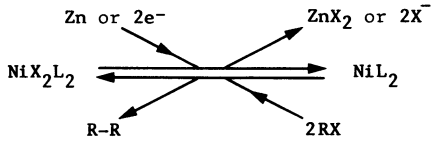
The *in situ*-Generated Nickel(0)-catalyzed Homo-coupling of Alkenyl Halides with Zinc Powder. A Specific Outcome in Stereochemistry

Kentaro TAKAGI,* Harutaka MIMURA,† and Saburo INOKAWA†
College of Liberal Arts and Science, Okayama University, Tsushima, Okayama 700
†*Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700*
(Received June 13, 1984)

The catalytic activity of nickel(0) generated *in situ* from nickel(II) salt was examined in a dehalogenative coupling of alkenyl halides with zinc powder. The reaction of alkenyl bromides took place provided that potassium iodide was present to assist the reduction of nickel(II) with zinc powder, and also to convert the alkenyl bromides to the corresponding alkenyl iodides. A speculative view concerning the disproportionation step is advanced in an attempt to explain the unique stereochemistry observed.

It is well known that a variety of transition-metal complexes react readily with such organic halides as aryl halides and alkenyl halides to afford dehalogenative coupling products, biaryls, and conjugated alkadienes.[1] The excellent reactivities of nickel(0) complexes to the Ullmann-type coupling have previously been proved, but the synthetic usefulness of the nickel-assisted reaction has been limited since stoichiometric amounts of unstable complexes are required to perform the reaction.[2] Recently, however, a catalytic procedure has been devised in which the dehalogenative coupling of aryl halides proceeds by the utilization of chemical reducing agents like zinc powder or electrochemically in the presence of a small amount of a stable nickel(II)-phosphine complex as a catalyst.[3]



L=PPh_3,[3] PR_3,[5] none[4]
R=Aryl, Alkenyl, Heteroaromatic

In a previous paper, we reported that a simple, phosphine-free nickel(II) compound like nickel(II) chloride or bromide is more effective for the dehalogenative coupling of aryl halides with zinc powder than the nickel(II)-phosphine complex.[4] In this paper, the simple nickel(II) catalyst is applied to a dehalogenative coupling of alkenyl halides with zinc powder hoping thus to achieve a convenient method of synthesizing conjugated dienes from alkenyl halides, but also to obtain insight into the mechanism of this kind of coupling reaction through the product analysis.[6]

Results and Discussion

Reaction Conditions. The reaction of 2-bromo-1,1-diphenylethene (**1**) with zinc powder in the presence of nickel(II) salt was examined under various conditions (Eq. 1). The results are listed in Table 1. It is noteworthy that the coupling product, 1,1,4,4-tetraphen-

$$\underset{\mathbf{1}}{2\,Ph_2C{=}CHBr} + Zn \xrightarrow{NiX_2} \underset{\mathbf{2}}{Ph_2C{=}CH{-}CH{=}CPh_2} + ZnX_2 \quad (1)$$

TABLE 1. NICKEL(0)-CATALYZED HOMO-COUPLING OF **1**[a]

Run	Nickel(II)[b]	Additive		Solvent	Time	**2**[c]
	Ni/**1**[d]	KI/**1**[d]	TMTU/**1**[d]		h	%
1	0.4	2.0	0	HMPA	4	96
2	0.4	2.0	0	NMP	4	94
3	0.4	2.0	0	TMU	4	90
4	0.4	2.0	0	DMF[e]	4	0
5	0.4	2.0	0	THF[f]	4	4
6	0.4	2.0	0	Toluene	4	0
7[g]	0.4	2.0	0	HMPA	7	99
8[h]	0.4	2.0	0	HMPA	10	72
9	0.4	0	0	HMPA	4	0
10	0.04	2.0	0	HMPA	3	97
11	0.04	0.4	0	HMPA	12	18
12	0.04	2.0	0.04	HMPA	1	89
13	0.04	0.4	0.04	HMPA	12	85

a) In the presence of 0.25 mmol of **1** and 0.25 mmol of Zn in 0.5 cm^3 of the solvent at 40 °C under nitrogen. b) Crystalline $NiCl_2$ (0.10 mmol) or 0.17 mol dm^{-3}-DMF solution of $NiBr_2$ (0.01 mmol) was used. c) Yields based on using **1** were determined by GLC using internal standards. d) Molar ratio. e) *N,N*-Dimethylformamide. f) Tetrahydrofuran. g) Run at 20 °C. h) Run using 0.15 mmol of Zn.

yl-1,3-butadiene (**2**), was obtained only in the runs where potassium iodide was present in the reaction mixture (Runs 1 and 9). This fact probably suggests that the metallic nickel generated *in situ* acted as an active catalyst, since the presence of potassium iodide is critical to reduce a nickel(II) salt with zinc powder under the conditions examined.[4] Thus, in the presence of catalytic amounts (0.04—0.4 molar equivalents to **1**) of nickel(II) salt and potassium iodide (2.0 molar equivalents to **1**), the coupling reaction proceeded smoothly using a stoichiometric amount of or a little more (0.6—1.0 molar equivalents to **1**) of zinc powder in such a solvent as hexamethylphosphoric triamide (HMPA), *N*-methyl-2-pyrrolidone (NMP) or 1,1,3,3-tetramethylurea (TMU) under mild conditions (20—40 °C) to afford **2** in a high yield. Thiourea (TU) or 1,1,3,3-tetramethylthiourea (TMTU), which assists the reduction of nickel(II) salt with zinc powder in the same manner as potassium iodide,[7] accelerated the reaction (Runs 1 and 11—13 and Table 2).

The results from various alkenyl halides are listed in Table 2. All the alkenyl bromides and iodides examined gave coupling products in fair to excellent yields, whereas alkenyl chlorides gave such products in extremely poor yields (Runs 16 and 17). No substitution pattern (α-, or β-substitution, α,β-, or β,β'-disubstitution, or functional group) significantly influenced the total reactivities. Unfortunately, the coupling products from β-substituted alkenyl halides always consisted of geometrical isomers (Runs 22—29). However, the major products were the desired ones, which were, in certain cases, obtained in geometrically pure forms from such mixtures after a simple procedure of purification (Runs 25, 26, and 28).[8]

Although readily available alkenyl bromides were the substrates of choice in most experiments, they might not afford coupling products directly. That is, under the present conditions, alkenyl bromides are known to react readily with iodide ions to yield the corresponding alkenyl iodides,[9] and, in fact, interrupted experiments showed that alkenyl bromides turned rapidly to alkenyl iodides (Run 35 in Table 3), and subsequently to coupling products at diminished rates (Runs 34 and 1). Furthermore, the reactions of alkenyl iodides did not necessarily need the presence of potsssium iodide in the reaction mixture if TU or TMTU was present in the place of potassium iodide (Runs 39 and 43).

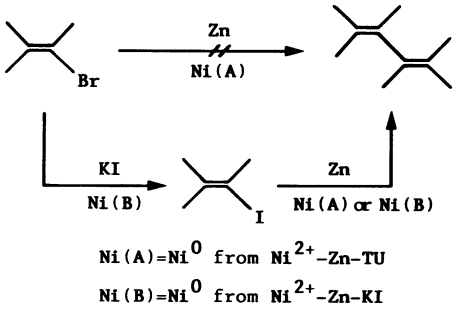


TABLE 2. NICKEL(0)-CATALYZED HOMO- COUPLING OF ALKENYL HALIDES[a]

Run	R^1	R^2	R^3	X	Temp °C	Time h	Alkadiene[b] %	Composition[b] (*E*,*E*)/(*E*,*Z*)/(*Z*,*Z*)
14	Ph	Ph	H	I	40	1.5	(96)	
15	Ph	Ph	H	Br	40	7	78	
16	CH_3	CH_3	H	Br	40	9	74	
17	CH_3	CH_3	H	Cl	40	24	(7)	
18[c]	$-(CH_2)_5-$		H	Br	40	5	72	
19[c]	H	$-(CH_2)_5-$		Br	40	6	40	
20[d]	H	$-(CH_2)_6-$		Br	50	2	80	
21[d]	H	H	CH_3	Br	50	1.5	(38)	
22	CH_3	H	H	Br	50	0.5	(64)	0/6/94
23	Ph	H	H	Br	40	2	(76)	4/30/66
24	H	Ph	H	Br	40	1	(78)	90/10/0
25	H	*p*-$CH_3C_6H_4$	H	Br	40	7	57	
26	H	*p*-ClC_6H_4	H	Br	40	4	48	
27	CH_3O_2C	H	H	Br	25	1.5	(90)	12/19/69
28	CH_3O_2C	H	H	Br	40	5	79	
29	CH_3O_2C	H	H	I	25	2	(90)	7/19/64
30	H	*p*-ClC_6H_4	H	Br	40			71/29/0
31	H	Ph	H	Br	40			78/22/0
32	H	*p*-$CH_3C_6H_4$	H	Br	40			82/18/0
33	Ph	H	H	Br	40			7/34/59

a) In the presence of 0.25 mmol of alkenyl halide in 0.5 cm^3 of HMPA (Runs 14, 17, 21—24, 27, and 29—33) or 1.0—10 mmol of alkenyl halide in 2—20 cm^3 of HMPA (Runs 15, 16, 18—20, 25, 26, and 28) under nitrogen. The molar ratios of the components were as follows: RX/$NiCl_2$/Zn/KI=1.0/0.4/1.0/2.0 (Runs 15—27 and 29), RX/$NiBr_2$/Zn/KI=1.0/0.04/1.0/2.0 (Runs 14 and 30—33), or RX/$NiBr_2$/Zn/KI=1.0/0.02/0.5/2.5 (Run 28). b) Isolated yields after purification. Yields in parentheses and compositions of isomers were determined by GLC using internal standards. c) Run with TMTU (molar ratio of TMTU/Ni=0.1). d) Run with TU (molar ratio of TU/Ni=0.1).

TABLE 3. COMPARISON OF REACTIVITIES OF ALKENYL BROMIDES WITH THOSE OF ALKENYL IODIDES IN NICKEL (0)-CATALYZED HOMO-COUPLING[a)]

Run	$R^1R^2C{=}CHX$			Additive		Time	Alkadiene[b)]
	R^1	R^2	X	KI	TMTU or TU	h	%
1	Ph	Ph	Br	+	−	4	96
34	Ph	Ph	Br	+	−	1.5	28[c)]
35	Ph	Ph	Br	+	−	0.5	1[d)]
36	Ph	Ph	Br	−	+	4	1[e)]
9	Ph	Ph	Br	−	−	4	0
12	Ph	Ph	Br	+	+	1	89
37	Ph	Ph	I	+	−	3.5	90
38	Ph	Ph	I	+	+	1.5	79
39	Ph	Ph	I	−	+	3.5	77
40	Ph	Ph	I	−	−	4	2[f)]
27	CH_3O_2C	H	Br	+	−	1.5	90[g)]
41	CH_3O_2C	H	Br	−	+	1.5	11[g)]
42	CH_3O_2C	H	Br	−	−	1.5	0
43	CH_3O_2C	H	I	−	+	2	78[g)]

a) In the presence of 0.25 mmol of alkenyl halide in 0.5 cm^3 of HMPA at 40 °C (Runs 34—42) or at 25 °C (Run 43) under nitrogen. The molar ratios of the components were as follows: $RX/NiCl_2/Zn/KI$(when used)/TMTU(Runs 36, 38, and 39) or TU(Runs 41 and 43)=1.0/0.4/1.0/2.0/0.04. b) Yields were determined by GLC using internal standards. c) The conversion was 96%. The yield of 2-iodo-1,1-diphenylethene was 62%. d) The conversion was 78%. The yield of 2-iodo-1,1-diphenylethene was 76%. e) The conversion was 6%. f) The conversion was 3%. g) Mixture of geometrical isomers.

This result is in marked contrast with that of the reaction of alkenyl bromides, where potassium iodide could not be replaced by TU or TMTU (Runs 36 and 41). These facts probably suggest that alkenyl iodides are reactive toward the coupling reaction, while alkenyl bromides are essentially not reactive under the conditions examined.

Stereochemistry. As is shown in Table 2, the reaction took place with some isomerization at the double bond. Although the low stereoselectivity considerably restricted the synthetic utility, the unique stereochemistry observed obviously ruled out the random scrambling of the configuration at sp^2-carbon; one of the two double bonds in a produced diene invariably retained the original geometry at the double bond except for the methyl 3-haloacrylates. For example, (*Z*)-1-bromopropene afforded (*Z,Z*)-2,4-hexadiene mainly, plus (*E,Z*)-isomer as a minor product, but little of the (*E,E*)-isomer (Run 22). It is apparent that the extent of concomitant isomerization ((*E,Z*)/(*E,E*) from (*E*)-alkenyl halide or (*E,Z*)/(*Z,Z*) from (*Z*)-alkenyl halide) was affected by both the steric and electronic effects of substituents bonded to the β positions. Then, the reaction of *p*-substituted β-bromostyrene was undertaken in order to examine the electronic effect on the composition of geometrical isomers exactly. Since the (*E,Z*)-isomer tended to isomerize to the (*E,E*)-isomer under the present reaction conditions, the composition at zero conversion had been determined (see Experimental). The results clearly showed that the extent of the concomitant isomerization increased with the increase in the electron-withdrawing ability of the substituents (Runs 30—32).

Reaction Path. For a nickel(0) or palladium(0)-assisted dehalogenative coupling of aryl halides or alkenyl halides, sequential steps of oxidative addition (Eq. 2), disproportionation (Eq. 3), and reductive elimination (Eq. 4) had been proposed as a reaction path:[4,10,11)]

$$\mathrm{Ni(0)} + \mathrm{RX} \rightleftharpoons \mathrm{R{-}Ni{-}X}, \qquad (2)$$

$$\mathrm{R{-}Ni{-}X} \longrightarrow 1/2\,\mathrm{R{-}Ni{-}R} + 1/2\,\mathrm{NiX_2}, \qquad (3)$$

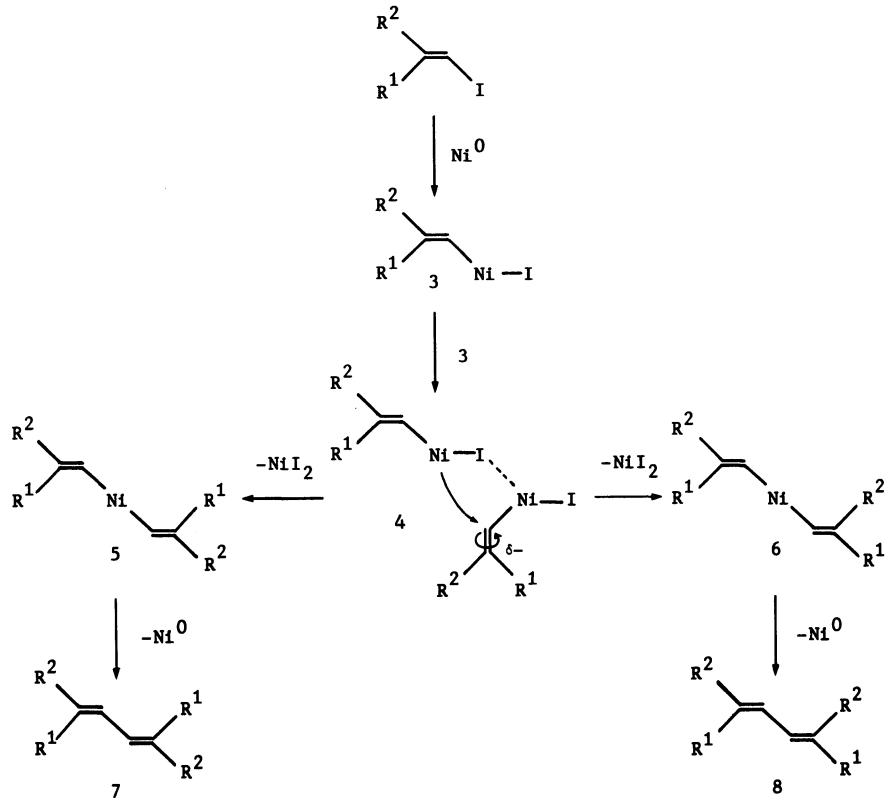
$$\mathrm{R{-}Ni{-}R} \longrightarrow 1/2\,\mathrm{R{-}R} + 1/2\,\mathrm{Ni(0)}. \qquad (4)$$

Each step is well-known and is frequently encountered in organotransition-metal chemistry. In our reaction, RX represents alkenyl iodides, and the nickel(II) generated in Eq. 3 may react further with excess zinc powder in the presence of potassium iodide, TU, or TMTU to regenerate the nickel(0) to ensure the catalytic cycle (Eq. 5). Some comments can be

$$\mathrm{NiX_2} + \mathrm{Zn} \xrightarrow{\text{KI or TU}} \mathrm{Ni(0)} + \mathrm{ZnX_2} \qquad (5)$$

made based on the obtained results.

The observed difference in reactivities between alkenyl bromides and alkenyl iodides may partly come from the difference in the bridging efficiencies of the halogen atoms. It is known that an iodide ligand can bridge two metal species far more effectively than a bromide ligand.[12)] Therefore, an iodide ligand in an oxidative adduct (**3**) may bring two nickel atoms close to (**4**), and such an association should be favorable for the succeeding disproportionation.



It has been established that the oxidative addition of alkenyl halides to low-valent transition-metal complexes proceeds with a retention of the configuration of the alkenyl groups,[13] and it is also believed that reductive elimination proceeds with the retention of the configuration of alkenyl ligands.[14] Therefore, the observed specific geometrical isomerization possibly took place at a stage of disproportionation; the double-bond character of the transferred alkenyl ligand might be partly released at the same stage, and, consequently, two kinds of dialkenylnickel complexes (**5** and **6**) may be produced from **3**. Another observation, that electron-withdrawing groups attached to the double bond tended to increase the ratio of isomerized diene (**8**), possibly suggests that an anionic character appeared synchronously on the transferred alkenyl ligand as the weakening of the double bond progressed.[15] Further investigations are, however, necessary to clarify the mechanistic details of this disproportionation step.

Experimental

All the reagents were used directly as obtained commercially, unless otherwise noted. The solvents were distilled and were dried over Molecular Sieve (3A). The 2-bromo-1,1-diphenylethene,[17] 2-iodo-1,1-diphenylethene,[18] 1-bromo-2-methyl-1-propene,[19] 1-bromo-1-cycloheptene,[20] 1-bromo-1-cyclooctene,[20] 1-bromomethylenecyclohexane,[21] (*E*)-β-bromostyrene (*Z*/*E*<1/99),[22] (*Z*)-β-bromostyrene (*Z*/*E*=98/2),[23] (*E*)-*p*-methyl-β-bromostyrene (*Z*/*E*<1/99),[24] (*E*)-*p*-chloro-β-bromostyrene (*Z*/*E*<1/99),[24] methyl (*Z*)-3-bromoacrylate (*Z*/*E*>99/1),[25] and methyl (*Z*)-3-iodoacrylate (*Z*/*E*>99/1),[25] were prepared according to the procedures in the literature. A Hitachi 160 gas chromatograph was used for the GLC analysis. The peak areas were determined with a Shimadzu Chromatopac 1A. The ^{1}H NMR spectra were obtained on a JOEL PMX 60 spectrometer, using Me_4Si as the internal standard. The IR spectra were recorded on a Hitachi 260-10 spectrometer. Photoisomerizations were carried out using a Rayonet Photochemical Reactor (Soutbern New England Ultraviolet Company).

General Procedure for Homo-coupling. Preparation of 1,1,4,4-Tetraphenyl-1,3-butadiene: A mixture of 2-bromo-1,1-diphenylethene (260 mg, 1.0 mmol), nickel(II) chloride (52 mg, 0.40 mmol), zinc powder (65 mg, 1.0 mmol), potassium iodide (332 mg, 2.0 mmol), and HMPA (2 cm^3) was evacuated, flushed with nitrogen, and kept at 40 °C with stirring for 7 h. To the mixture, dilute hydrochloric acid (1 mol dm^{-3}, 6 cm^3) was then added and the organic materials were extracted with a mixture of ether (10 cm^3) and chloroform (4 cm^3), washed with two portions of aqueous sodium chloride (4 cm^3), and dried over anhydrous magnesium sulfate. The subsequent evaporation of the solvents gave a pale yellow solid, which was triturated with a small amount of hexane to leave 143 mg of 1,1,4,4-tetraphenyl-1,3-butadiene (78%). Both the NMR and IR spectra were consistent with those of an authentic sample. Mp 193—196 °C (lit,[26] 207—210 °C). Found: C, 94.00; H, 6.07%. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19%.

2,5-Dimethyl-2,4-hexadiene: Mp 13—15 °C (lit,[27] 14.5 °C). Found: C, 86.68; H, 12.67%. Calcd for 0.9935 C_8H_{14}: C, 86.62; H, 12.73%.

1,1'-(1,2-Ethanediylidene)biscyclohexane: Mp 42—44 °C (lit,[28] 45—47 °C). Found: C, 88.47; H, 11.60%. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65%.

1,1'-Bi(1-cycloheptenyl): Bp 110—113 °C/1.5 mmHg (1 mmHg=133.322 Pa) (lit,[29] 133 °C/10 mmHg). Found: C,

88.57; H, 11.56%. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65%.

1,1'-Bi(1-cyclooctenyl): Mp 38 °C (lit,[30] 43 °C). Found: C, 87.73; H, 11.93%. Calcd for $C_{16}H_{26}$: C, 88.00; H, 12.00%.

Preparation of (E,E)-1,4-Bis(4-methylphenyl)-1,3-butadiene: A mixture of (*E*)-*p*-methyl-β-bromostyrene (493 mg, 2.5 mmol), nickel(II) chloride (130 mg, 1.0 mmol), zinc powder (163 mg, 2.5 mmol), potassium iodide (880 mg, 5.0 mmol), and HMPA (2.5 cm^3) was kept at 40 °C for 6 h with stirring under nitrogen. Subsequent treatment similar to that described above gave 290 mg of 1,4-bis(4-methylphenyl)-1,3-butadiene (1:5 mixture of (*E,Z*)- and (*E,E*)-isomers). Recrystallization from ethanol gave 168 mg of pure (*E,E*)-diene (57%). The absence of (*E,Z*)-diene was ascertained by means of GLC. The NMR spectrum was consistent with the previously reported one.[31] Mp 210—211 °C (lit,[32] 198 °C). IR (KBr) 994, 852, and 796 cm^{-1}. Found: C, 92.88; H, 7.45%. Calcd for $C_{14}H_{10}$: C, 92.26; H, 7.74%.

(E,E)-1,4-Bis(4-chlorophenyl)-1,3-butadiene:[33] Mp 214—215 °C. IR (KBr) 1093, 997, 855, and 801 cm^{-1}. ^1H NMR (THF-d_8) δ=6.2—7.1 (m, 4H, olefinic H), and 7.4 (s, 8H, aromatic H). Found: C, 69.89; H, 4.63%. Calcd for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40%.

Dimethyl (Z,Z)-2,4-Hexadienedioate: Mp 70.5—72 °C (lit,[34] 73 °C). Found: C, 56.42; H, 5.87%. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92%.

Composition of Geometrical Isomers at Zero Conversion. The Reaction of (E)-p-Methyl-β-bromostyrene: A mixture of (*E*)-*p*-methyl-β-bromostyrene (49 mg, 0.25 mmol), nickel(II) bromide (0.059 cm^3 of 0.17 mol dm^{-3}-DMF solution, 0.01 mmol), potassium iodide (83 mg, 0.50 mmol), zinc powder (16 mg, 0.25 mmol), and HMPA (0.5 cm^3) was heated at 40 °C for 20 min. To the mixture, ether (8 cm^3) and dibenzyl ether (10 mg, internal standard) were then added. GLC analysis of the mixture showed that 0.9% of (*E,Z*)-diene and 4.5% of (*E,E*)-diene were produced. (Authentic samples of (*E,Z*)-dienes were prepared following the previously reported methods.[31,35]) In a similar mixture which had been heated for 35 min or 45 min, 3% or 5% of (*E,Z*)-diene and 16% or 28% of (*E,E*)-diene were produced. From the plot of the molar ratio of the two isomers *vs.* the total yield ((*E,Z*)/(*E,E*):yield=4.8:5.4%, 5.1:19%, 5.4:33%), the molar ratio of the two isomers at 0% was estimated to be 4.6.

References

1) See, *e.g.*, J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," 2nd ed, McGraw-Hill, New York (1977), pp. 408 and 606; P. W. Jolly, "Nickel Catalyzed Coupling of Organic Halides and Related Reactions," in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon Press, Oxford (1982), Vol. 8, p. 723.

2) M. F. Semmelhack, P. M. Helquist, and L. D. Jones, *J. Am. Chem. Soc.*, **93**, 5909 (1971); M. F. Semmelhack, P. M. Helquist, and J. D. Gorzynski, *ibid.*, **94**, 9234 (1972); M. F. Semmelhack, P. Helquist, L. D. Jones, L. Keller, L. Mendelson, L. S. Ryono, J. G. Smith, and R. D. Stauff, *ibid.*, **103**, 6460 (1981).

3) A. S. Kende, L. S. Liebeskind, and D. M. Braitsch, *Tetrahedron Lett.*, **1975**, 3375; M. Zembayashi, K. Tamao, J. Yoshida, and M. Kumada, *ibid.*, **1977**, 4089; P. W. Jennings, D. G. Pillsbury, J. L. Hall, and V. T. Brice, *J. Org. Chem.*, **41**, 719 (1976); M. Mori, Y. Hashimoto, and Y. Ban, *Tetrahedron Lett.*, **21**, 631 (1980).

4) K. Takagi, N. Hayama, and S. Inokawa, *Chem. Lett.*, **1979**, 917; *Bull. Chem. Soc. Jpn.*, **53**, 3691 (1980).

5) K. Takagi, N. Hayama, and K. Sasaki, *Bull. Chem. Soc. Jpn.*, **57**, 1887 (1984).

6) For a preliminary communication on a portion of this work, see K. Takagi and N. Hayama, *Chem. Lett.*, **1983**, 637.

7) G. P. Chiusoli and L. Cassar, *Angew. Chem. Int. Ed. Engl.*, **6**, 124 (1967).

8) Certain σ-donor ligands seem likely to improve the stereoselectivity. See Ref. 5 and P. Caubere, *Angew. Chem. Int. Ed. Engl.*, **22**, 599 (1983).

9) This reaction proceeds with a retention of the configuration; K. Takagi, N. Hayama, and S. Inokawa, *Chem. Lett.*, **1978**, 435; T. T. Tsou and J. K. Kochi, *J. Org. Chem.*, **45**, 1930 (1980).

10) G. W. Parshall, *J. Am. Chem. Soc.*, **96**, 2360 (1974); F. R. S. Clark, R. O. C. Norman, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 121; H. Matsumoto, S. Inaba, and R. D. Rieke, *J. Org. Chem.*, **48**, 840 (1983).

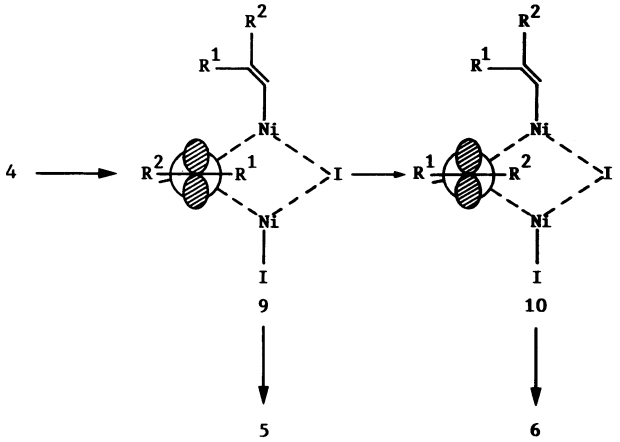
11) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 7547 (1979).

12) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, New York (1967), p. 495.

13) J. K. Stille, "Principles of Transition Metal Chemistry," in "Modern Synthetic Methods," ed by R. Scheffold, Otto Salle Verlag, Frankfurt am Main (1983), Vol. 3, p. 10.

14) Ref 13, p. 22; M. K. Loar and J. K. Stille, *J. Am. Chem. Soc.*, **103**, 4174 (1981); J. W. Labadie and J. K. Stille, *ibid.*, **105**, 6129 (1983).

15) The negative charge might arise from a nucleophilic attack of a neighboring nickel on the π* orbital of the transferred alkenyl group. Thus, structure **9** may be attributable to a canonical form of the transient intermediate. A similar structure had been proposed in organocopper chemistry to explain a stereoselective substitution.[16]



16) J. Klein and R. Levene, *J. Am. Chem. Soc.*, **94**, 2520 (1972); See also D. Dodd, M. D. Johnson, B. S. Meeks, D. M. Titchmarsh, K. N. Van Duong, and A. Gaudemer, *J. Chem. Soc., Perkin Trans. 2*, **1976**, 1261.

17) P. Lipp, *Ber.*, **56**, 567 (1923).

18) K. Takagi, N. Hayama, and T. Okamoto, *Chem. Lett.*, **1978**, 191.

19) H. A. Dieck and R. F. Heck, *J. Am. Chem. Soc.*, **96**, 1133 (1974).

20) K. Schank and B. Eistert, *Ber.*, **99**, 1414 (1966).
21) J. Wolinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).
22) L. J. Dolby, C. Wilkins, and T. G. Frey, *J. Org. Chem.*, **31**, 1114 (1966).
23) S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **75**, 2645 (1953).
24) M. K. Loar and J. K. Stille, *J. Am. Chem. Soc.*, **103**, 4180 (1981).
25) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).
26) C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **49**, 546 (1927).
27) C. Prevost, *Compt. Rend.*, **184**, 1460 (1927).
28) I. T. Harrison, B. Lythgoe, and S. Trippett, *J. Chem. Soc.*, **1955**, 4016.
29) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, **1962**, 2298.
30) D. S. Greidinger and D. Grinsburg, *J. Org. Chem.*, **22**, 1406 (1957).
31) T. V. Singh, G. P. Pandey, and K. N. Mehrotra, *Indian J. Chem.*, **18**, 8 (1979).
32) V. V. R. Rao, C. V. Kumar, and D. Devaprabhakara, *J. Organomet. Chem.*, **179**, C7 (1979).
33) E. K. Fields (Standard Oil Co.), U. S. Patent 4, 174, 447 (1979); *Chem. Abstr.*, **92**, P110636u (1980).
34) J. A. Elvidge, R. P. Linstead, P. Sims, and B. A. Orkin, *J. Chem. Soc.*, **1950**, 2235.
35) G. Zweifel, N. L. Polston, and C. C. Whitney, *J. Am. Chem. Soc.*, **90**, 6244 (1968).