Nickel-Phosphine Complex-Catalyzed Grignard Coupling. I. Cross-Coupling of Alkyl, Aryl, and Alkenyl Grignard Reagents with Aryl and Alkenyl Halides: General Scope and Limitations

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It has been established that dihalodiphosphinenickel(II) complexes exhibit extremely high catalytic activity for selective cross-coupling of Grignard reagents with aryl and alkenyl halides. This catalytic reaction can be employed in synthetic practice for reasons of simple procedures, mild reaction conditions, high yields and high purity of the coupling products, and the wide applicability to reactions involving primary and secondary alkyl (regardless of the presence or absence of β-hydrogen(s)), aryl, and alkenyl Grignard reagents and nonfused, fused, and substituted aromatic halides and haloolefins. Limitations lie in sluggish reactions between alkyl Grignard reagents and dihaloethylenes. The most effective catalysts are $[Ni\{(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2\}Cl_2]$ for alkyl and simple aryl Grignard reagents, $[Ni\{(CH_3)_2P(CH_2)_2P(CH_3)_2\}Cl_2]$ for alkenyl and allylic Grignard reagents and $[Ni\{P(C_6H_5)_3\}_2Cl_2]$ for sterically hindered aryl Grignard reagents and halides. Great stabilizing effects of phosphine ligands on the catalytic species are demonstrated by no effect observed after aging the catalyst. Organic chlorides are generally the most suitable halide in view of the reasonable reactivities and limited side reactions. Ether is favored over tetrahydrofuran as solvent. About sixty experimental results are presented and several features are discussed.

The metal-promoted coupling reactions of organic halides are one of the most attractive and useful procedures for formation of the carbon-carbon σ bond.$^{1)}$ In recent years low valent transition metals and organotransition metallics hold an important position as coupling agents for such processes. Representatives include the Ullmann reaction,$^{2,3)}$ the nickel(0)-promoted coupling reactions,$^{4-7)}$ and cross-coupling using π-allylnickel complexes,$^{6)}$ organocuprates,$^{3,8,9)}$ or organoferrates.$^{10)}$ Reactions of active organometallic reagents, such as organolithium and Grignard reagents, with transition metal salts also provide a route to the formation of the carbon–carbon bond; salts of Cu(I), Cu(II),$^{3,9,11)}$ Ag(I), and various Group VIII metals$^{12,13)}$ have been used successfully. These reactions, however, have the disadvantages that they require at least stoichiometric amounts of transition metals.

It has been known for thirty years that catalytic amounts of transition metal salts induce the coupling reaction of Grignard reagents with organic halides.$^{12)}$ In spite of a number of mechanistic studies,$^{14)}$ such catalytic reactions, "Kharasch reaction," have been seldom employed in synthetic practice, because of the formation of a complex mixture of products consisting of homo coupling products and a variety of disproportionation products in substantial amounts. Since 1971, when Tamura and Kochi reported that "soluble catalysts" consisting of silver,$^{15,16)}$ iron$^{15,16a)}$ or copper$^{15)}$ in tetrahydrofuran were extremely effective for selective coupling of Grignard reagents with organic halides, the synthetic applicability of these catalytic reactions has received much attention.$^{17b,18,19)}$ In 1972, Corriu and Masse$^{20)}$ and we$^{21)}$ independently reported that nickel–phosphine complexes catalyze the selective cross-coupling of Grignard reagents with aryl and alkenyl halides:

$$RMgX + R'X' \xrightarrow{[NiL_2Cl_2]} R\text{-}R' + MgXX'$$

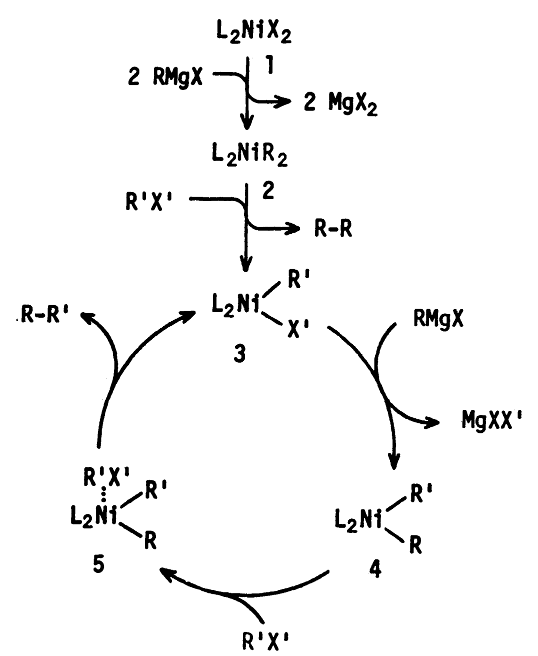
More recently, Murahashi *et al.*$^{22)}$ examined the catalytic activity of a palladium–phosphine complex for the similar Grignard cross-coupling. It was rather surprising that little attention had been paid to the catalytic activity of phosphine–modified transition metals for the Kharasch type reactions, despite extensive studies on a variety of homogeneous catalyses.

The nickel–phosphine complex-catalyzed Grignard coupling has opened up the possibility of preparing a large variety of unsaturated organic compounds from two different organic halides$^{23,24)}$ and there have been reported several characteristic features of the reaction, including the alkyl group isomerization,$^{25)}$ stereochemical aspects,$^{26)}$ asymmetric synthesis,$^{27)}$ and applications to the cyclophane synthesis$^{28)}$ and to the heterocycle coupling.$^{29)}$ In this paper, we report, aside from the mechanistic aspects, the general scope and limitations of the nickel–phosphine complex-catalyzed Grignard cross-coupling.

Results and Discussion

I. Design of a Catalytic Cycle. When undertaking this series of studies, we designed the catalytic process of the cross-coupling reaction as pictured in Scheme 1 by combining two important observations on the chemistry in relation to σ-organonickel complexes bearing "supporting" ligand(s): (1) two organic groups on a nickel complex L_2NiR_2 are released by the action of, for example, a halobenzene R′X′ to undergo coupling, along with the formation of $L_2Ni(R')(X')$,$^{30,31)}$ and (2) such a halogen–nickel bond is readily replaced by a Grignard reagent to form the corresponding organonickel bond, $L_2Ni(R')(R)$.$^{32)}$

Thus, a dihalodiphosphinenickel reacts with a Grignard reagent to form the intermediate diorganonickel complex **2** which is subsequently converted to the halo(organo)nickel complex **3** by an organic halide.



Scheme 1.

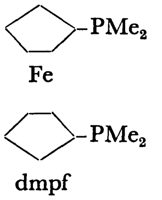
Reaction of **3** with the Grignard reagent then forms a new diorgano complex **4** from which the cross-coupling product is released by the attack of the organic halide, possibly *via* the pentacoordinated intermediate **5**, and thereby the original complex **3** is regenerated to complete the catalytic cycle.

The reaction, indeed, could be achieved by the addition of Grignard reagent to a vinylic or an aromatic halide in the presence of a catalytic amount of a dihalodiphosphinenickel and the yields were generally very high. Throughout this paper, the following phosphines and other ligands are described in their abbreviations shown here.

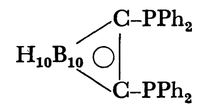
$Ph_2P(CH_2)_nPPh_2$
$n=1$, dppm
$n=2$, dppe
$n=3$, dppp
$n=4$, dppb

$Me_2P(CH_2)_2PMe_2$
dmpe

cis-$Ph_2PCH{=}CHPPh_2$
cis-dpen



dmpf



dppc

2,2′-Bipyridyl: bipy
Pyridine: py
Acetylacetonate: acac

II. Coupling of Butylmagnesium Bromide with Halobenzenes. To a mixture of chlorobenzene (1 part) and a catalytic amount of [Ni(dppp)Cl_2] (0.01—0.001 part) in anhydrous ether was added the butyl Grignard reagent (1.2 part) at 0 °C under nitrogen to give a tan clear mixture. The mixture was stirred at room temperature and a mildly exothermic reaction set in. After refluxing for 20 h and hydrolysis, GLPC analysis showed that the starting chlorobenzene was no longer present and butylbenzene was formed in quantitative yield. The product was easily isolated pure by simple distillation; there was no contamination with a structural isomer, such as *sec*-butylbenzene.

In the light of the fact that the above reaction readily goes to completion, the coupling of the butyl Grignard reagent with halobenzenes was chosen as a model reaction for the examination of the catalytic ability of various nickel–phosphine complexes and of the reactivity of halobenzenes.

TABLE 1. CATALYTIC ACTIVITY OF VARIOUS [NiL_2Cl_2] FOR CROSS-COUPLING OF n-C_4H_9MgBr WITH C_6H_5Cl[a)]

L_2	Conversion (%)[b)]	Yield (%) of n-$C_4H_9C_6H_5$[b)]
dppp	100	100
dmpf	100	94
$2Ph_3P$	91	84[c)]
$2Ph_3P$[d)]	90	50[e)]
dppe	73	79
dppe[f)]	78	77
dmpe	53	47
dppc	30	28
dppb	38	28
cis-dpen	19	20
$2Et_3P$	63	6[g)]
$2Ph_2MeP$	[h)]	4[e)]

a) Unless otherwise noted, to a mixture of C_6H_5Cl (~10 mmol), [NiL_2Cl_2] (~0.1 mmol) and anhydrous ether (10 ml) was added n-C_4H_9MgBr (~12 mmol), and then the mixture was heated for 20 h under nitrogen. b) Determined by GLPC using mesitylene as an internal standard based on the chlorobenzene used. c) Benzene 10%. d) Used as a mixture of PPh_3 (0.21 mmol) and anhydrous $NiCl_2$ (0.16 mmol). e) Benzene was not determined. f) Petroleum ether was used as additional solvent. g) Benzene 52%. h) GLPC showed the presence of a large amount of unchanged chlorobenzene.

Catalytic Activity of Various Nickel-Phosphine Complexes: Under the similar conditions, catalytic activity of various nickel(II) complexes was examined (Table 1). The catalytic activity of the nickel complexes depends strongly upon the nature of the ligands. This ligand-dependency clearly indicates that a catalytically active species does contain phosphine ligand(s) on nickel. In Table 1, the phosphine ligands are listed in the order of decreasing catalytic activity of their nickel complexes.

Bidentate phosphines as ligands exhibit much higher catalytic activity than unidentate ones; the efficiency of the bidentate phosphine ligands decreases roughly in the sequence: dppp>dmpf>dppe>dmpe>dppb>dppc>*cis*-dpen. It seems of particular interest to note that the catalytic activity depends on the length of the methylene bridge between two diphenylphosphino groups in a homologous series of $Ph_2P(CH_2)_nPPh_2$, *viz.*, $n=3>n=2>n=4$. The prominence of [Ni(dppp)Cl_2] as a catalyst is commonly observed also in different combinations of other Grignard reagents and halides (*vide infra*).

Of the unidentate phosphines as ligands, only triphenylphosphine is practically active for the coupling.

Although with [Ni(PEt$_3$)$_2$Cl$_2$] chlorobenzene is consumed to the same extent as with [Ni(PPh$_3$)$_2$Cl$_2$], benzene is formed as a major product.

The following nickel complexes and salts are practically inactive for the coupling: [Ni(PPh$_2$Me)$_2$Cl$_2$], [Ni(PPhMe$_2$)$_2$Cl$_2$], [Ni(dppm)$_2$Cl$_2$], [Ni(bipy)Cl$_2$], [Ni(py)$_2$Cl$_2$], Ni(acac)$_2$, and NiCl$_2$. With [Ni(bipy)Cl$_2$] as a catalyst the reaction mixture remained a deeply green color characteristic of diorganonickel complexes with the bipy ligand,[33] indicating that the intermediate is too stable to react further with chlorobenzene. It should be noted that an equimolar mixture of [Ni(dppe)Cl$_2$] and the dppe free ligand exhibited no catalytic activity, apparently owing to the blocking of catalytically active vacant sites on the nickel catalyst by the extra phosphine. Interestingly, Ni(acac)$_2$, which was reported to be efficient for the coupling of aryl Grignard reagents with aryl and alkenyl halides,[20] showed no activity at all for the coupling of simple alkyl Grignard reagents with chlorobenzene.

[Pd(PPh$_3$)$_2$Cl$_2$], [Pd(PEt$_3$)$_2$Cl$_2$], *cis*-[Pt(PPh$_3$)$_2$Cl$_2$], and [Co(dppp)Cl$_2$] exhibited no catalytic activity, which may be attributable primarily to the fact that chlorobenzene hardly undergoes oxidative addition to the low valent species of these metals.[31d,34] The recently reported palladium(0)catalyzed Grignard coupling may be restricted to more reactive bromides.[22]

Table 2. Effect of aging on the catalytic activity in the coupling of n-C$_4$H$_9$MgBr with C$_6$H$_5$Cl[a]

Aging time (h)	Reaction time after addition of C$_6$H$_5$Cl (h)	Conversion (%)	Yield (%)	
			C$_4$H$_9$-C$_6$H$_5$	C$_6$H$_6$
		[Ni(dppp)Cl$_2$]		
1/30	3	>99	99	trace
1	3	>99	97	trace
3.5	3	>99	>99	trace
16	3	>99	98	trace
		[Ni(PPh$_3$)$_2$Cl$_2$]		
0[b]	3	63	52	N.d.
0[b]	20	87	72	N.d.
1/20	3	78	58	22
1	3	71	55	20
16	3	53	21	N.d.
16	20	94	69	35

a) To a mixture of the catalyst (0.05 mmol) and ether (5 ml) was added n-BuMgBr in ether (6 mmol) at 0 °C. The mixture was stirred at room temperature for a given period of aging time: [Ni(dppp)Cl$_2$] gave a yellowish clear solution, while [Ni(PPh$_3$)$_2$Cl$_2$] gave a dark brown mixture. Chlorobenzene (5 mmol) was then added at room temperature in one portion and the mixture was stirred at room temperature for 30 min and then refluxed for a given period of time. After hydrolysis the mixture was analyzed by GLPC. b) To a mixture of the catalyst, chlorobenzene and ether was added the n-C$_4$H$_9$MgBr solution.

Aging of Catalysts: Stability of the catalytically active species has been examined for [Ni(dppp)Cl$_2$] and [Ni(PPh$_3$)$_2$Cl$_2$] (Table 2). Thus, a catalytic amount of the nickel complex was firstly added to the butyl Grignard reagent, the resulting mixture was allowed to stand at room temperature under nitrogen for a given period of time, and then chlorobenzene was added. Rather surprisingly, the yellowish clear catalyst solution generated from [Ni(dppp)Cl$_2$] and the butyl Grignard reagent did not decrease in efficiency even after 16 h at room temperature. Upon addition of chlorobenzene at this point, an exothermic reaction set in and exactly the same results were obtained as the case where the Grignard reagent was finally added to a mixture of chlorobenzene and [Ni(dppp)Cl$_2$] (without aging).

In contrast with this result, a dark-brown mixture generated from [Ni(PPh$_3$)$_2$Cl$_2$] and the butyl Grignard reagent gradually diminished in activity with time. However, the prolonged coupling-reaction time led to essentially the same results as observed in experiments with no aging.

These results demonstrate a great stabilizing effect on the catalytically active species by, notably, the bidentate phosphine ligand.

Reactivity of Halobenzenes: Reactivity of halobenzenes, from fluoro- to iodo-benzene, was examined for the coupling with the butyl Grignard reagent in the presence of [Ni(dppp)Cl$_2$] or [Ni(dppe)Cl$_2$] as catalyst.

Table 3. Reactivity of halobenzenes in the coupling with n-C$_4$H$_9$MgBr[a]

X in C$_6$H$_5$X	Reaction time (h)	Conversion[b] (%)	Yield (%)[b]	
			n-C$_4$H$_9$C$_6$H$_5$	C$_6$H$_6$
		[Ni(dppp)Cl$_2$]		
F	2	c)	31	c)
Cl	1	54	50	trace
Cl	2	80	81	trace
Cl[d]	3	93	95	trace
Br	1	47	39	6
Br	2	56	46	7
Br	4.5	62	54	9
I[d]	3[e]	99	80	19[f]
		[Ni(dppe)Cl$_2$]		
F	20	c)	18	c)
Cl	20	59	60	trace
Br	20	75	51	23

a) To a mixture of C$_6$H$_5$X (~5 mmol) and [NiL$_2$Cl$_2$] (~0.05 mmol) in 15 ml of ether was added a solution of n-C$_4$H$_9$MgBr (6.3 mmol) in ether at 0 °C and then refluxed for a given period of time, unless otherwise noted. b) Determined by quantitative GLPC based on C$_6$H$_5$X. c) Conversion and benzene could not be determined by GLPC, because C$_6$H$_5$F and benzene appeared in a single peak. d) Carried out in a 10-mmol scale. e) The reaction occurred vigorously even at 0 °C. Stirred at room temperature for 3 h. f) Biphenyl 2%.

The reactivity of halobenzenes appears to be dependent upon the nature of the catalyst. Thus, while with [Ni(dppp)Cl$_2$] a rather abnormal reactivity order PhI>PhCl>PhBr>PhF was observed, with [Ni(dppe)Cl$_2$] the order was normal: PhBr>PhCl>PhF (Table 3). However, from the competitive reactions (Table 4), the normal reactivity order was observed also with [Ni(dppp)Cl$_2$]. This strange behavior is difficult to

Table 4. Competitive reaction between two kinds of halobenzenes with n-C_4H_9MgBr[a)]

Combination of C_6H_5X	Reaction time (h)	Conversion (%)[b)] run 1	2	3
	[Ni(dppp)Cl_2]			
C_6H_5F	1	25	24	26
C_6H_5Cl		52	58	47
C_6H_5Cl	1	25	25	24
C_6H_5Br		45	45	46
	[Ni(dppe)Cl_2]			
C_6H_5F	20	19	20	—
C_6H_5Cl		58	58	—
C_6H_5Cl	20	29	30	29
C_6H_5Br		78	80	75[c)]

a) For the procedure, see footnote a) of Table 3: C_6H_5X, 5 mmol each; Grignard reagent, 6.4 mmol; catalyst, ~0.05 mmol; ether, 15 ml. b) Determined by GLPC. c) Benzene 22%.

explain, but implies that there are two or more rate-limiting steps in the reaction.

In view of the extremely low reactivity of organofluoro compounds toward metals, it seems of particular interest that even fluorobenzene, if not completely, does undergo the metal-catalyzed coupling reaction. To our knowledge, oxidative addition of a fluorine–carbon bond to a transition metal complex has not yet been reported.[31e)] Iodobenzene reacts very vigorously even at 0 °C, with biphenyl being formed only in trace amounts. The formation of benzene also depends on the nature of the halides in the order: $PhF < PhCl \ll PhBr < PhI$.

The foregoing results demonstrate that chlorobenzene exhibits a reasonable reactivity, gives a high yield of the cross-coupling product with no by-product, and hence is the halide that was chosen for the present reaction. The superiority of chlorobenzene as a halide is particularly worthy of note, because bromides or iodides have been used so far in almost all types of coupling reactions of organic halides using metals as coupling agents.

Table 5. Solvent effects on the coupling of C_2H_5MgBr with C_6H_5Cl[a)]

Solvent	Reaction time (h)	Conversion[b)] (%)	Yield (%)[b)] $C_2H_5C_6H_5$	C_6H_6
		[Ni(dppe)Cl_2]		
$(C_2H_5)_2O$	16	99	98	trace
THF	22	78	66	11
		[Ni(PPh_3)$_2$$Cl_2$]		
$(C_2H_5)_2O$	16	86	59	20
THF	22	51	10	35

a) C_6H_5Cl, 12 mmol; C_2H_5MgBr, 12—14 mmol; catalyst, 0.1 mmol; solvent 20 ml. Refluxed for a given period of time. b) Determined by GLPC.

Solvent Effects: Grignard reagents are usually prepared either in diethyl ether or in THF, and hence these two solvents were examined in regard to solvent effects. The effects on the coupling of the ethyl Grignard reagent with chlorobenzene in the presence of [Ni(dppe)Cl_2] or [Ni(PPh_3)$_2$$Cl_2$] as catalyst are summarized in Table 5. For both of the catalysts used, the reactions tend to proceed considerably faster in diethyl ether than in THF and the undesired product, benzene, is formed in a larger amount in THF. Therefore, diethyl ether is better than THF as a solvent.

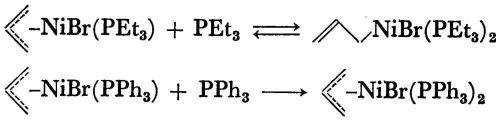
Although reasons for the observed solvent effects are not clear presently, it seems likely that a more basic solvent ($THF > Et_2O$) interacts more tightly with the nickel center to prevent the approach of the halide and/or the Grignard reagent to it.

III. Coupling of Other Alkyl, Aryl, and Alkenyl Grignard Reagents with Aryl and Alkenyl Halides. The generality of the nickel-phosphine complex-catalyzed Grignard cross-coupling is apparent from the results summarized in Tables 6 and 7.

Catalytic Activity of Nickel–Phosphine Catalysts: Table 6 summarizes a comparison of the catalytic activities of some selected nickel-phosphine complexes for several representative combinations of Grignard reagents and organic halides. The efficiency of the catalysts appears to be dependent mainly on the structure of the organic moieties of Grignard reagents and little on the nature of the organic halides. Several features are worthy of note.

Here again, [Ni(dppp)Cl_2] is the most effective for primary alkyl (regardless of the presence or absence of β-hydrogen(s) (*vide infra*)), secondary alkyl, and aryl Grignard reagents.

Two rather exceptional cases arise. Firstly, [Ni(dmpe)Cl_2], which contains a basic bidentate ligand, is the most suitable catalyst for allylic and vinylic Grignard reagents. Interestingly, both the Grignard reagents contain an unsaturated group potentially capable of coordination with the nickel center of the catalyst. This exceptional behavior may be related to the observations that basic ligands can cause π–σ conversion of an allyl-nickel complex, whereas less basic ligands form a relatively stable five-coordinate π-allyl-nickel complex, as exemplified by the following equations:[35)]

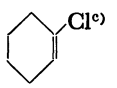

-NiBr(PEt_3) + PEt_3 ⇌ NiBr(PEt_3)$_2$
-NiBr(PPh_3) + PPh_3 ⟶ -NiBr(PPh_3)$_2$

It should be noted that the former is coordinatively unsaturated, while the latter saturated.

The other exceptional case is observed in the coupling of the mesityl Grignard reagent for which a unidentate phosphine is better than bidentate phosphine ligands. It has long been recognized that *ortho*-substituted aryl-nickel complexes are of high kinetic stability[36)] and hence the enhanced stability of a mesityl-nickel intermediate to be expected with a bidentate phosphine ligand may be responsible for the diminished reaction rates in this case. A reversible ligand dissociation from a dimesitylnickel complex of a unidentate phosphine has been observed.[37)]

The pronounced differences in catalytic activity between [Ni(dppp)Cl_2] and [Ni(dppe)Cl_2] were observed for the coupling of the trimethylsilylmethyl Grignard reagent with chlorobenzene; with the former catalyst the coupling product was obtained in quantitative yield.

TABLE 6. CATALYTIC ACTIVITY OF $[NiL_2Cl_2]$ FOR THE COUPLING OF VARIOUS GRIGNARD REAGENTS WITH ORGANIC HALIDES[a]

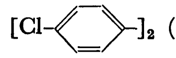
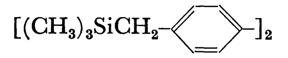
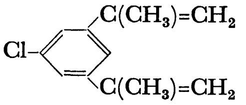
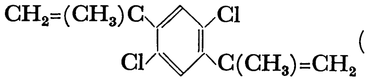
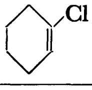
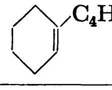
RMgX	Halide	Yield (%) of coupling product[b]				
		dppp	dppe	dmpe	$2Ph_3P$	$2Et_3P$
n-PrMgBr	PhCl[c]	94	—	19	72[d]	—
i-PrMgCl	PhCl[c,e]	89	74	81	20[f]	trace
MeMgBr	PhCl[c]	100	65[g]	—	—	—
MeMgBr	 [c]	98	24	—	—	—
Me_3SiCH_2MgCl	PhCl[c]	100	0	16[h]	53[i]	95
CH_2=$CHCH_2MgBr$	PhBr[j]	trace	trace	63	36	37[k]
CH_3CH=CHMgBr	PhBr[l,m]	16	—	84	15	—
Mes–MgBr[n]	PhBr[c]	78	—	85	96	—
n-$C_8H_{17}MgCl$	CH_2=CHCl	—	95	—	72	48
PhMgBr	CH_2=CHCl	—	89	—	63	58

a) $[NiL_2Cl_2]/RMgX/R'X' \simeq 10^{-2}/1.2/1.0$. The reactions were carried out in a 5—10 mmol scale in diethyl ether, unless otherwise noted. b) Determined by quantitative GLPC based on the organic halide. c) Refluxed for 20 h. d) Benzene 20%. e) For the alkyl group isomerization, see Ref. 25. f) Benzene 24%. g) Recovered PhCl 24%. h) Refluxed for 37 h. i) Recovered PhCl 41%. j) Refluxed for 50 h. k) L_2=2n-Bu_3P. l) For 40 h at 50 °C in THF. m) Stereochemistry has been discussed in Ref. 26. n) Mes=mesityl.

TABLE 7. COUPLING OF ALKYL, CYCLOALKYL, ARYL, ALKENYL GRIGNARD REAGENTS WITH ARYL AND ALKENYL HALIDES:[a] CATALYST A; $[Ni(dppp)Cl_2]$, B; $[Ni(dppe)Cl_2]$, C; $[Ni(PPh_3)_2Cl_2]$, D; $[Ni(dmpe)Cl_2]$

Halide (mmol)	Grignard reagent (mmol)	Catalyst (mmol)	Time,[b] h	Product(s)	Yield[c] (%)
Aryl halide					
1,2-$Cl_2C_6H_4$ (200)	n-C_4H_9MgBr (500)	A (0.5)	6	1,2-$(C_4H_9)_2C_6H_4$ 1,2-$C_4H_9C_6H_4Cl$	79—83 *ca.* 10
1,2-$Cl_2C_6H_4$ (53)	n-C_4H_9MgBr (120)	B (0.38)	20	1,2-$(C_4H_9)_2C_6H_4$ 1,2-$C_4H_9C_6H_4Cl$	89 *ca.* 5
1,3-$Cl_2C_6H_4$ (51)	n-C_4H_9MgBr (120)	B (0.39)	20	1,3-$(C_4H_9)_2C_6H_4$ 1,3-$C_4H_9C_6H_4Cl$	94 < 5
1,4-$Cl_2C_6H_4$ (9.3)	n-C_4H_9MgBr (24)	B (0.04)	20	1,4-$(C_4H_9)_2C_6H_4$ 1,4-$C_4H_9C_6H_4Cl$	95 < 5
1,4-$Cl_2C_6H_4$ (102)	n-C_4H_9MgBr (224)	C (0.90)	26	1,4-$(C_4H_9)_2C_6H_4$	30[d]
1,2-$ClC_6H_4CH_3$ (49)	n-C_4H_9MgBr (72)	B (0.23)	20	1,2-$C_4H_9C_6H_4CH_3$	37
1,3-$ClC_6H_4CH_3$ (51)	n-C_4H_9MgBr (72)	B (0.22)	20	1,3-$C_4H_9C_6H_4CH_3$	48
1,4-$ClC_6H_4CH_3$ (48)	n-C_4H_9MgBr (72)	B (0.24)	20	1,4-$C_4H_9C_6H_4CH_3$	58
1,4-$ClC_6H_4CH_3$ (10)	n-C_4H_9MgBr (13)	A (0.05)	15	1,4-$C_4H_9C_6H_4CH_3$	(39)[e]
1,4-$ClC_6H_4OCH_3$ (24)	n-C_4H_9MgBr (38)	A (0.07)	6	1,4-$C_4H_9C_6H_4OCH_3$	(90)
1,4-$ClC_6H_4CF_3$ (12)	n-C_4H_9MgBr (13)	A (0.05)	15	1,4-$C_4H_9C_6H_4CF_3$	(56)[f]
1-Np-Br[g] (91)	n-C_4H_9MgBr (120)	B (0.42)	20	1-Np–C_4H_9	88
1-Np–Br (101)	n-C_4H_9MgBr (113)	C (0.91)	23	1-Np–C_4H_9	44[h]
1-Np–Br (99)	C_6H_5MgBr (125)	B (0.41)	20[i]	1-Np–C_6H_5	91
C_6H_5Br (92)	1-Np–MgBr[j] (126)	B (0.37)	20	1-Np–C_6H_5	98
C_6H_5Cl (5.5)	Mes–MgBr[k] (6)	A (0.04)	20	C_6H_5–Mes	(6)
1-Np–Br (4.1)	Mes–MgBr (6)	A (0.04)	20	1-Np–Mes	(45)
1,2-$CH_3OC_6H_4Br$ (5.2)	Mes–MgBr (6)	A (0.05)	20	1,2-$CH_3OC_6H_4$–Mes	(74)
Mes–Br[k] (4.2)	C_6H_5MgBr (6)	A (0.05)	20	C_6H_5–Mes	(48)
Mes–Br (4.7)	n-C_4H_9MgBr (6)	C (0.08)	20	Mes–H	(40)
C_6H_5Cl (9.6)	$(CH_3)_5Si_2CH_2MgCl$ (12)	A (0.03)	23	$(CH_3)_5Si_2CH_2C_6H_5$	(92)
1,2-$Cl_2C_6H_4$ (10)	$(CH_3)_3SiCH_2MgCl$ (24)	A (0.1)	20	1,2-$[(CH_3)_3SiCH_2]_2C_6H_4$	75
1,3-$Cl_2C_6H_4$ (30)	$(CH_3)_3SiCH_2MgCl$ (70)	A (0.3)	20	1,3-$[(CH_3)_3SiCH_2]_2C_6H_4$	83
1,4-$Cl_2C_6H_4$ (30)	$(CH_3)_3SiCH_2MgCl$ (70)	A (0.3)	20	1,4-$[(CH_3)_3SiCH_2]_2C_6H_4$	81
1-Np–Br (20)	$(CH_3)_3SiCH_2MgCl$ (24)	A (0.2)	21	1-Np–$CH_2Si(CH_3)_3$	66
9-Ant–Br[l] (4.0)	$(CH_3)_3SiCH_2MgCl$ (5)	C (0.05)	18[m]	9-Ant–$CH_2Si(CH_3)_3$	71

Table 7. Continued

Halide (mmol)	Grignard reagent (mmol)	Catalyst (mmol)	Time,[b] h	Product(s)	Yield[c] (%)
 (2.4)	$\mathrm{(CH_3)_3SiCH_2MgCl}$ (7.5)	A (0.02)	20		65
$\mathrm{C_6H_5Cl}$ (30)	*c*-$\mathrm{C_6H_{11}MgBr}$[n] (41)	A (0.15)	20	*c*-$\mathrm{C_6H_{11}C_6H_5}$	(97)[o]
$\mathrm{C_6H_5Cl}$ (5.0)	*c*-$\mathrm{C_6H_{11}MgBr}$ (7.3)	D (0.03)	20	*c*-$\mathrm{C_6H_{11}C_6H_5}$	(80)
1,2-$\mathrm{Cl_2C_6H_4}$ (9.6)	*c*-$\mathrm{C_6H_{11}MgBr}$ (22)	A (0.02)	22	*c*-$\mathrm{C_6H_{11}C_6H_5}$ 1,2-*c*-$\mathrm{C_6H_{11}C_6H_4Cl}$	(31) (8.5)[p]
1,3-$\mathrm{Cl_2C_6H_4}$ (30)	*c*-$\mathrm{C_6H_{11}MgBr}$ (66)	A (0.03)	20	1,3-(*c*-$\mathrm{C_6H_{11})_2C_6H_4}$	73
1,4-$\mathrm{Cl_2C_6H_4}$ (10)	*c*-$\mathrm{C_6H_{11}MgBr}$ (22)	A (0.02)	22	1,4-(*c*-$\mathrm{C_6H_{11})_2C_6H_4}$	63
1–Np–Br (30)	*c*-$\mathrm{C_6H_{11}MgBr}$ (36)	A (0.03)	20	1-Np–*c*-$\mathrm{C_6H_{11}}$	47
$\mathrm{C_6H_5Cl}$ (6.4)	*c*-$\mathrm{C_3H_5MgBr}$[q] (7.3)	A (0.03)	81	*c*-$\mathrm{C_3H_5C_6H_5}$	9
$\mathrm{C_6H_5Br}$ (4.0)	*c*-$\mathrm{C_3H_5MgBr}$ (4.8)	D (0.05)	70	*c*-$\mathrm{C_3H_5C_6H_5}$	37
$\mathrm{C_6H_5Br}$ (8.4)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (11)	D (0.08)	20[s]	$\mathrm{C_6H_5C(CH_3){=}CH_2}$	(85)
1,4-$\mathrm{ClBrC_6H_4}$ (10)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (11)	D (0.08)	20[s]	1,4-$\mathrm{CH_2{=}(CH_3)CC_6H_4Cl}$	(68)
1,4-$\mathrm{Br_2C_6H_4}$ (10)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (22)	D (0.08)	20[s]	1,4-$\mathrm{[CH_2{=}(CH_3)C]_2C_6H_4}$ 1,4-$\mathrm{CH_2{=}(CH_3)CC_6H_4Br}$	(72) (28)
1,2-$\mathrm{BrC_6H_4CH_3}$ (10.6)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (11.7)	D (0.04)	20[s]	1,2-$\mathrm{CH_3C_6H_4C(CH_3){=}CH_2}$	(30)
1,3,5-$\mathrm{Cl_3C_6H_3}$ (5.6)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (16.5)	D (0.04)	20[s]		(25)
1,2,4,5-$\mathrm{Cl_4C_6H_2}$ (4.6)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (20.2)	D (0.08)	20		(70)
1–Np–Br (10)	$\mathrm{CH_2{=}C(CH_3)MgBr}$[r] (11)	D (0.08)	20[s]	1-Np–$\mathrm{C(CH_3){=}CH_2}$	(78)
$\mathrm{C_6H_5Br}$ (55)	$\mathrm{CH_2{=}CHMgCl}$[r] (12.5)	D (0.05)	20[m]	$\mathrm{C_6H_5CH{=}CH_2}$	(28)[t]
Alkenyl halide					
$\mathrm{CH_2{=}CHCl}$[u]	1–Np–MgBr[k] (55)	B (0.34)	20[m]	1-Np–$\mathrm{CH{=}CH_2}$	80[t]
$\mathrm{CH_2{=}CHCl}$[u]	*c*-$\mathrm{C_6H_{11}MgBr}$ (10)	A (0.03)	2.5[m]	*c*-$\mathrm{C_6H_{11}CH{=}CH_2}$	(47)[t]
$\mathrm{CH_2{=}CHCl}$ (240)	4-$\mathrm{ClC_6H_4MgBr}$ (200)	A (0.1)	1.5[m]	4-$\mathrm{ClC_6H_4CH{=}CH_2}$	79[t]
$\mathrm{CH_2{=}CHCl}$[u]	$\mathrm{(CH_3)_3SiCH_2}$-MgCl (10)	A (0.1)	20	$\mathrm{(CH_3)_3SiCH_2CH{=}CH_2}$	78[t]
$\mathrm{CH_2{=}CHCl}$[u]	Mes–MgBr (14)	A (0.1)	20[s]	Mes–$\mathrm{CH{=}CH_2}$	(78)[t]
$\mathrm{CH_2{=}CCl_2}$ (95.8)	$\mathrm{C_6H_5MgBr}$ (220)	B (0.62)	16.5	$\mathrm{CH_2{=}C(C_6H_5)_2}$	82
$\mathrm{CH_2{=}CCl_2}$ (50)	$\mathrm{C_6H_5CH_2MgCl}$ (130)	B (0.20)	20	$\mathrm{CH_2{=}C(CH_2C_6H_5)_2}$	43
$\mathrm{CH_2{=}CCl_2}$ (20)	$\mathrm{(CH_3)_3SiCH_2MgCl}$ (44)	A (0.40)	20	[v]	
(*Z*)-ClCH=CHCl (5.0)	$\mathrm{C_6H_5MgBr}$ (12)	B (0.05)	2[m]	$\mathrm{C_6H_5CH{=}CHC_6H_5}$ *Z*: *E*=90: 10[w]	(91)
(*E*)-ClCH=CHCl (5.0)	$\mathrm{C_6H_5MgBr}$ (12)	B (0.05)	2[m]	$\mathrm{C_6H_5CH{=}CHC_6H_5}$ *Z*: *E*=80: 20[w]	(100)
(*E*)-ClCH=CHCl (7.2)	*n*-$\mathrm{C_4H_9MgBr}$ (32)	A (0.07)	24[m]	$\mathrm{C_4H_9CH{=}CHC_4H_9}$ $\mathrm{C_8H_{18}}$	(23) (48)
(*E*)-ClCH=CHCl (8.3)	$\mathrm{C_6H_5CH_2MgCl}$ (38)	A (0.07)	63[m]	$\mathrm{(C_6H_5CH_2)_2}$	(75)[x]
(*Z*)-ClCH=CHCl (12)	*c*-$\mathrm{C_6H_{11}MgBr}$ (25)	A (0.02)	21	(*E*)-*c*-$\mathrm{C_6H_{11}CH{=}}$ CH-*c*-$\mathrm{C_6H_{11}}$	(14)[y]
(*E*)-ClCH=CHCl (11)	*c*-$\mathrm{C_6H_{11}MgBr}$ (23)	A (0.02)	21	(*E*)-*c*-$\mathrm{C_6H_{11}CH{=}}$ CH-*c*-$\mathrm{C_6H_{11}}$	(43)[y]
$\mathrm{CH_2{=}C(CH_3)Br}$ (12)	$\mathrm{CH_2{=}C(CH_3)MgBr}$ (25)	A (0.1)	20	$\mathrm{[CH_2{=}C(CH_3)]_2}$	(79)
$\mathrm{CH_2{=}C(Cl)CH{=}CH_2}$[z] (108)	$\mathrm{C_6H_5MgBr}$ (125)	B (0.43)	20[m,z']	$\mathrm{CH_2{=}C(C_6H_5)CH{=}CH_2}$	65
 (83)	*n*-$\mathrm{C_4H_9MgBr}$ (120)	B (0.42)	20		67

a) Carried out under nitrogen atmosphere. Unless otherwise mentioned, solvent is diethyl ether. The Grignard reagent was added to a mixture of a halide, a catalyst, and solvent. The reaction conditions are not necessarily optimum. b) Unless otherwise noted, refluxed for the given period of time. c) Isolated yield based on the halide, unless otherwise noted. Yields determined by quantitative GLPC are given in parentheses. d) Conversion 58%. e) Conversion 44%. f) Conversion 59%. g) Np=naphthyl. h) Naphthalene 43%. i) An exothermic reaction occurred. j) In a mixed solvent of benzene, ether, and THF (3: 2: 1). k) Mes=mesityl. l) Ant=anthryl. m) Room temperature. n) *c*-$\mathrm{C_6H_{11}}$=cyclohexyl. o) Contaminated with a few per cent of dicyclohexyl. p) 1,2-Dicyclohexylbenzene was not formed. q) *c*-$\mathrm{C_3H_5}$=cyclopropyl. r) In tetrahydrofuran. s) 40—50 °C. t) Based on the Grignard reagent. u) About 2 fold excess. v) A complex mixture of products were formed. w) For a detailed stereochemical aspects, see Ref. 26. x) Little $\mathrm{C_6H_5CH_2CH{=}CHCH_2C_6H_5}$ was formed. y) Dicyclohexyl 8—9% yield. z) A *m*-xylene solution. z') A vigorous reaction occurred at 0 °C.

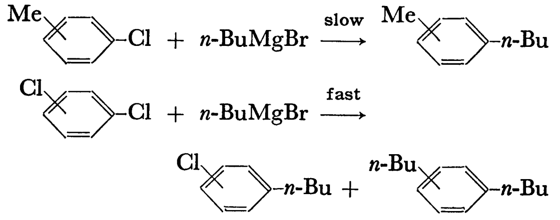
whereas with the latter no reaction occurred at all under similar conditions, the reaction mixture remaining a clear yellow solution. In view of the recently recognized concept that Me_3SiCH_2–transition metal complexes are the best examples of "elimination-stabilized alkyls,"[38] the lack of the catalytic activity of [Ni(dppe)Cl_2] in this case may be attributable primarily to the great stability of the initially formed bis(trimethylsilylmethyl)nickel intermediate. This hypothesis could be partially supported by the isolation of [Ni(dppe)$(CH_2SiMe_3)_2$] as a stable complex in high yield from the reaction of Me_3SiCH_2MgCl with [Ni(dppe)Cl_2] even in chlorobenzene as solvent.[39] However, with the experimental results at hand, it seems hard to find valid reasons for the higher efficiency of dppp as ligand as compared with dppe.[40]

Finally, of particular interest, but rather hard to understand, is that [Ni(dmpe)Cl_2] is among the poor catalysts for reactions with primary alkyl Grignard reagents, but one of the best ones for reactions with secondary alkyl Grignard reagents, although in the latter case extensive isomerization of the alkyl group from secondary to primary takes place during the cross-coupling.[25] This strange trend can not easily be interpreted in terms of the stability order of the organonickel intermediates involved.

Organic Halides and Grignard Reagents: Results summarized in Table 7 contain several features worthy of note.

(1) The present Grignard cross-coupling is equally applicable to substituted halobenzenes, polyhalobenzenes, and condensed aromatic halides. In these cases no positional scrambling is observed. Thus, the organic moiety of the Grignard reagent becomes bonded to the carbon atom which has borne the halogen atom. Therefore, the isomeric purity of the coupling products is very high.

(2) The reactivity order of substituted aryl halides has not yet been studied quantitatively, but judging from the exothermicity of reactions, dichloro- and dibromo-benzene and 1-bromonaphthalene are among the most reactive aryl halides examined, while chlorotoluenes are the least reactive ones. Interestingly, in spite of the low reactivity of monoalkylchlorobenzenes, dichlorobenzenes are smoothly *dialkylated* even in the presence of two-fold excess of dichlorobenzene over the alkyl Grignard reagent to give, for example, a 94: 6 mixture of dibutylbenzene and butylchlorobenzene. The result suggests that the second alkylation step in dichlorobenzene is mechanistically different from the alkylation of chlorotoluenes.

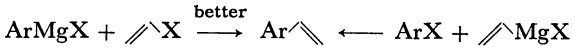


6 94

(3) Vinyl chloride is one of the most reactive halides and reacts with aryl and alkyl Grignard reagents with equal efficiency. The reactions using vinyl chloride are usually conducted either in a pressure glass-tube or in an ordinary reaction vessel, as described in Experimental section. These are strongly exothermic reactions and may proceed with violence unless controlled by the dropwise addition of Grignard reagents: care must be taken NOT to add a catalyst to a mixture of the halide and a Grignard reagent, particularly, in a large scale preparation. For example, the addition of a small amount of [Ni(dppp)Cl_2] to a mixture of vinyl chloride and 4-chlorophenylmagnesium bromide in ether at 0 °C led, after a few minutes' induction period, to an uncontrollable violent reaction.

While 1,1- and 1,2-dichloroethylenes react very smoothly with *aryl* Grignard reagents, reactions with *alkyl* Grignard reagents proceed sluggishly to give a mixture of products, usually the homo coupling product of the Grignard reagent predominating. The sluggish and complicated nature of these reactions constitutes, unfortunately, one of the most serious limitations of the present nickel–phosphine catalyzed Grignard coupling.

(4) Vinylic Grignard reagents exhibited relatively low reactivity and vinylmagnesium chloride in THF is one of the least reactive ones. Dihalobenzenes are not completely converted to dialkenylbenzenes even in the presence of [Ni(dmpe)Cl_2]. Therefore, from a synthetic viewpoint, styrene and its derivatives should be prepared from an aryl Grignard reagent and a vinylic halide rather than from an aryl halide and a vinylic Grignard reagent:



Stereochemical aspects of the coupling using vinylic halides or vinylic Grignard reagents have been reported briefly[26] and will be discussed in more detail elsewhere.

(5) The cyclohexyl Grignard reagent couples with almost all of the aryl halides studied, excepting 1,2-dichlorobenzene which gave no dicyclohexylbenzene, but a mixture of cyclohexylbenzene and cyclohexylchlorobenzene. The cyclopropyl Grignard reagent is reluctant to react with halobenzenes; a fair yield of cyclopropylbenzene was obtained with the [Ni(dmpe)Cl_2] catalyst. It seems of interest to note that the relatively high activity of [Ni(dmpe)Cl_2] in this case is similar to the situation observed for vinylic Grignard reagents, and may be related partially to the special hybridization of cyclopropyl carbon atoms.[43]

(6) Sterically hindered, *ortho*-substituted aryl halides (especially bromides) and Grignard reagents also couple smoothly to afford *ortho*-substituted unsymmetrical biaryls. Chlorobenzene is reluctant to react with the mesityl Grignard reagent. Generally, better yields can be obtained from a combination of a hindered aryl Grignard reagent and a less hindered bromide rather than the reverse combination.

Unfortunately, the action of the *n*-butyl Grignard reagent on mesityl bromide resulted in the formation of mesitylene.

IV. Summary of General Scope and Limitations.

The foregoing experimental results reveal that the present nickel–phosphine complex catalyzed Grignard coupling reaction is widely applicable to a variety of

Grignard reagents and various C(sp^2)-halides, with only a few limitations. Generally, for the direct alkylation and arylation of C(sp^2)-halides are required drastic reaction conditions, unless either they are strongly activated by some substituents or certain sophisticated reagents, such as organocuprates, are used.[44] The present reaction requires only a catalytic amount of a nickel–phosphine complex, uses mild reaction conditions, and gives high yields of cross-coupling products of high purity. It seems of interest to compare the present one-step preparation of, for example, the isomeric pure di-*n*-alkylbenzenes with the traditional multistep preparative methods starting with cyclohexenone or phthalic anhydride.[45]

The most serious limitation is that the substituents on the organic halides and on the Grignard reagents are restricted to those which cannot react with Grignard reagents. Reactions of appropriately masked halocarbonyl compounds are now being investigated with a view to overcoming the limitations.

V. A Brief Comment on the Mechanism. Although the mechanism of the present reaction has not yet been fully clarified, almost all of the foregoing results can be rationalized by Scheme 1. The most recent mechanistic studies by Morrell and Kochi[46] also provide results essentially consistent with this Scheme.

On the other hand, Felkin and Corriu and their coworkers have proposed a mechanism involving the oxidative addition of a Grignard reagent to Ni(0) species for a series of nickel-catalyzed Grignard reactions.[19,47]

We recently observed that organolithium reagents cannot be used in place of the corresponding Grignard reagents in the present coupling reaction.[48] Therefore, it seems likely that magnesium moieties of the Grignard reagents may play an important role in the high yield, selective cross-coupling reaction. While much remains to be studied for the elucidation of the mechanism, it seems apparent at least that diorganonickel intermediates are involved in this reaction.

In connection with these mechanistic aspects, it seems of interest to discuss a few special features of this reaction, based on the facts so far recognized concerning organonickel complexes. Firstly, the most remarkable feature of the present reaction is that even alkyl Grignard reagents containing the β-hydrogen(s) give selectively the cross-coupling products in high yields, because a transition metal alkyl containing β-hydrogen(s) is commonly unstable and tends to undergo β-elimination to form a metal hydride and an olefin;[38,49] nickel alkyls being also the case:

$$\mathrm{M{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}H \longrightarrow M{-}H + {>}C{=}C{<}}$$

For the same reasons, no aging effect on the catalytic activity is also noteworthy. Here again, an important role of magnesium components may be envisaged, as well as the stabilizing effect of the phosphine ligands.

Secondly, the aforementioned reactivity of vinylic halides in striking contrast to vinylic Grignard reagents implies the importance of the interaction between the diorganonickel intermediate and the unsaturated organic component (*cf.* **5** in Scheme 1). Thus, a strong interaction between a vinylic halide and a diorganonickel intermediate favors the catalytic process. On the other hand, the vinylic Grignard reagent as an olefinic component may well compete with the organic halide of comparable or lower coordinating ability for coordination onto the diorganonickel intermediate. This type of interaction may be responsible for the inhibited catalysis encountered with [Ni(dppp)Cl_2] catalyst. The high efficiency of [Ni(dmpe)Cl_2] in this case may be attributable to the expected weak interaction between the electron-rich olefin in the vinylic Grignard reagent and the nickel species bearing the electron-donating phosphine.

Experimental

Materials. Phosphine–nickel(II), –palladium(II), –platinum(II), and –cobalt(II), and amine–nickel(II) complexes were prepared by known methods. In the following list, the references given after the compounds are to the source or method of preparation: [Ni(PPh_3)$_2$$Cl_2$],[50] [Ni($PPh_2Me$)$_2$$Cl_2$],[51] [Ni($PPhMe_2$)$_2$$Cl_2$],[52] [Ni{P($n$-Bu)$_3$}$_2$$Cl_2$],[53] [Ni($PEt_3$)$_2$$Cl_2$],[53] [Ni(dppm)$_2$$Cl_2$],[54] [Ni(dppe)$Cl_2$],[54] [Ni(dppp)$Cl_2$],[54] [Ni(dppb)$Cl_2$],[55] [Ni(*cis*-dpen)$Cl_2$],[56] [Ni(dmpe)$Cl_2$],[57] [Ni(dmpf)$Cl_2$],[58] [Ni(dppc)$Cl_2$],[59] [Ni(bipy)$Cl_2$],[30b,60] [Ni(py)$_2$$Cl_2$],[61] [Pd($PPh_3$)$_2$$Cl_2$],[62] [Pd($PEt_3$)$_2$$Cl_2$],[62] [Pt($PPh_3$)$_2$$Cl_2$],[62] and [Co(dppp)$Cl_2$].[63] Cyclopropyl bromide,[64] 1-bromo-[65] and 2-bromo-propene,[65] mesityl bromide,[66] 1-chlorocyclohexene,[67] chloromethyl-trimethylsilane,[68] and -pentamethyldisilane[69] were prepared as reported previously. 9-Bromoanthracene was generously gifted by Dr. T. Kawamura, Department of Hydrocarbon Chemistry, Kyoto University. 4,4′-Dichlorobiphenyl and a solution of chloroprene in *m*-xylene were generously supplied by Kanegafuchi Chemical Industry Co., Ltd. and Toyo Soda Manufacturing Co., Ltd., respectively. Other organic halides were commercially available. Chlorobenzene, bromobenzene, and butyl bromide were purified by distillation before use, but others were used without further purification. Magnesium ribbons were commercially available (Nakarai Chemical). Ether was dried over sodium wire and distilled before use. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ before use.

Grignard Reagents. Grignard reagents were prepared in a standard manner by adding a solution of an organic halide to magnesium ribbons which had been dried under a rapid stream of dry nitrogen by flaming. Magnesium was usually used in 10—20% excess over the halide in order to exhaust the latter. After completion of the addition the mixture was refluxed for about one hour to ensure the reaction. Concentrations of the Grignard reagents were determined by adding one ml of the solution to an excess of standard hydrochloric acid followed by back titration with a standard sodium hydroxide solution.

Coupling Reactions. Detailed procedure for coupling of 1,2-dichlorobenzene with *n*-butylmagnesium bromide will appear in Organic Syntheses,[23] and only several typical procedures are described in detail below. All other reactions were carried out in essentially the same manner. Conversions of reactions and yields of products were determined either by careful distillation or by quantitative GLPC using an appropriate internal standard calibrated against the pure samples. Quantitative GLPC was performed on a Hitachi GC 4B gas-chromatograph using a 3 m×4 mm column 30% Silicone DC 550 on Celite (60—80). Preparative GLPC was performed on a Varian Aerograph Model 90-P gas-chromatograph, using a 3 or 6 m×9 mm column packed with 30% Silicone DC 550 on Celite (60—80). Infrared spectra were obtained on a Hitachi EPI G3 Grating spectrophotometer, NMR spectra were obtained with a Varian T-60, EM-360, or HA-100 spectrometer in CCl_4 solutions with TMS, cyclohexane, or benzene as internal standard. Mass spectra were recorded on a Hitachi RMS-4 mass spectrometer.

The following coupling products were identified by spectral (NMR and/or IR) comparison with commercial authentic samples or established spectral data;[70] toluene, ethylbenzene, propylbenzene, cumene, 1,1-diphenylethylene, (*E*)- and (*Z*)-stilbene, styrene, cyclohexylbenzene, 1-phenylnaphthalene, vinylcyclohexane, cyclopropylbenzene, 1-decene, 1-, 2-, and 3-phenylpropene, 1,4-bis(isopropenyl)benzene, 4-isopropenylchlorobenzene and 2,3-dimethyl-1,3-butadiene. Authentic samples of 1-methylcyclohexene,[71] allyltrimethylsilane,[72] benzyltrimethylsilane,[73] and benzylpentamethyldisilane[74] were prepared by reported methods.

Other coupling products are listed below together with some physical constants, spectral and/or analytical data.

A. Procedure for the Examination of Catalytic Activity of Phosphine-Nickel Complexes, Reactivity of Halobenzenes and Solvent Effects. A catalyst was placed in a 50-ml two-necked flask equipped with a stirring bar, a serum cap and a reflux condenser fitted with a three way stopcock. The reaction vessel was then filled with nitrogen after evacuation and charged with an organic halide, anhydrous ether, and an appropriate internal standard (normal alkane) through the serum cap with a syringe. To the mixture was then added a Grignard reagent in a similar way at 0 °C with stirring. The resulting mixture was refluxed for a given period of time and hydrolyzed with a dilute acid. The organic layer was analyzed by GLPC.

B. Procedure for the Examination of Catalytic Activity on Aging. Essentially the same procedure was employed as above, excepting that to the catalyst were added first anhydrous ether and the butyl Grignard reagent at 0 °C, the resulting mixture was allowed to stand at room temperature under nitrogen for a given period of time (aging time), and finally chlorobenzene was added. After refluxing for a given period of time, the mixture was hydrolyzed and an internal standard was added. Data obtained by GLPC analysis are listed in Table 2.

C. Procedures for the Reaction of Aryl Halides. *(a) Butylbenzene*: In a 300-ml two-necked flask, equipped with a pressure-equalizing dropping funnel, a reflux condenser attached to a nitrogen line and a stirring bar, were placed 430 mg (0.81 mmol) of $[Ni(dppe)Cl_2]$, 10.78 g (95.8 mmol) and 100 ml of anhydrous ether; the nickel complex was insoluble in the mixture. To the mixture was added dropwise butylmagnesium bromide in ether (110 mmol; 40 ml of 2.8 M solution) at room temperature with stirring under nitrogen over 20 min. The mixture changed immediately to an yellow clear and then brown solution. After, 22 h-reflux the mixture was hydrolyzed with diluted hydrochloric acid under cooling with an ice bath. The organic layer and ether extracts from the aqueous layer were combined, washed with water, saturated sodium hydrogencarbonate solution and water, and then dried over calcium chloride. After evaporation of solvent distillation gave 9.80 g (76% yield based on the chlorobenzene) of butylbenzene boiling at 70 °C/19 mmHg;[75] n_D^{15} 1.4928. NMR (CCl_4, TMS): δ 7.11 (s, 5H), 2.59 (t, 7 Hz, 2H), 2.0—0.8 (m, 7H); IR: for monosubstituted benzene; 1945 (w), 1875 (w), 1802 (w), 1750 (w), 746 (s), 702 (s) cm^{-1}. Careful GLPC analysis and mass spectrometry, showing a base peak *m/e* 91 in addition to a parent peak *m/e* 134, but no *m/e* 105, clearly indicated no contamination with *sec*-butylbenzene.[76]

(b) 9-Trimethylsilylmethylanthracene: In a 50-ml two-necked flask equipped as described in A were placed $[Ni(PPh_3)_2Cl_2]$ (32 mg; 0.06 mmol), 9-bromoanthracene (1.017 g; 3.95 mmol) and 5 ml of anhydrous ether. To the stirred mixture was added dropwise an ether solution of trimethylsilylmethylmagnesium chloride (5.14 mmol) through a serum cap with a syringe at room temperature. Immediately an exothermic reaction occurred. The resulting brownish mixture was stirred at room temperature for 18 h. usual work-up and distillation afforded 0.74 g (71% yield based on the halide) of 9-trimethylsilylmethylanthracene as slightly yellow crystals, mp 59—60 °C, NMR (CCl_4) δ: 8.3—7.2 (m, 9H), 3.09 (s, 2H), −0.03 (s, 9H). Found: C, 81.62; H, 7.41. Calcd for $C_{18}H_{20}Si$: C, 81.75; H, 7.62%.

D. Procedures for the Reaction of Vinyl Chloride. *(a) In a Pressure Glass Tube*; *1-Vinylnaphthalene*: Vinyl chloride (6 ml) was dried by passing the gas through a phosphorus pentoxide–calcium chloride column and condensed at −78 °C in a graduated, 100-ml pressure glass tube containing 178 mg (0.34 mmol) of $[Ni(dppe)Cl_2]$. To it were added at the same temperature 10 ml of anhydrous ether and a solution of 1-naphthylmagnesium bromide (55 mmol) in 50 ml of a mixed solvent of benzene, ether, and THF (3: 2: 1). The glass tube was stoppered and allowed to warm up to 0 °C. The resulting homogeneous solution was then kept standing at room temperature for 20 h. Work-up as above and distillation under reduced pressure gave 6.8 g (80% based on the Grignard reagent) of 1-vinylnaphthalene boiling at 89 °C/5 mmHg, n_D^{25} 1.6418 (lit,[78] bp 87 °C/2 mmHg, n_D^{25} 1.6436).

(b) In a Three-necked Flask; *4-Chlorostyrene*: A solution of 4-chlorophenylmagnesium bromide was prepared in the usual manner from 4.9 g (0.20 g-atom) of magnesium and 38.3 g (0.20 mol) of 4-chloro-1-bromobenzene in 150 ml of anhydrous ether.

A 500-ml three-necked flask was equipped with a mechanical stirrer, a reflux condenser attached to a drying tube, and a gas inlet tube reaching the bottom. In the flask were placed about 50 mg ($\approx$0.1 mmol) of $[Ni(dppp)Cl_2]$ and 100 ml of dry ether. The flask was cooled in an ice bath. Through the inlet tube was introdued 15 g (0.24 mol) of vinyl chloride which had been dried by passing the gas through a phosphorus pentoxide–calcium chloride column (about 40 cm × 2 cm diameter). The gas inlet tube was replaced by a pressure-equalizing dropping funnel, to which was transferred the Grignard solution prepared above under a nitrogen atmosphere. The Grignard solution was then added dropwise to the mixture containing the nickel catalyst, with stirring and cooling in an ice bath, over 45 min. The reaction mixture changed to yellow-brown with formation of two liquid layers. After completion of the addition the mixture was stirred at 0 °C for 30 min and then at room temperature for 1.5 h. The mixture was then cooled in an ice bath hydrolyzed by slow addition of about 150 ml of about 2 M-hydrochloric acid. After the usual work-up, distillation in the presence of a small amount of hydroquinone through a short Vigreux column under reduced pressure gave 21.5—22.0 g (78—79%) of 4-chlorostyrene, bp 78—80 °C/18 mmHg or 85—85.5 °C/25 mmHg, n_D^{20} 1.5664, (lit,[79] bp 38 °C/2.2 mmHg, n_D^{20} 1.5650), as a colorless to light yellow liquid.

1,2-Dibutylbenzene: bp 76—81 °C/3.5 mmHg, n_D^{20} 1.4920 (lit,[45a,b] n_D^{20} 1.4916). NMR: 7.00 (s, 4H), 2.60 (t, J=8.5 Hz, 4H), 1.7—0.7 (m, 14H). (Found: C, 88.31; H, 11.75%.) *1,3-Dibutylbenzene*: bp 84 °C/5 mmHg, n_D^{20} 1.4873 (lit,[45c] n_D^{25} 1.4860), d_4^{20} 0.8564. NMR: 7.1—6.8 (m, 4H), 2.57 (t, J=8 Hz, 4H), 1.9—0.7 (m, 14H). (Found: C, 88.19; H, 11.41%.) *1,4-Dibutylbenzene*: bp 93 °C/6 mmHg, n_D^{20} 1.4905 (lit,[80] n_D^{20} 1.4883). NMR: 6.93 (s, 4H), 2.54 (t, J=8 Hz, 4H), 1.8—0.6 (m, 14H). (Found: C, 88.65; H, 11.84%.) *2-Butyl-1-chlorobenzene*: n_D^{20} 1.5115 (lit,[81] n_D^{25} 1.5087). NMR: 7.4—6.9 (m, 4H), 2.70 (t, J=7.5 Hz, 2H), 1.9—0.7 (m, 7H). *3-Butyl-1-chlorobenzene*: n_D^{20} 1.5093. NMR: 7.3—6.88 (m, 4H), 2.60

(t, J=7.5 Hz, 2H), 1.9—0.7 (m, 7H). Found: C, 71.83; H, 8.15%. Calcd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77%. *4-Butyl-1-*chlorobenzene: n_D^{20} 1.5091. NMR: 7.11 (cent. of m, 4H), 2.56 (t, J=7.5 Hz, 2H), 1.9—0.7 (m, 7H). Found: C, 71.48; H, 7.86%. Calcd for $C_{10}H_{13}Cl$: C, 71.21; H, 7.77%. *2-Butyltoluene*: bp 85—86.5 °C/20 mmHg, $n_\mathrm{D}^{18.5}$ 1.4981 (lit,[82] $n_\mathrm{D}^{18.4}$ 1.49662). NMR: 7.03 (s, 4H), 2.58 (t, J=8 Hz, 2H), 2.11 (s, 3H), 1.8—0.8 (m, 7H). *3-Butyltoluene*: bp 90 °C/20 mmHg, $n_\mathrm{D}^{18.5}$ 1.4937 (lit,[82] $n_\mathrm{D}^{18.4}$ 1.49315). NMR: 7.2—6.8 (m, 4H), 2.55 (t, J=7 Hz, 2H), 2.33 (s, 3H), 1.8—0.7 (m, 7H). *4-Butyltoluene*: bp 81 °C/20 mmHg, n_D^{14} 1.4939 (lit,[82] $n_\mathrm{D}^{14.2}$ 1.4912). NMR: 6.95 (s, 4H), 2.54 (t, J=8 Hz, 2H), 2.29 (s, 3H), 1.8—0.8 (m, 7H). (Found: C, 88.90; H, 10.99%.) *4-Butylanisole*: bp 165—170 °C/100 mmHg, n_D^{20} 1.5013 (lit,[83] bp 120 °C/19 mmHg, n_D^{15} 1.5027). NMR: 6.94, 6.66 (q, $A_2'B_2'$, 4H), 3.68 (s, 3H), 2.50 (t, J=7 Hz, 2H), 1.9—0.7 (m, 7H). (Found: C, 80.60; H, 10.06%.) *4-Butyl-1-trifluoromethylbenzene*: n_D^{20} 1.4402. NMR: 7.50, 7.21 (q, $A_2'B_2'$, 4H), 2.68 (t, J=7 Hz, 2H), 1.9—0.7 (m, 7H). Found: C, 65.00; H, 6.69%. Calcd for $C_{11}H_{14}F_3$: C, 65.04; H, 6.95%. *1-Butylnaphthalene*: bp 97.5—100.5 °C/5 mmHg (lit,[84] bp 287—288 °C/745 mmHg). NMR: 8.1—7.2 (m, 7H), 3.03 (t, J=9 Hz, 2H), 2.0—0.7 (m, 7H). *1,2-Bis(trimethylsilylmethyl)benzene*: mp 2—3 °C, n_D^{20} 1.4967 (lit,[85] mp 2—3 °C, n_D^{20} 1.4950). NMR: 6.87 (s, 4H), 1.99 (s, 4H), −0.01 (s, 18H). *1,3-Bis(trimethylsilylmethyl)-benzene: mp 4—10 °C,* n_D^{20} *1.4925 (lit,*[86] *mp 4 °C,* n_D^{20} *1.4919).* NMR: 7.17—6.47 (m, 4H), 1.97 (s, 4H), −0.02 (s, 18H). *1,4-Bis(trimethylsilylmethyl)benzene*: mp 64—64.5 °C (lit,[86] mp 61—63 °C). NMR: 6.80 (s, 4H), 1.93 (s, 4H), −0.02 (s, 18 H). *1-Trimethylsilylmethylnaphthalene*: n_D^{20} 1.5751. NMR: 8.04—6.98 (m, 7H), 2.52 (s, 2H), −0.02 (s, 9H). Found: C, 78.18; H, 8.39%. Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46%. *4,4'-Bis(trimethylsilylmethyl)biphenyl*: mp 82—83 °C. NMR: 7.22, 6.84 ($A_2'B_2'$ q, J=8 Hz, 8H), 1.95 (s, 4H), −0.09 (s, 18H). Found: C, 73.65; H, 9.20%. Calcd for $C_{20}H_{22}Si_2$: C, 73.54; H, 9.26%. *2-(*o*-Anisyl)mesitylene*: mp 55—56 °C. NMR: 7.3—6.8 (m, 4H), 6.76 (s, 2H), 3.67 (s, 3H), 2.24 (s, 3H), 1.89 (s, 6H). Found: C, 84.81; H, 7.76%. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.01%. *2-(1-Naphthyl)mesitylene*: mp 70—72 °C. NMR: 7.9—7.05 (m, 7H), 6.88 (s, 2H), 2.33 (s, 3H), 1.85 (s, 6H). Found: C, 92.14; H, 7.71%. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.36%. *2-Phenylmesitylene*: NMR: 7.5—6.95 (m, 5H), 6.80 (s, 2H), 2.28 (s, 3H), 1.97 (s, 6H). *2-Cyclohexylchlorobenzene*: n_D^{20} 1.5421 (lit,[77] n_D^{20} 1.5436). (Found: C, 73.85; H, 7.64%.) *1,3-Dicyclohexylbenzene*: n_D^{20} 1.5370 (lit,[77] n_D^{20} 1.5356). NMR: 7.27—6.77 (m, 5H), 2.8—2.2 (br, 2H), 2.2—0.6 (m, 20H). *1,4-Dicyclohexylbenzene*: mp 103—103.5 °C (lit,[87] mp 101—102 °C). NMR: 7.05 (s, 4H), 2.8—2.2 (br, 2H), 2.2—0.6 (m, 20H). *1-Cyclohexylnaphthalene*: bp 172—174 °C/8 mmHg, n_D^{20} 1.6044 (lit,[88] bp 178—183 °C/12 mmHg, $n_\mathrm{D}^{19.3}$ 1.6040). *4-Isopropenyl-1-bromobenzene*: n_D^{20} 1.5830 (lit,[89] n_D^{20} 1.5834). NMR: 7.57—7.17 (m, 4H), 5.31 (br, 1H), 5.06 (m, 1H), 2.13 (br, 3H). *2-Isopropenyltoluene*: n_D^{20} 1.5152 (lit,[90] n_D^{20} 1.5155). NMR: 7.06 (s, 4H), 5.13 (m, 1H), 4.83 (m, 1H), 2.18 (s, 3H), 2.03 (br, 3H). *3,5-Diisopropenyl-1-chlorobenzene*: n_D^{20} 1.5695. NMR: 7.40—7.23 (m, 3H), 5.37 (m, 2H), 5.11 (m, 2H), 2.13 (m, 6H). Found: C, 74.58; H, 6.89%. Calcd for $C_{12}H_{13}Cl$: C, 74.80; H, 6.80%. *1,4-Dichloro-2,5-diisopropenylbenzene*: n_D^{20} 1.5601. NMR: 7.25 (s, 2H), 5.13 (m, 2H), 5.03 (m, 2H), 2.03 (m, 6H). Found: C, 63.61; H, 5.47%. Calcd for $C_{12}H_{12}Cl_2$: C, 63.45; H, 5.32%. 1-*Isopropenylnaphthalene*: n_D^{20} 1.6075 (lit,[91] n_D^{20} 1.6085). NMR: 8.10—7.13 (m, 7H), 5.37 (m, 1H), 5.07 (m, 1H), 2.20 (m, 3H). (Found: C, 92.55; H, 7.37%.) *2-Benzyl-3-phenylpropene*: bp 120—123 °C/5 mmHg, n_D^{20} 1.5652. NMR: 7.10 (br. s, 10H), 4.80 (s, 2H), 3.20 (s, 4H). Found: C, 92.00; H, 7.97%. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74%. (E)-*1,2-dicyclohexylethylene*: n_D^{20} 1.4881. NMR: 5.04 (dd, J=2 and 6 Hz, 2H), 2.5—2.0 (br, 2H), 2.0—0.7 (m, 20H). IR (neat): 965 cm^{-1} (*trans* olefin). Found: C, 87.33; H, 12.61%. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58%. *2-Phenyl-1,3-butadiene*: bp 62.5 °C/20 mmHg, n_D^{20} 1.5487 (lit,[92] n_D^{20} 1.5489). NMR: 7.30 (s, 5H), 7.0—6.2 (m, 1H), 5.4—4.9 (m, 4H). *1-Butylcyclohexene*: bp 102 °C/65 mmHg, n_D^{20} 1.4610 (lit,[71] bp 180.8—182.9 °C, n_D^{20} 1.4591). NMR: 5.37 (br, 1H), 2.2—0.6 (m, 17H). IR (neat): 1670 cm^{-1} (trisubstituted olefin).

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