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A Novel Cyclodimerization of Butadiene. A Synthetic Route to 2-Methylenevinylcyclopentane

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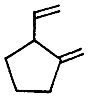
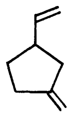
In the presence of a controlled amount of alcohol, the dimerization of butadiene to produce 2-methylenevinylcyclopentane has been shown to occur by means of several nickel catalysts. The most effective nickel catalysts are: (1) $(Bu_3P)_2NiX_2$ (X=Cl and Br) and organolithium, (2) (*o*-tolyl)NiX$(PEt_3)_2$ (X=Cl, Br, and I), and (3) π-allylnickel bromide and tri-*n*-butylphosphine. A detailed study of the role of alcohol during the reaction by the arylnickels is presented. In the presence of butadiene, the aryl-nickel bond of (*o*-tolyl)NiX$(PEt_3)_2$ is reductively cleaved by methanol to give toluene, and then the dimerization of butadiene occurs. With CH_3OD as the reducing reagent, toluene is not deuterated, but with CD_3OD the aromatic ligand is deuterated on the carbon originally bonded to nickel to give monodeuterotoluene.

The dimerizations of butadiene in the presence of transition metals to cyclic or linear products have been extensively studied in the last decade by many workers.[1] The principal products are isomeric *n*-octatrienes, methylheptatrienes, 4-vinylcyclohexene, 1,5-cyclooctadiene, and 1,2-divinylcyclobutane. Until now, however, no effective catalysts have been reported to convert butadiene into a five-membered cyclic dimer, 2-methylenevinylcyclopentane (I) or 3-methylenevinylcyclopentane (II), except for the works of Müller[2] and Feldman,[3] who isolated the five-membered cyclic dimers of butadiene in low yields as a by-product.


I


II

The formation of intermediates which give several different products is expected when butadiene is allowed to react under the influence of transition-metal catalysts. Therefore, it is of considerable interest to compare the courses of the dimerization of butadiene by the different transition metals. The critical importance of appropriate auxiliary ligands to the catalytic effectiveness of Ziegler-Natta polymerization catalysts is well known. From our interest in the mechanism of transition-metal-catalyzing oligomerization and polymerization, we have examined the effects of appropriate ligands, using the reaction of butadiene by means of nickel catalysts as a model system. In the course of this work, we have confirmed the formation of 2 methylenevinylcyclopentane (MVCP) from the dimerization of butadiene by several nickel catalysts. A part of this study has already been reported in preliminary reports.[4,5] The new route to MVCP from butadiene is of interst in connection with certain synthetic problems and with the catalysis of transition metals.

In this paper we wish to report on the formation of MVCP and on some mechanistic studies of the cyclodimerization.

Results and Discussion

The following types of nickel catalysts in the presence of alcohol were effective for the cyclodimerization of butadiene to MVCP: (1) bis(trialkylphosphine)dihalo-

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[1] C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York (1967), p. 30.

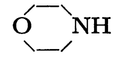
[2] H. Müller, D. Wittenberg, H. Seibt, and E. Scharf, *Angew. Chem., Int. Ed. Engl.*, **4**, 327 (1965).

[3] J. Feldman, O. Frampton, B. Saffer, and M. Thomas, ACS Preprints, Division of Petroleum Chemistry, **9**, A55 (1964).

[4] J. Kiji, K. Masui, and J. Furukawa, *Tetrahedron Lett.*, **1970**, 2561.

[5] J. Kiji, K. Masui, and J. Furukawa, *Chem. Commun.*, **1970** 1310.

Table 1. Dimerization of butadiene by various nickel catalysts in the presence of protonic compounds[a]

Expt. No.	Ni Compd.	(mmol)	Organo-lithium[b]	(mmol)	Protonic compd.	(mmol)	Butadiene (mmol)	Produces[c] yield (%)
1	$(Bu_3P)_2NiCl_2$	(1.4)	*n*-BuLi	(0.72)	CH_3OH	(40)	80	MVCP (50)
2	$(Bu_3P)_2NiCl_2$	(1.3)	*n*-BuLi	(1.3)	CH_3OH	(40)	70	MVCP (70)
3	$(Bu_3P)_2NiCl_2$	(1.3)	*n*-BuLi	(2.6)	CH_3OH	(40)	70	MVCP (70)
4	$(Bu_3P)_2NiCl_2$	(1.3)	*n*-BuLi	(5.1)	CH_3OH	(40)	70	MVCP (50)
5	$(Bu_2P)_2NiBr_2$	(1.4)	*n*-BuLi	(1.4)	CH_3OH	(40)	120	MVCP (90)
6	$(Bu_3P)_2NiI_2$[d]	(0.58)	*n*-BuLi	(0.68)	CH_3OH	(25)	70	1,3,7-OT[e]
7	$(Bu_3P)_2Ni(NO_2)_2$	(1.1)	*n*-BuLi	(1.0)	CH_3OH	(25)	100	——
8	$(Bu_3P)_2Ni(SCN)_2$	(2.0)	*n*-BuLi	(2.0)	CH_3OH	(25)	100	——
9	$(Bu_3P)_2NiCl_2$	(1.5)	DMBALi	(1.5)	CH_3OH	(2.5)	80	VCH,[e] COD[e]
10	$(Bu_3P)_2NiCl_2$	(1.5)	DMBALi	(1.5)	CH_3OH	(25)	80	MVCP (70)
11	$(Bu_3P)_2NiCl_2$	(1.5)	DMBALi	(1.5)	CH_3OH	(75)	80	MVCP (45)
12	$(Bu_3P)_2NiCl_2$	(2)	DMBALi	(2)	C_6H_5OH	(10)	70	MVCP (20)
13	$(Bu_3P)_2NiCl_2$	(1.5)	DMBALi	(1.5)	$C_6H_5CH_2OH$	(5)	130	MVCP (5)
14	$(Bu_3P)_2NiCl_2$	(1.5)	DMBALi	(1.5)	$C_6H_5CH_2OH$	(20)	110	MVCP (70)
15	$(Bu_3P)_2NiCl_2$	(1.1)	*n*-BuLi	(1.1)		(17)	10	MVCP (10) VCH,[e] COD[e]
16	$(Et_2PhP)_2NiCl_2$	(1.1)	*n*-BuLi	(1.1)	CH_3OH	(25)	50	MVCP (60) VCH (5)
17	$(Cy_3P)_2NiCl_2$	(0.5)	*n*-BuLi	(0.5)	CH_3OH	(12)	30	1,3,7-OT (33) 1,3,6-OT (15)
18	$(Bu_3P)_2NiCl_2$	(1.3)	*n*-BuLi	(3.2)	H_2O	(28)	—	VCH (22) COD (28)
19	$(Bu_3P)_2NiCl_2$	(1.3)	*n*-BuLi	(1.3)	CH_3COOH	(17)	100	——
20	$(Bu_3P)_2NiCl_2$	(1.3)	*n*-BuLi	(1.3)	CF_3COOH	(10)	100	——

a) All reactions were carried out in benzene (1.8—5 m*l*) solution at 60—75°C for 40—50 hr.
b) *n*-BuLi, *n*-butyllithium; DMBALi, *o*-lithio-*N*,*N*′-dimethylbenzylamine.
c) MVCP, 2-methylenevinylcyclopentane; VCH, 4-vinyl-1-cyclohexene; COD, 1,5-cyclooctadiene; OT, octatriene.
d) Crystalline compound could not be obtaind.
e) In low yield.

nickel and organolithium, (2) *trans*-bis(triethylphosphine)halo-(*o*-tolyl)nickel, and (3) π-allylnickel bromide and tributylphosphine. The dimerization with these catalysts proceeded smoothly at 60—70°C, and MVCP free from significant by-products was easily obtained by distillation. No obvious dimerization was observed at room temperature. We have not tried to carry the reaction out above 100°C because the Diels-Alder reaction is expected to occur at higher temperatures. The most characteristic features of these catalysts are that they contain a halogen atom and should be used in the presence of a considerable and controlled amount of alcohol. Without alcohol, 4-vinylcyclohexene (VCH) and 1,5-cyclooctadiene (COD) were formed in low yields. The infrared spectrum of MVCP showed strong absorptions at 910 and 990 cm^{-1} due to a vinyl group and at 880 cm^{-1} due to a terminal methylene group. The absorption band at 1370 cm^{-1} for the methyl group was absent in the spectrum. The main product of hydrogenation over palladium-carbon was identical with *trans*-1-methyl-2-ethylcyclopentane.

Bis(tertiaryphosphine)dihalonickel Compounds and Organolithium. The results are summarized in Table 1. An inspection of Table 1 leads to the following conclusions concerning the factors which affect this cyclodimerization.

(a) It is essential to add alcohol in a 25—40 molar amount. In an experiment in which an amount of methanol equimolar to the nickel catalyst was added, no MVCP was formed except that vinylcyclohexene and cyclooctadiene were formed in low yields. On the other hand, the use of too large an amount of methanol resulted in the formation of higher-boiling products in addition to MVCP. Alcohols other than methanol can be used, but acids, phenols, and amines were less effective.

(b) The cyclodimerization proceeds satisfactorily in the presence of strong σ-donor phosphines without a bulky substituent. Strong electron donors, such as triethylphosphine and tri-*n*-butylphosphine, were effective as auxiliary ligands. On the contrary, bis(tricyclohexylphosphine)dichloronickel catalyzed not the cyclodimerization, but the linear dimerization, as is indicated by No. 17. Presumably, the marked difference in the behavior of $(Bu_3P)_2NiCl_2$ and $(Cy_3P)_2NiCl_2$ is a consequence of the difference in the bulkiness of the substituents on phosphorus, because the electron donor-acceptor properties of these two phosphines are similar; *i.e.*, no indication of any significant difference is provided by a comparison of the infrared CO stretching frequencies of $Ni(CO)_2(Phosphine)_2$ for tricyclohexylphosphine, 1973 cm^{-1}, with that for tri-*n*-butylphosphine, 1976 cm^{-1}.[6]

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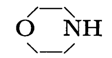
6) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

Table 2. Dimerization with (o-tolyl)NiX$(PEt_3)_2$ in the presence of protonic compounds[a)]

Expt No.	Catalyst	(mmol)	Protonic compd.	(mmol)	Butadiene (mmol)	Dimer distribution (%)			
						MVCP	VCH	COD	OT
1	IIIa X=Cl	(0.85)	CH_3OH	(20)	60	86	9	5	—
2	IIIb X=Br	(2.4)	CH_3OH	(40)	100	95	4	1	—
3	IIIc X=I	(0.5)	CH_3OH	(12)	50	92	5	3	—
4	IIId X=NO_2	(0.3)	CH_3OH	(12)	50	—	6	22	72
5	IIIe X=NCS	(1.1)	CH_3OH	(25)	70	—	14	16	70
6	IIIb X=Br	(1.4)		(17)	100	29	46	25	—
7[b)]	IIIb X=Br	(0.4)	CH_3OD	(15)	15	—	—	—	—

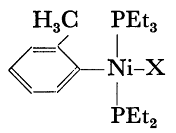
a) All reactions except No. 7 were carried out in benzene (1—5 ml) solution at 70—75°C for 40 hr; yield of dimers, 50—70%.

b) Reaction at 70°C for 3 hr. Butadiene was recovered unchanged (not deuterated) and decomposition of the catalyst was not observed.

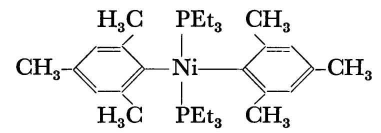
(c) The substituent, X, in $(R_3P)_2NiX_2$ is very important, although its behavior is obscure. It is essential for the nickel complex to contain a chlorine or bromine atom. No MVCP was formed, but linear dimers were formed in low yields when the substituents, the X's, were I, NO_2, CO, and SCN.

(d) o-Substituted aryllithium such as o-lithio-N,N'-dimethylbenzylamine[7)] was effective, as was n-butyllithium. The other alkylation reagents, such as alkylaluminums, were ineffective.

Arylnickel Compounds. It is generally agreed that the first step in the reaction of transition metal halides and alkylmetals (*i.e.*, the first step in the preparation of Ziegler-Natta-type catalysts) is an alkylation. This mechanistic concept prompted us to examine the catalytic properties of the stable o-substituted arylnickels (III and IV) prepared by Chatt and Shaw,[8)] because an arylnickel is presumed to be formed on the reaction of o-lithio-N,N'-dimethylbenzylamine with $(Bu_3P)_2NiCl_2$.



III



IV

a: X=Cl d: X=NO_3
b: X=Br e: X=NCS
c: X=I

These arylnickels (III and IV) are so stable that they can be handled in the open air. In spite of their chemical stability, they readily dimerized butadiene in the presence of alcohol.[5)] The results are summarized in Table 2.

The iodine complex (IIIc) effected the cyclodimerization, while $(Bu_3P)_2NiI_2$ and organolithium catalyzed a linear dimerization. Interestingly, nitrironickel (IIId), isothiocyanatonickel (IIIe), and bis(triethylphosphine)-di(mesityl)nickel (IV) no longer brought about the cyclodimerization, but effected linear dimerization. Thus, in this catalytic system only halogen-bearing arylnickels were effective for the dimerization to the five-membered cycle (I). In the present study, however, the role of the halogen atom in the cyclodimerization has not been well understood so we cannot here discuss its behavior.

Bis(triethylphosphine)halo-(o-tolyl)nickels were recovered unchanged after heating the solution of methanol if butadiene was absent. Under the dimerization conditions in the presence of butadiene, the o-tolylnickels were decomposed to give toluene almost quantitatively, and were converted to a substance possessing the catalytic activity. In the working state of the catalysts, the aryl group originally attached to nickel is eliminated. Therefore, the presence of the aryl-nickel bond is not essential for the cyclodimerization, though the initiation of the dimerization may be affected by the aryl group. When the reaction with IIIb was stopped at an early stage (after three hours), toluene and the dimer, I, were not detected. Thus, the elimination of the aryl group and the cyclodimerization are associated with each other. This is consistent with the fact observed in the case of diethylbis(dipyridyl)iron, which catalyzes the dimerization of butadiene after the elimination of the ethyl group as butane, ethane, or ethylene.[9)]

Of considerable importance is the observation that no deuterium was incorporated in toluene even if CH_3OD and CD_2=CH-CH=CD_2 were used instead of CH_3OH and CH_2=CH-CH=CH_2 respectively. The results are summarized in Table 3. This observation suggests that the cleavage of the arylnickel σ-bond in the presence of butadiene is not due to simple methanolysis. Since the use of CD_3OD resulted in the formation of monodeuterotoluene, it is clear that a hydrogen (deuterium) is transferred from a methoxide group to the coordinated o-tolyl group originally attached to nickel, thus liberating toluene. Accordingly, we began to consider the reductive cleavage of the aryl-nickel bond. Indeed, we have observed that the aryl-nickel bond of IIIb is cleaved by molecular hydrogen. Though the reaction was slow and a considerable amount of IIIb was recovered unchanged after the reaction, toluene was isolated in a 33% yield (based on the IIIb used); the complex under the influence of hydrogen showed a catalytic activity toward the dimerization of butadiene similar to that of IIIb combined with methanol.

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7) A. Kasahara and T. Izumi, This Bulletin, **42**, 1765 (1969).

8) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1960**, 1718.

9) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **90**, 1878 (1968).

TABLE 3. REACTIONS OF (*o*-TOLYL) $NiX(PEt_3)_2$ WITH REDUCING AGENTS IN THE PRESENCE OF BUTADIENE[a)]

III	(mmol)	Reductive cleavage of C-Ni bond Reagent	(mmol)	Toluene[b)] (%)	D % in toluene	Catalytic dimerization Butadiene (mmol)	MVCP [5)] (%)
X=Br	0.4	——	——	0	——	C_4H_6 10	0
X=Cl	3.0	CH_3CD	40	67[c)]	0	C_4H_6 15	25[c)]
X=Br	1.0	CH_3OH	13	n.d[d)]	0	$C_4H_2D_4$ 6	55
X=Cl	1.5	CD_3OD	24	85[e)]	*ca.* 95	C_4H_6 10	80
X=Br	0.4	H_2	30 (kg/cm²)	33[e)]	0	C_4H_6 10	5

a) All reactions were carried out in benzene solution (1 m*l*) at 70—75°C for 24—48 hr.
b) Yield based on nickel complex used.
c) Isolated yield after distillation.
d) Not determined.
e) Gas chromatographic analysis using benzene as an internal standard.
f) Yield based on butadiene used.

While, in the cleavage of the aryl-nickel bond, no products other than toluene have been identified, the reaction evidently proceeds, by analogy to that of palladium,[10)] through an oxidation of methanol, thus producing toluene and an active nickel catalyst which is effective for the dimerization to MVCP. The reduction of IIIb with molecular hydrogen also gives toluene and the active nickel catalyst. The dimerization using molecular hydrogen as the reducing agent is interesting in the point that a hydrogen migration during the dimerization is involved even in an aprotic solvent. In addition, dimers other than MVCP were not formed, though the formation of vinylcyclohexene and cyclooctadiene has been anticipated, because vinylcyclohexene and cyclooctadiene are the usual products of the dimerization of butadiene using nickel catalysts in an aprotic solvent.[1)] In order to cyclodimerize butadiene to MVCP, the migration of one hydrogen must be involved. To our knowledge, for the dimerization of butadiene using nickel catalysts, protonic solvents such as alcohol,[2)] phenol[3)] and amine[11)] must be always used for the formation of linear dimers. The experiment with molecular hydrogen suggests that alcohol is not necessary to the migration of hydrogen during the dimerization.

Bis(triethylphosphine)di(mesityl)nickel showed a different catalytic behavior from that of III (Table 4); even in the absence of the reducing agent, IV catalyzed the dimerization of butadiene to give 4-vinylcyclohexene and 1,5-cyclooctadiene in high yields.

TABLE 4. CATALYSIS OF $(MESITYL)_2Ni(PEt_3)_2$[a)]

Catalyst (mmol)	Reducing agent (mmol)	Butadiene (mmol)	Products (%)	
0.3	——	9	Vinylcyclohexene	50
			Cyclooctadiene	27
1.0	Methanol 25	100	1,3,6-*n*-Octatriene	14
			Higher boiling products[b)]	
0.4	H_2 30 (kg/cm²)	10	Butane	*ca.* 30
			Ethylcyclohexane	33
			Cyclooctane	24

a) All reactions were carried out in benzene solution at 70—75°C for 24 hr.
b) The yields were not determined.

Similarly, the aryl-nickel bond of bis(triethylphosphine)di(mesityl)nickel (IV) was cleaved by molecular hydrogen to form mesitylene. The mesityl complex, IV, was also an excellent catalyst precursor for the dimerization of butadiene described below, though the reaction catalyzed by IV differed from that by III. The catalytic behavior of IV would be consistent with the catalysis of $Fe(dipyl)_3$[9)] or "naked nickel" combined with an electron-donating ligand[12)]in the points that the distribution of the products is similar and IV is the precursor of an active catalyst containing no halogen atom.

On the other hand, if the mesityl complex, IV, was treated with hydrogen in the presence of butadiene, mesitylene was liberated and the reaction of butadiene was observed. In this case, however, instead of 4-vinylcyclohexene and 1,5-cyclooctadiene, only butane, ethylcyclohexane, and cyclooctane were formed as hydrogenated products. This is in marked contrast to the catalysis of III, which is inactive for hydrogenation.

π-Allylnickel Halide and Electron Donors. It is well known that π-allylic complexes are converted to dynamic σ-allylic ones.[13)]

$$\pi\text{-Allyl}\cdot M\cdot X\cdot PR_3 + PR_3 \rightleftharpoons \sigma\text{-Allyl}\cdot M\cdot X\cdot(PR_3)_2$$

M: Ni and Pd. X: Halogen.

Thus, the π-allylnickel complex combined with strong electron donors was expected to show catalytic activities similar to those of the arylnickels described above. In fact, π-allylnickel bromide combined with tri-*n*-butylphosphine converted butadiene catalytically to MVCP. The results are summarized in Table 5. It is noteworthy that π-allylnickel iodide gave no MVCP but *trans*-1,4-polybutadiene. We examined the effect

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[10)] D. A. White and G. W. Parshall, *Inorg. Chem.*, **9**, 2358 (1970).

[11)] P. Heimbach, *Angew. Chem.*, **80**, 967 (1968).

[12)] W. Brenner, P. Heimbach, H. Hey, E. W. Müller, and G. Wilke, *Ann. Chem.*, **727**, 161 (1969).

[13)] G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, Methuen, London (1968). p. 46.

[14)] R. G. Miller, R. D. Stauffer, D. R. Fahey, and D. R. Parnell, *J. Amer. Chem. Soc.*, **92**, 1511 (1970).

[15)] E. O. Fischer and G. Bürger, *Z. Naturforsch.*, **166**, 77 (1961).

TABLE 5. DIMERIZATION BY π-ALLYLNICKEL BROMIDE AND ELECTRON DONORS[a)]

Expt No.	Catalyst $(\pi\text{-}C_3H_5NiBr)_2$ (mmol)	Catalyst Donor (mmol)		Products yield (%)
1	0.75	PBu_3	3	MVCP, 50
2	0.75	PPh_3	3	MVCP, 5; 1,3,6-OT, 9
3	0.75	$P(OPh)_3$	3	——
4	0.75	NEt_3	3	——

a) All reactions were carried out in 5 m*l* of benzene at 70—75°C for 40 hr. 80 mmol of butadiene was used.

of some other electron donors. Phosphite and tertiary amine were ineffective.

Reaction Mechanism. The catalysts studied by us are different from the conventional nickel catalysts, which give linear dimers in protonic solvents.[1)] The essential features of our nickel catalysts giving the five-membered cycle (I) are that they contain a halogen atom and are to be used in the presence of a controlled amount of alcohol. The cyclodimerization involves a hydrogen migration caused by a protonic compound. This is confirmed by the reaction using deuteromethanol. The dimerization was duplicated using deuteromethanol (CH_3OD) in place of methanol (CH_3OH). A monodeuterated dimer was thus obtained. Fig. 1B shows a part of the NMR spectrum. The absorptions of 3.9 to 5.3 τ were unaffected by the deuteration. The signal centered at 7.6 τ is assigned to the hydrogens on the 3-carbon atom. The analysis of this dimer using mass spectrometry and the NMR technique demonstrated that it is about 50% deuterated in the 3 position.

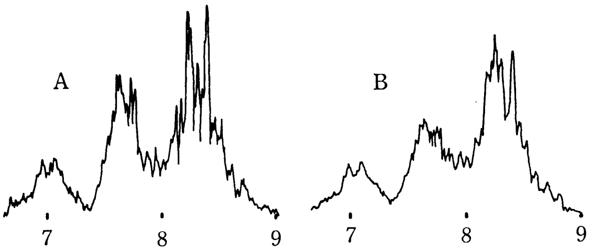
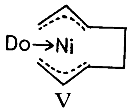


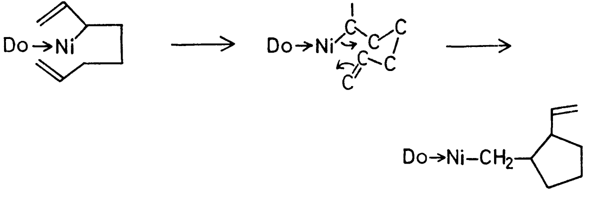
Fig. 1. NMR spectra of (A) normal- and (B) monodeuterated-MVCP.

Dimerization with nickel catalysts to cyclic or linear dimers is believed to proceed through a bis-π-allylic intermediate (V).[12)]



V

In our case, the internal insertion of a double bond into the nickel-carbon σ-bond to form a five-membered cycle has been proposed.[4)]



However, since halogen is essential to this catalyst, the structure of the intermediate of the dimerization may be more complicated.

Experimental

trans-Bis(tertiaryphosphine)dichloronickel and the bromo analog were prepared by adding the phosphine (2 mol) to a solution of the nickel halide (1 mol) in methanol. The derivatives of NO_2, SCN, and I were afforded by displacement reactions in which the appropriate metal salt was mixed with the dihalocomplex in acetone.[14)] Arylnickel complexes were prepared from a Grignard reagent according to the method of Chatt and Shaw.[8)] π-Allylnickel halides were prepared from the reaction of allyl halide with nickel carbonyl.[15)] Commercially-available *n*-butyllithium in hexane was used. *o*-Lithio-*N*,*N'*-dimethylbenzylamine was prepared from *N*, *N'*-dimethylbenzylamine and *n*-butyllithium in benzene.[7)] Commercially-available deuteromethanol was used without further purification. Tetradeuterobutadiene was prepared by H–D exchange between butadiene-β-sulfone and deuterium oxide.[9)] Commercially-available butadiene was used after drying with a 3 Å molecular sieve.

Gas-chromatographic analyses were carried out on a column, Silicon DC 550 on Celite, 1 m, at 100°C. The identification of vinylcyclohexene, cyclooctadiene, and *n*-octatrienes was done by comparing the retention time on the gas chromatogram and the infrared and NMR spectra with those of authentic samples. The identification of 2-methylenevinylcyclopentane was done by comparing the retention time and the infrared and NMR spectra of the hydrogenation product over palladium-carbon with those of *trans*-1-methyl-2-ethylcyclopentane.[16)]

*Dimerization by Bis(tri-*n*-butylphosphine)dichloronickel and* n*-Butyllithium.* Bis(tri-*n*-butylphosphine)dicloronickel, 0.67 g (1.3 mmol), was placed in a glass tube (20 mm in diameter). The tube was immediately fitted with a three-way stopcock through which solvent and reagents were introduced through a syringe. The system was placed under argon by evacuating it and filling it with argon several times. At room temperature, 5 m*l* of benzene and 1.3 mmol of *n*-butyllithium in 0.54 m*l* of *n*-hexane were added. The reaction mixture became warm and turned dark red. It was then stirred at room temperature for 30 min, and this was followed by the addition of 1.5 m*l* (40 mmol) of methanol. The solution was cooled to −78°C in a dry ice-acetone bath; then, 3.9 g (70 mmol) of liquefied butadiene was added and the tube was sealed with a flame. The reaction mixture was heated at 65—70°C for 40 hr. Distillation without separation of the catalyst gave 2.7 g (70%) of MVCP as a colorless liquid; bp 121—122°C, n_D^{24} 1.4553. (lit,[17)] n_D^{27} 1.4557)

General Procedure for Dimerization by Various Nickel Catalysts and Organolithium. The above procedure is illustrative. The amounts of reagents used and the reaction conditions are shown in Table 1. The reactions were carried out in the glass tube described above. The yields of the products were determined gas-chromatographically. The separation of the products, if necessary, was carried out by preparative gas chromatography, and the structure of the products was confirmed by comparing the NMR and infrared spectra of the products with those of authentic samples.

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16) W. D. Huntsman, V. C. Solomon, and D. Eros, *J. Amer. Chem. Soc.*, **80**, 5455 (1958).

17) W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, **27**, 1988 (1962).

Dimerization by trans-*Bis(triethylphosphine)chloro-(*o*-tolyl)-nickel.* In the glass tube, 0.36 g (0.85 mmol) of *trans*-bis(triethylphosphine)chloro-(*o*-tolyl)nickel was dissolved in 1.5 m*l* of benzene under an argon atmosphere; this was followed by the addition of 0.85 m*l* of methanol. The solution was cooled to −78°C in a dry ice-acetone bath, and then 3.5 g of liquefied butadiene were added. The sealed tube was heated at 70—75°C for 40 hr. Distillation gave 2.4 g of dimers. Gas-chromatographic analysis showed the presence of MVCP (86%), VCH (9%), and COD (5%).

The above procedure is illustrative. Reactions by other arylnickels are summarized in Table 2.

Reaction of Ia with CD_3OD and Dimerization of Butadiene. In a glass tube 0.61 g (1.5 mmol) of IIIa was placed. Under a nitrogen atmosphere 0.9 g of benzene and 1 m*l* of CD_3OD were added. The mixture was cooled in a dry ice-acetone bath to −78°C, and then 10 mmol of liquefied butadiene were added. The tube was heated at 70—75°C for 42 hr. Gas-chromatographic analysis (2 m Apiezon, 100°C), using benzene as an internal standard, showed the formation of 0.11 g (85% based on IIIa) of toluene and 0.48 g of MVCP. After the removal of the catalyst by distillation, toluene was separated by preparative gas chromatography. Mass spectroscopic analysis showed C_7H_7D of *ca.* 95% isotopic purity.

Reaction of IIIb with Hydrogen and Dimerization of Butadiene. In a 30-m*l*, stainless-steel pressure reactor, 0.21 g (0.41 mmol) of IIIb was dissolved in 2 m*l* of benzene. The reactor was cooled to −78°C, and then 10 mmol of liquefied butadiene was added under a nitrogen atmosphere. Hydrogen was charged up to 30 kg/cm^2 at that temperature. The mixture was heated at 70—75°C for 24 hr. Gas-chromatographic analysis showed the formation of toluene (33% yield on IIIb) and MVCP (5% yield on butadiene). From the reaction mixture, a yellow-brown solid was obtained. Recrystallization from methanol gave 0.03 g of the pure IIIb as yellow-brown needles, mp 102—103°C (lit,[8] mp 102—103°C).

Reaction of IV and Reaction of Butadiene Catalyzed by IV. All reactions using methanol (or without methanol) or hydrogen were carried out in ways similar to those described above in the glass tube or the stainless-steel pressure reactor respectively. The products were identified by comparing the infrared spectra and retention time with those of authentic samples. The formation of butane, ethylcyclohexane, and cyclooctane was confirmed by a study of the infrared and mass spectra.

Dimerization by π-Allylnickel Halide and an Electron Donor. The following procedure is a typical one. To 5 m*l* of benzene solution containing 0.75 mmol of π-allylnickel bromide, 0.61g (3 mmol) of tri-*n*-butylphosphine, 25 mmol of methanol and 80 mmol of liquefied butadiene were added, in this order. The glass tube was then sealed and heated at 70—75°C for 40 hr. Distillation gave MVCP in a 50% yield.

Dimerization by other π-allylnickel compounds were carried out in a similar way. The reaction conditions are summarized in Table 5.