceeded after the conversion noted in Table II, but the catalyst lost its selectivity. This indicates that some irreversible changes occur with the catalyst after prolonged times of reaction. When $AlBr_3$ was used as the Lewis acid cocatalyst (molar ratio to $Zn[Co(CO)_4]_2$ 1:1) 408 moles of bicycloheptadiene were converted to "Binor-S" per mole of the catalyst. Increasing the amount of $AlBr_3$ decreased the catalyst life and some polymers were formed.

---

(7) Also see L. G. Cannell, *Tetrahedron Letters*, in press, for a revision of the structure of dimer no. VIII in ref 4b.

(8) Spectroscopic work performed by Dr. A. C. Jones, Emeryville.

Table II. Effect of $BF_3O(C_2H_5)_2$/$Zn[Co(CO)_4]_2$ (mmoles of BCH Converted to "Binor-S")/(mmoles of $Zn[Co(CO)_4]_2$)

Molar ratio $BF_3O(C_2H_5)_2$/ $Zn[Co(CO)_4]_2$	mmoles of BCH converted to "Binor-S"/ mmoles of $Zn[Co(CO)_4]_2$
1.2	257
4.08	852
5.17	684
8.08	938

Effect of the Heterometal

The heterometal cobalt carbonyl compounds of cadmium and indium gave mixtures of dimers including "Binor-S" at the same catalyst concentrations where $Zn[Co(CO)_4]_2$ also gave dimer mixtures. However, both catalysts also responded to Lewis acid cocatalysis. Normally $Hg[Co(CO)_4]_2$ dimerizes bicycloheptadiene to a mixture of four dimers, the two isomers each of structures III and IV. No "Binor-S" is formed. However, in the presence of Lewis acids this catalyst gives "Binor-S" exclusively.

Effect of Bases

Bases such as amines, phosphines, phosphites, and arsines react with cobalt carbonyl compounds. Depending on the carbonyl compound and the base three characteristic reactions are observed: displacement of carbon monoxide, disproportionation, or coordination of the heterometal. The mercury cobalt carbonyl is less stable and reacts with amines and phosphites eliminating elemental mercury. Qualitative experiments indicate that the cobalt compounds with Zn or Cd form adducts with phosphites, alkylphosphines, and nitrogen bases without the displacement of carbon monoxide, in which the central metal is becoming coordinated. Triphenylphosphine and triphenylarsine displace carbon monoxide to give complexes of the type $M[Co(CO)_3Lig]_2$. In the presence of these bases a different reaction pattern than with the parent carbonyl compounds is observed. The dimerization activity is generally decreased, and in extreme cases (excess of phosphine or phosphite) completely suppressed. At tributylphosphine levels of 1 to 4 moles per mole of catalyst other dimers are formed (see Table IV in Experimental Section) and only little of "Binor-S." The specific product distribution varies from base to base. The dimerization to IVb is quite selective with either pyridine or 3,5-lutidine, while 2,6-lutidine favors formation of dimer IIIa under comparable conditions. The aforementioned stereoselectivity to dimer IVb with 3,5-lutidine was also observed with the cobalt carbonyl derivatives of Hg, Cd, or In. The product distribution is also dependent on the catalyst concentration employed. Under conditions of more dilute catalyst there is a tendency to form more of isomer IIIa. These examples may suffice to indicate how sensitively the composition and structure of the "Binor-S" transition state is affected by coordinating agents.

Effect of Solvents

To obtain "Binor-S" the dimerization must be conducted in nonpolar solvents such as heptane or toluene. In tetrahydrofuran, dioxane, *t*-butyl alcohol, ethanol, or ethylene glycol dimethyl ether, dimers III and IV are formed instead, which suggests that these solvents have a similar action as the bases mentioned above. In alcohols solvolysis (formation of $HCo(CO)_4$) is also possible in addition to coordination effects.

Other Metal Carbonyl Catalysts

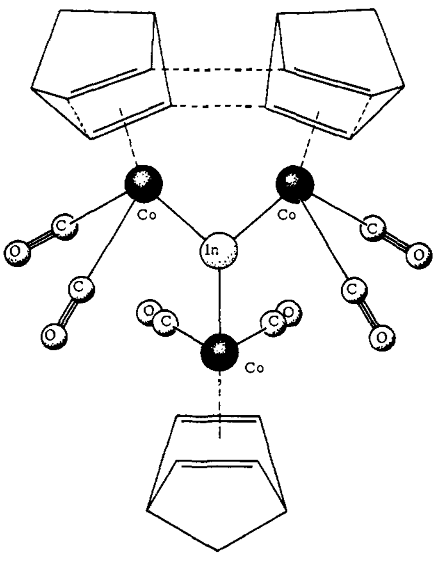
Although cobalt carbonyl is a dimer and hence potentially a binuclear catalyst, it was found to dimerize norbornadiene only to a mixture characteristic of mononuclear catalysts. A complex of composition $(BCH)_2Co_2(CO)_4$ (VIII) has been described[9] which contains bridging carbonyl groups, but whose structure is not yet known in detail. Decomposition of VIII was found to give no "Binor-S." Spectroscopic evidence indicated the formation of ketonic materials. However, thermal decomposition in the presence of aluminum bromide or $BF_3O(C_2H_5)_2$ leads to the exclusive formation of "Binor-S." The effect appears to be one involving a change in complex structure. Other metal carbonyls and their mixtures with Lewis acids were evaluated for their catalytic activities in the bicycloheptadiene dimerization. Low conversion to dimers other than "Binor-S" was noted; in most cases, however, polymerization reactions occurred. The catalyst systems studied included $Ni(CO)_4$, $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in conjunction with $BF_3O(C_2H_5)_2$ as cocatalyst.

Discussion

The dimerization of bicycloheptadiene catalyzed by $Zn[Co(CO)_4]_2$ shows an induction period during which carbon monoxide deficient intermediates are formed. The evolution of CO occurs immediately upon adding the catalyst to a solution containing bicycloheptadiene and slowly continues during the reaction until at a later stage it is reabsorbed or otherwise reacts. Accordingly, carbon monoxide was found to slow down the rate of dimerization as its competes with the initial substitution of the metal-bound CO by norbornadiene. It was observed that the rate of dimer formation increased by a factor of 6.65 if conducted under nitrogen sweep, as compared to a control dimerization in a closed system. In the latter case spectroscopic examination revealed the presence of ketonic materials which were absent in the products obtained from the "open" reaction. These findings are consistent with the formation of norbornadiene catalyst π complexes prior to the actual formation of the dimers. The catalytically important species must be VI which cannot be isolated and is expected to collapse into "Binor-S" and the ligand-deficient species "$Zn[Co(CO)_2]_2$," which is readily resolvated by the bicycloheptadiene in the reaction mixture. Under these circumstances it is clear that the formation of the "Binor-S" transition state will be seriously impaired by the presence of other coordinating ligands such as amines or phosphines. It is at first surprising that the compound $In[Co(CO)_4]_3$ also catalyzes the dimerization of bicycloheptadiene to "Binor-S." However, assuming that an intermediate $In[Co(CO)_2BCH]_3$ is formed, it may be shown that the only transition state in which norbornadiene molecules come sufficiently close is that shown in IX. Formation

---

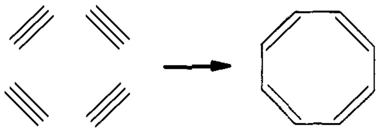
[9] G. Winkhaus and G. Wilkinson, *J. Chem. Soc.*, 602 (1961).



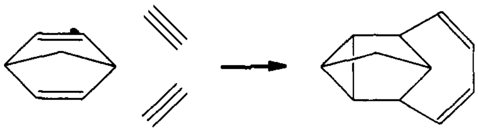
IX

of a trimer of norbornadiene is eliminated on steric grounds, but also because this would require three substrate molecules to react simultaneously. Although trimerization could take place in principle, it is nevertheless not likely to occur in this particular system. To explain the effect of added Lewis acids we assume that BF_3 acts as a cocatalyst which may cause a faster displacement of the coordinated carbon monoxide or a stabilization of the catalytically active complex.[10] A 1:1 addition compound of $AlBr_3$ with $Co_2(CO)_8$ has been reported;[11] it is of interest that this complex catalyzes the formation of "Binor-S", as well, whereas $Co_2(CO)_8$ alone does not. Boron trifluoride etherate did not seem to react with $Zn[Co(CO)_4]_2$ in cold toluene; addition of $AlBr_3$ to the carbonyl complex in the same solvent immediately produced a tan precipitate containing Al, Co, and Zn in the ratio of 1:2:1.4 which could not be isolated in crystalline form. The interaction of $Zn[Co(CO)_4]_2$ with $AlBr_3$ thus appears to be more complicated as metathetical reactions leading to aluminum–cobalt carbonylates may occur. The catalytically active species seem to be binuclear as well. However, "Binor-S" so far could not be obtained with catalyst systems that could with some assurance be regarded as "mononuclear." It thus appears that "Binor-S" formation may be generally indicative for the presence of binuclear catalytically active species in norbornadiene dimerization.

Finally, a similarity between "Binor-S" formation and Reppe's cyclooctatetraene synthesis may be postulated. It is known that the C=C bonds in bicycloheptadiene are about as reactive as carbon–carbon triple bonds. The formation of cyclooctatetraene (X) from acetylene most probably occurs in a labile π complex of Ni^{2+} containing four acetylene molecules.[12] Accordingly, norbornadiene is an inhibitor of the Reppe reaction and cocyclooligomerization to XII occurs instead.[13] Formally, the formation of "Binor-S" (XII) thus corresponds to Reppe's cyclooctatetraene synthesis in the bicycloheptadiene system. As a consequence, it was also attempted to synthesize cyclooctatetraene using $Zn[Co(CO)_4]_2$ as the catalyst. Although the main volatile product was benzene, about 3% of cyclooctatetraene was also detected. Since this is the first reported formation of cyclooctatetraene on a catalyst not containing nickel it is possible that binuclear catalysis is involved in this case. In these reactions it is reasonable to assume that the new C–C bonds are formed simultaneously. Several related reactions, *e.g.*, the catalytic dimerization of norbornadiene to the dimers III and IV, or the nickel-catalyzed addition of vinylogs or alkines to norbornadiene, and certain reactions of alkynes with metal carbonyls were similarly proposed to proceed as "π complex multicenter reactions."[5,13,14] It thus seems that this mechanistic principle is indeed a useful one.



X



XI

XII

Experimental Section

Reagents. Preparation of $Zn[Co(CO)_4]_2$, $Cd[Co(CO)_4]_2$, and $In[Co(CO)_4]_3$. A 705-ml autoclave was charged with zinc dust (12 g, 0.184 g-atom) and a toluene solution of $Co_2(CO)_8$, 400 ml, 10%, under nitrogen. Carbon monoxide (3000 psi, 20°) was introduced and the autoclave was heated with shaking to 200° (4750 psi) for 12 hr. Carbon monoxide was vented from the cooled reactor, and the golden yellow solution was filtered under nitrogen into a low-temperature (−78°) crystallizer. The yellow crystalline $Zn[Co(CO)_4]_2$, 30.95 g, was isolated by filtration and stored under dry, oxygen-free nitrogen. The same procedure was used for the preparation of the cadmium and indium compounds. Experimental conditions are given in Table III. The mercury compound, $Hg[Co(CO)_4]_2$, was prepared by the method in ref 2.

Table III

Compound	Toluene–10% $Co_2(CO)_8$, ml	Metal, g	Carbon monoxide, psi		Time, hr	Yield, g
			20°	200°		
$Cd[Co(CO)_4]_2$	200	7.40	2940	4800	16	12.50
$In[Co(CO)_4]_3$	200	4.56	3000	4800	10	2.96

Small-Scale Dimerization of Bicycloheptadiene. The reagents listed in Table IV were charged to 50-ml flasks equipped with rubber serum caps, containing, *e.g.*, 10 ml of toluene and 5 ml of bicyclo-

---

[10] The interaction of metal carbonyl compounds with Lewis acids is not without precedent. G. W. Parshall (*J. Am. Chem. Soc.*, **86**, 361 (1964)) reported addition compounds of borane with various salts of manganese and rhenium carbonyls.

[11] P. Chini and R. Ecoli, *Gazz. Chim. Ital.*, **88**, 1170 (1958).

[12] G. N. Schrauzer, *Angew. Chem.*, **76**, 28 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

[13] G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

[14] G. N. Schrauzer, *ibid.*, **94**, 1403 (1961).

Table IV. Examples of Small-Scale Dimerizations in Toluene Solution

Catalyst, mmoles	Cocatalyst, mmoles		Time, hr	Temp, °C	Wt %					
	Lewis acid	Base			BCH	IIIa	IIIb	IVa	IVb	"Binor-S"
$Zn[Co(CO)_4]_2$ 2.0	. . .	. . .	3.50	100	0.7	0	0	0	0	99.3
1.0	. . .	. . .	17	95	4.0	15.2	6.3	14.0	8.9	52.5
0.5	. . .	. . .	16	100	4.3	30.5	9.2	26.8	14.6	14.6
0.25	. . .	. . .	16	100	0	60.3	13.6	16.7	7.4	1.9
0.05	. . .	. . .	16	100	75.1	17.5	3.2	3.2	1.0	0
1.0	$BF_3O(C_2H_5)_2$ 0.5	. . .	2.25	100	0	0	0	0	0	100
1.0	$AlBr_3$ 0.66	. . .	0.50	100	0	0	0	0	0	100
$Cd[Co(CO)_4]_2$ 0.5	. . .	. . .	4.1	100	11.1	18.4	3.9	8.4	7.9	50.3
0.5	$BF_3O(C_2H_5)_2$ 0.71	. . .	0.25	100	0	0	0	0	0	100
0.5	. . .	Pyridine 23.8	5.25	100	41.5	1.8	5.6	51.0	0	0
$Zn[Co(CO)_4]_2$ 1.0	. . .	C_2H_5OH 10 ml	3.00	80	79.2	7.8	3.0	6.8	3.0	0
1.0	. . .	$P(n\text{-}C_4H_9)_3$ 1.0	4.25	95	19.9	19.7	6.5	23.9	21.2	0.4
1.0	. . .	$P(n\text{-}C_4H_9)_2$ 2.0	4.25	95	0	44.3	13.4	21.1	12.9	0.5
1.0	. . .	Pyridine 21.4	4.67	100	16.6	1.0	Trace	7.8	71.4	0
1.0	. . .	$N(C_2H_5)_3$ 10.5	4.00	100	42.8	15.0	14.6	17.0	10.7	0
1.0	. . .	$S(C_2H_5)_2$ 9.0	4.00	100	0	0	7	0	0	93
1.0	. . .	$P(OC_6H_5)_3$ 4.3	4.00	100	100	0	0	0	0	0
1.0	. . .	$P(n\text{-}C_4H_9)_3$ 4.6	4.00	100	100	0	0	0	0	0
$Hg[Co(CO)_4]_2$ 1.0	. . .	. . .	3.50	100	0.1	29.1	22.5	25.0	23.5	0
$In[Co(CO)_4]_3$ 0.5	$BF_3O(C_2H_5)_2$ 0.5	. . .	0.1	30[a]	6.0	0	0	0	5.5	88.5
0.5	. . .	3,5-Lutidine 9.3	72	100	77.8	0	0	1.4	20.8	0
$Zn[Co(CO)_4]_2$ 0.5	. . .	2,6-Lutidine 9.1	17	100	5.9	44.0	9.9	25.1	14.0	1.2
0.5	. . .	3,5-Lutidine 8.1	17	100	43.2	2.8	0	5.4	45.7	0
0.5	. . .	3,5-Lutidine 8.9	0.1	95	47.4	(3.3)[b]		5.5	43.8	0
$Cd[Co(CO)_4]_2$ 0.5	. . .	3,5-Lutidine 8.6	72	100	47.8	7.4	0	6.4	38.5	0
$Co_2(CO)_8$ 1.0	. . .	. . .	3.0	100	0	23.2	16.8	27.2	26.4	0
1.0	$BF_3O(C_2H_5)_2$ 0.56	. . .	0.1	25[a]	0	0	0	0	0	100
0.5	$AlBr_3$ 0.5	. . .	1	60	0	0	0	0	0	100
0.5	SbF_5 0.5	. . .	1.75	85	93.1	0	0	0	0	6.9
1.0	BF_3 gas 0.5	. . .	2	70	6.8	0	0	0	0	93.2

[a] Temperature at which exotherm began; temperature rose to approximately 110°. [b] Weight for dimers IIIa and IIIb.

heptadiene under dry nitrogen or argon and heated in an oil bath. In certain cases the reactants were heated gently to initiate the dimerization and no external heat was necessary to bring the reactions to completion. The solutions were analyzed by glpc, and the dimers identified by comparison of the retention times and the infrared spectra of authentic samples kindly furnished by L. Cannell. Glpc analyses were carried out on an F and M Model 810 dual column chromatograph using a 6-ft column of SE-30 silicone rubber or Carbowax-20M polyethylene glycol on Chromosorb W.

Preparation and Properties of "Binor-S." A 500-ml nitrogen-filled reactor equipped with stirrer, reflux condenser, thermometer, addition funnel, and a nitrogen sweep was charged with toluene (100 ml), $Zn[Co(CO)_4]_2$ (0.81 g, 2.0 mmoles), and $BF_3O(C_2H_5)_2$ (2.28 g, 1.62 mmoles). Bicycloheptadiene (226 g, 2.45 moles) was added slowly with stirring, and the reaction vessel was heated to 70°. The addition was completed in 90 min during which an ice bath was periodically applied to maintain the desired temperature of about 70–80°. Heat was applied to keep the reaction at this temperature for another 21 hr. The mixture was washed with 5% aqueous HCl, dried over anhydrous Na_2CO_3, decolorized with Norit and vacuum distilled, bp 73° (1–2 mm). The "Binor-S" (174.01 g, 76.4%) was recrystallized from ethanol and dried over P_2O_5 (mp 65°). Glpc analysis on a 6-ft Carbowax column showed only the presence of "Binor-S." Parent peak in the mass spectrum is at 184. *Anal.* Calcd for $C_{14}H_{16}$: C, 91.3; H, 8.7. Found: C, 91.3; H, 8.8. Infrared spectrum in C–H region (thin layer film): 3074, 3063 (cyclopropyl), 3058, 3056 (both sh), 2999, 2984 (cyclopropyl), 2940, 2928 (CH_2 assym), 2914 (sh), 2900 (C–H), 2863 cm^{-1} (CH_2, sym); nortricyclene bands appeared at 800 and 788 cm^{-1}.

In addition to the 11 definite C–H stretching bands, a total of 43 definite bands between 1600 and 300 cm^{-1} plus 18 questionable weak bands or shoulders were observed. For C_{2v} symmetry (*cis* structure), 13 infrared active C–H stretching vibrations and 52 vibrations below 1600 cm^{-1} are expected. For C_{2h} symmetry (*trans* structure) 8 and 34 infrared active vibrations, respectively, are predicted. "Binor-S" therefore should have C_{2v} symmetry.

Nmr Spectrum. The nuclear magnetic resonance spectrum of "Binor-S" is simple and consists of only four peaks. Observed φ values, intensities, and suggested assignments are given below.

φ_{obsd}, ppm	1.05	1.28	1.60	1.88
Intensity	6	4	2	4
Assignment	Cyclopropyl protons	Bridging $-CH_2-$	$\geqslant$C–H adjacent to $-CH_2-$ bridges	$\geqslant$C–H at C atoms connecting the two nortricyclene units

Hydrogenation of "Binor-S." "Binor-S" shows reactivity characteristic of cyclopropyl systems. It is hydrogenated to a mixture of liquid hydrocarbons over Pt at 200°, 4600 psi. The products, isomers of composition $C_{14}H_{20}$ (94%) and $C_{14}H_{18}$ (6%), had bp 76–83° (0.25 mm) and were not separated into the individual components. The composition was proved by mass spectrometric and elemental analyses.

Decomposition of $Co_2(CO)_4(C_7H_8)_2$. The compound was prepared from bicycloheptadiene by the method of Winkhaus and Wilkinson[9] and was decomposed in toluene in the presence and absence of $AlBr_3$. In the former case, glpc analysis showed no dimers although three small peaks were observed which had retention times between bicycloheptadiene and the dimers. The infrared spectrum of the products showed a small peak at 5.76 μ. Glpc analysis of the thermal decomposition products of $Co_2(CO)_4(C_7H_8)_2$ in the presence of $AlBr_3$ (1:1 molar ratio) showed the formation of 0.386 mmole of "Binor-S" from 1.00 mmole of complex (77%) after heating (95°) for 2 hr. "Binor-S" was the only organic product observed.

Reaction of Acetylene with $Zn[Co(CO)_4]_2$ (Experiments performed in cooperation with Dr. P. W. Glockner, Emeryville). A 300-ml autoclave was charged with 50 ml of dry tetrahydrofuran and 3 g of $Zn[Co(CO)_4]_2$ and treated with acetylene (~200 psi) for 3 hr at 190–200°. The uptake was 60 psi. After filtration from solid products ("cuprene"), glpc analysis of the solution indicated the presence of 6 g of benzene and 0.4 g of cyclooctatetraene.

Reaction of $Zn[Co(CO)_4]$ and $AlBr_3$. Aluminum bromide (1.33 g, 5.0 mmoles) was added to a toluene (25 ml) solution of $Zn[Co(CO)_4]_2$ under dry oxygen-free nitrogen. The resulting tan precipitate, which was formed without gas evolution, was collected on a filter, washed with petroleum ether, and dried in a stream of dry nitrogen. Analysis gave 12.6% Zn, 16.9% Co, and 3.8% Al.