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Cross-coupling Reaction of Aryl Grignard Reagents with Aromatic Halides catalyzed by Bis(acetylacetonato)nickel(II)[1]

Eiichi Ibuki, Shigeru Ozasa,* Yasuhiro Fujioka, and Yoshihiko Yanagihara

Kyoto College of Pharmacy, Misasagi-nakauchi-cho, Yamashina-ku, Kyoto 607, Japan

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A series of cross-coupling reactions of aryl Grignard reagents with aromatic iodides catalyzed by bis(acetylacetonato)nickel(II) was studied to establish reaction conditions under which the cross-coupling proceeded selectively and quantitatively. Under the standard conditions thus selected, the coupling reactions proceeded within a few hours by a simple procedure and gave very pure product in high yield. Thus, the Kharash-type cross-coupling reaction was found to be very useful for the synthesis of a variety of polyphenyls. With some reactants of more or less crowded geometry, the reaction resulted in rather low yields of polyphenyls. This cross-coupling was successfully applied to the synthesis of a new compound, 2,6,2′,6′-tetraphenylbiphenyl, having a highly non-planar arrangement of π-systems.

Keywords——Grignard reaction; Ni-complex-catalyzed cross-coupling; terphenyl; sexiphenyl; polyphenyls

To investigate the relationship between the number and arrangement of benzene rings and the physical properties of polyphenyls and polyphenylenes, we have prepared a series of quinque- to octiphenyls.[2] The Ullmann reaction of aryl halide[3] was employed for most of the preparations, which generally gave fairly good yields of polyphenyls in cases of homo-coupling. The Ullmann cross-coupling, however, tended to give low yields due to inevitable by-product formation and involved tedious purification procedures.[2a,b] In 1972, an alternative aryl–aryl cross-coupling method was reported by Corriu and Masse.[4] Thus, the reaction of phenylmagnesium bromide and *p*-dibromobenzene in the presence of bis(acetylacetonato)-nickel(II), $Ni(acac)_2$, provides *p*-terphenyl in good yield.

In the present study, we attempted to apply this Kharash-type Grignard cross-coupling reaction for the syntheses of various types of polyphenyls. The optimum reaction conditions as well as the limitations of the reaction were thoroughly investigated. The standard reaction conditions, which generally resulted in quantitative yield in the coupling reaction within a few hours, were identified. As a result, syntheses of a variety of very pure polyphenyls in high yields were found to be possible, though the coupling reaction with reactants having highly crowded geometry inevitably gave low yields.[5]

The coupling reaction consists of C_{ar}–C_{ar} bond formation by the combination of the aromatic moieties of aryl Grignard reagent and aromatic halide catalyzed by nickel(II) complex as follows:

$$Ar^1MgX + Ar^2X' \xrightarrow{\text{Ni(II) complex}} Ar^1\text{–}Ar^2 + MgXX'$$

We have developed several new catalysts, which are more efficient than $Ni(acac)_2$,[6] for the coupling reaction. In the present work, however, $Ni(acac)_2$ was used because it is commercially available.

Coupling of Phenylmagnesium Halides with Halobiphenyls

A series of C_{ar}–C_{ar} bond formations by the cross-coupling of phenylmagnesium halides with halobiphenyls in the presence of $Ni(acac)_2$ was examined under various conditions.

Reactivity of Halobiphenyls——In two sets of coupling reactions using 2- and 4-halobiphenyls, phenylmagnesium bromide was coupled with each iodobiphenyl in the presence of

Table I. Coupling of C_6H_5MgBr with Halobiphenyls[a]

n[b]	X in $XC_6H_4C_6H_5$[c]	Conversion of halide (%)[d]	Products (yield, %)[d]		
			$C_6H_5C_6H_4C_6H_5$[e]	$C_6H_5(C_6H_4)_2C_6H_5$[e]	$C_6H_5C_6H_5$[f]
2	4-Cl	6	3(*p*-)	0	29
2	4-Br	55	36(*p*-)	0	34
2	4-I	100	95(*p*-)	4(*p*-)	32
2	2-Cl	0	0	0	23
2	2-Br	42	14(*o*-)	0	50
2	2-I	100	91(*o*-)	0	38

a) Solvent: ether–benzene (1:1, v/v) mixture for *p*-terphenyl, and ether for *o*-terphenyl synthesis. Catalyst: 1% of the C_6H_5MgBr used. A solution of halide and catalyst was added to the Grignard solution all at once at 0°C under a nitrogen atmosphere, and the mixture was stirred for 1 h at 0°C, then refluxed for 3 h.
b) *n*: molar ratio (C_6H_5MgBr/halide).
c) Concentration of halide: 0.3—0.5 mol/l. Concentration of C_6H_5MgBr: 1 mol/l.
d) Determined by quantitative GLPC.
e) Based on the halide used.
f) Based on the C_6H_5MgBr used.

$Ni(acac)_2$ almost quantitatively to give *o*- or *p*-terphenyl (91—95%) (Table I). Under similar conditions, the bromides gave only low yields of terphenyls (14—36%) together with appreciable amounts of unchanged bromides. The chlorides, however, gave little or no terphenyl, indicating that they have very low reactivities under these reaction conditions. Thus, aryl iodides were proved to be the most suitable halide for coupling with aryl Grignard reagent.

Molar Ratio of Reactants——The equimolar coupling of phenylmagnesium bromide with 2-iodobiphenyl resulted in a poor conversion of iodide and a low yield of *o*-terphenyl together with undesired formation of *o*-quaterphenyl. The use of two equivalent amounts of the Grignard reagent, however, gave a high yield of *o*-terphenyl (91%) accompanied with only a small amount of easily separable biphenyl (Table II). Table II also shows that Grignard reagent prepared from aryl iodide had relatively low reactivity under the reaction conditions used.

From a synthetic point of view, therefore, the coupling of aryl iodide and two equivalents of arylmagnesium bromide seems to be preferable.

Solvent Effects——The effects of solvents on the coupling of phenylmagnesium bromide with 2-iodobiphenyl were examined in diethyl ether, diethyl ether–benzene (1:1) mixture,

Table II. Effects of the Molar Ratio of C_6H_5MgX to $2\text{-}IC_6H_4C_6H_5$ on the Coupling Reaction[a]

n[b]	X in C_6H_5MgX	Conversion of iodide (%)[c]	Products (yield, %)[c]		
			o-$C_6H_5C_6H_4C_6H_5$[d]	*o*-$C_6H_5(C_6H_4)_2C_6H_5$[d]	$C_6H_5C_6H_5$[e]
1	Br	64	43	11	35
1.5	Br	100	67	3	36
2	Br	100	91	0	38
2	I	71	45	3	21
		75	50[f]	2[f]	24[f]
3	I	100	63	0	28

a) Solvent: ether. Catalyst: 1% of the C_6H_5MgX used. Both reactants were allowed to react at 0°C under a nitrogen atmosphere, and the mixture was stirred for 1 h at 0°C, then refluxed for 3 h.
b) *n*: molar ratio (C_6H_5MgX/halide).
c) Determined by GLPC, unless otherwise noted.
d) Based on the halide used.
e) Based on the C_6H_5MgX used.
f) Isolated yield.

Table III. Solvent Effects on the Coupling of C_6H_5MgBr with 2-$IC_6H_4C_6H_5$[a]

Solvent[b]	Method of coupling[c]	Conversion of halide (%)[d]	Products (yield, %)[d]		
			o-$C_6H_5C_6H_4C_6H_5$[e]	*o*-$C_6H_5(C_6H_4)_2C_6H_5$[e]	$C_6H_5C_6H_5$[f]
E	Usual	100	91	0	38
E–B	A	100	97	0	36
E–B	B	100	82	3	35
THF	C	100	12	5	121[g]
THF	D	100	15	8	114[g]

a) Catalyst: 1% of the C_6H_5MgBr used. Molar ratio (C_6H_5MgBr/halide): 2.
b) E–B: ether–benzene (1: 1, v/v) mixture.
c) Usual: The ether solution of halide and catalyst was added all at once to the ethereal Grignard reagent at 0°C. The mixture was stirred for 1 h at 0°C, then refluxed for 3 h.
A: Same as the usual method except that benzene solution of halide and catalyst was used.
B: Same as A except that the Grignard reagent was used in an ether–benzene mixture.
C: The THF solution of halide and catalyst was added all at once to the Grignard reagent in THF at 0°C.
D: The THF solution of catalyst was added dropwise during a period of 1.5 h at 0°C to the mixture of Grignard reagent, halide, and THF.
d) Determined by GLPC.
e) Based on the halide used.
f) Based on the C_6H_5MgBr used.
g) Includes apparent reduction product of halide.

and tetrahydrofuran (THF). As shown in Table III, coupling in an ether–benzene (1: 1) mixture as the solvent proceeded nearly quantitatively, as in the case of using diethyl ether. This result is of significance, because the solubilities of reactants should be appreciably increased by using such a mixture, and this should make it possible to synthesize less soluble higher polyphenyls. Coupling using THF as a solvent, however, resulted in very low yields of *o*-terphenyl (12—15%) together with the formation of appreciable amounts of biphenyl, attributable to apparent reduction rather than cross-coupling of the halide.

Activity of the Catalyst——The coupling experiments of phenylmagnesium bromide with 2-iodobiphenyl catalyzed by different amounts of catalyst are summarized in Table IV. The table shows that the cross-coupling proceeded selectively and quantitatively in the presence of 0.01—1.0% of $Ni(acac)_2$ with negligible formation of by-products other than biphenyl. It seems of interest to note that after aging of the catalyst for 3 h at 0°C in the Grignard reagent, the catalyst did not show any appreciable change in its activity for such a coupling reaction.

Table IV. Catalytic Activity of $Ni(acac)_2$ for the Coupling of C_6H_5MgBr with 2-$IC_6H_4C_6H_5$[a]

Solvent[b]	$Ni(acac)_2$ (%)	Method of coupling[c]	Conversion of halide (%)[d]	Products (yield, %)[d]		
				o-$C_6H_5C_6H_4C_6H_5$[e]	*o*-$C_6H_5(C_6H_4)_2C_6H_5$[e]	$C_6H_5C_6H_5$[f]
E–B	None	Usual	13	3	0	22
E–B	0.001	Usual	22	7	0	20
E	0.01	Usual	100	96	1	29
E	0.1	Usual	100	89	1	34
E	1.0	Usual	100	91	0	38
E–B	1.0	Usual	100	91	0	35
E–B	1.0	A	100	92	0	62

a) Molar ratio (C_6H_5MgBr/halide): 2.
b) E–B: ether–benzene (1: 1) mixture.
c) Usual: The benzene or ether solution of halide and/or catalyst was added all at once to the ethereal Grignard reagent at 0°C. The mixture was stirred for 1 h at 0°C, then refluxed for 3 h.
A: The benzene solution of halide was added all at once to the ethereal Grignard reagent, which had previously been mixed with $Ni(acac)_2$ and stirred for 3 h at 0°C. Then the mixture was worked up as usual.
d) Determined by GLPC.
e) Based on the halide used.
f) Based on the C_6H_5MgBr used.

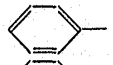
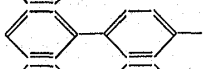
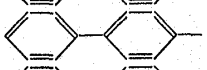
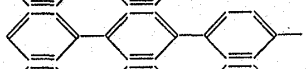
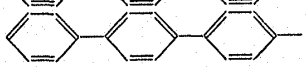
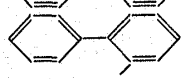
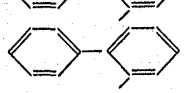
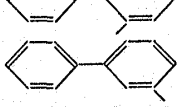
Coupling of Other Aryl or Arylene Grignard Reagents with Aromatic Iodides

Structural Effects in Aromatic Iodides——In order to ascertain the scope of the coupling reaction, the effects of halide structure upon the cross-coupling of phenylmagnesium bromide with a variety of halides were examined.

The coupling of the Grignard reagent with differently substituted iodobiphenyls proceeded quantitatively and independently of the position of the iodo-substituent (Table V). Generally, both ether and an ether-benzene mixture could be used as efficient solvents for the cross-coupling reactions. In the case of a halide with *p*-phenylene ring(s), the use of an ether–benzene mixture improved the yield of cross-coupling.

As shown in Table VI, the cross-coupling of Grignard reagent with diiodide proceeded stoichiometrically. The reaction with dibromide proceeded to a considerable extent, while

Table V. Coupling of C_6H_5MgBr with Aryl Iodides[a]

Ar′ in Ar′I	Concentration (mol/l) C_6H_5MgBr	Concentration (mol/l) Ar′I	Solvent[b]	Conversion of iodide (%)[c]	Products (yield, %)[c] Ar′–C_6H_5[d]	Ar′–Ar′[d]	$C_6H_5C_6H_5$[e]
	1.0	0.4	E	100	124[f]	0	—
	1.0	0.1	E	100	88	8	38
	1.0	0.4	E-B (1:1)	100	95	4	32
	0.3	0.003	E	21	16	0	33
	0.7	0.03	E-B (1:15)	58	51	0	35
	1.0	0.4	E	100	91	0	38
	1.0	0.4	E-B (1:1)	100	97	0	36
	1.0	0.4	E	100	90	8	31
	1.0	0.4	E-B (1:1)	100	90	7	29

a) Molar ratio (C_6H_5MgBr/halide): 2. The ether or benzene solution of halide and catalyst (1%) was added all at once to the ethereal Grignard reagent at 0°C. The mixture was stirred for 1 h at 0°C, then refluxed for 3 h.
b) E: ether; B: benzene.
c) Determined by GLPC.
d) Based on the halide used.
e) Based on the C_6H_5MgBr used.
f) Includes biphenyl originated from C_6H_5MgBr only.

Table VI. Coupling of C_6H_5MgBr with 1,4-Dihalobenzenes[a]

Halide	Conversion of halide (%)[b]	Products (yield, %)[b] *p*-$C_6H_5C_6H_4C_6H_5$[c]	*p*-$XC_6H_4C_6H_5$[c]	$C_6H_5C_6H_5$[d]
1,4-$Cl_2C_6H_4$	1	0.2	0.1	60
1,4-$Br_2C_6H_4$	98	35	0	42
1,4-$I_2C_6H_4$	100	92	0	15

a) Molar ratio (C_6H_5MgBr/halide): 4. The benzene solution of halide and catalyst (1%) was added all at once to the ethereal Grignard reagent at 0°C. The mixture was stirred for 1 h at 0°C, then refluxed for 3 h. Concentrations of C_6H_5MgBr and halide were 1.4 and 0.4 mol/l respectively.
b) Determined by GLPC.
c) Based on the halide used.
d) Based on the C_6H_5MgBr used.

that with dichloride hardly occurred. In the case of similar coupling with 1,2,3-triiodobenzene, 1,2,3-triphenylbenzene was obtained in only low yields (15—18%) even under forcing conditions[7] using a nine-fold excess of the Grignard reagent. In addition, the formation of *o*- and *m*-terphenyl as by-products was observed, presumably as a result of partial coupling followed by reduction of the iodo-substituent (Table VII).

Table VII. Coupling of C_6H_5MgX with $1,2,3\text{-}I_3C_6H_3$[a]

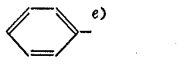
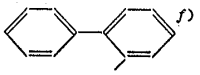
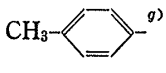
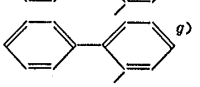
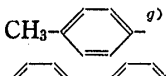
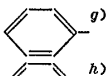
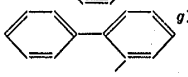
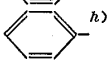
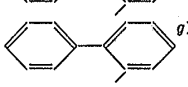
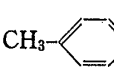
X in C_6H_5MgX	Conversion of halide (%)[b]	Products (yield, %)[b]			
		1,2,3-$(C_6H_5)_3C_6H_3$[c]	*m*-$C_6H_5C_6H_4C_6H_5$[c]	*o*-$C_6H_5C_6H_4C_6H_5$[c]	$C_6H_5C_6H_5$[d]
Br	100	15	21	11	36
I	100	18	32	15	28

a) Molar ratio (C_6H_5MgX/halide): 9. The benzene solution of triiodide and catalyst (0.5%) was added all at once to the boiling Grignard reagent prepared in an ethereal solution, followed by the addition of a half volume of benzene. The mixture was then refluxed for 3 h.
b) Determined by GLPC.
c) Based on the halide used.
d) Based on the C_6H_5MgX used.

In contrast to the above experiments, attempted coupling of *m*-terphenyl-2′-ylmagnesium iodide with 2′-iodo-*m*-terphenyl proceeded in high yield (77%) to give 2,6,2′,6′-tetraphenylbiphenyl (mp 396°C), having a highly nonplanar and crowded system, without any by-product formation except for small amount of *m*-terphenyl. The exceptionally efficient coupling despite crowded geometry of the reactants is presumably due to the remarkably low solubility of the resultant polyphenyl in an ether–benzene mixture.

Design for Polyphenyl Synthesis——In order to find suitable combinations of the reactants, Grignard reagent and aromatic halide, for polyphenyl synthesis, several cross-coupling reactions were examined. The results obtained are summarized in Tables VIII and IX. Table VIII shows that better yields can be obtained from a combination of a crowded aryl Grignard reagent and a less crowded halide than from the reverse combination. Furthermore,

Table VIII. Coupling of Ar^1MgBr with Ar^2I[a]

Ar^1 in Ar^1MgBr	Ar^2 in Ar^2I	Conversion of halide (%)[b]	Products (yield, %)[b]				
			$Ar^1\text{–}Ar^2$[c]	$Ar^2\text{–}Ar^2$[c]	Ar^2H[c]	$Ar^1\text{–}Ar^1$[d]	Ar^1H[d]
 e)	 f)	100	91	0	38		—i)
CH_3–  g)	 g)	100	89	5	6	41	—
CH_3–  g)	 g)	99	93	5	—	15	—
 g)	 h)	90	57	j)	—	12	48
 g)	CH_3–  h)	99	73	4	—	5	46

a) Molar ratio (Ar^1MgBr/Ar^2I): 2. The ether solution of halide and catalyst (1%) was added all at once to the ethereal Grignard reagent at 0°C. The mixture was worked up as in the general procedure.
b) Determined by GLPC.
c) Based on the Ar^2I used.
d) Based on the Ar^1MgBr used.
e) Concentration: 1 mol/l.
f) Concentration: 0.4 mol/l.
g) Concentration: 0.7 mol/l.
h) Concentration: 0.3 mol/l.
i) Not determined.
j) A small amount was probably included in Ar^1H.

Table IX. Coupling of 1,4-$XMgC_6H_4MgX$ with C_6H_5I[a]

X in 1,4-$(XMg)_2C_6H_4$	Conversion of C_6H_5I(%)[b]	Products (yield, %)[b]	
		p-$C_6H_5C_6H_4C_6H_5$[c]	$C_6H_5C_6H_5$[c]
Br	100	17	65
I	100	16	69

a) Molar ratio (Grignard reagent/C_6H_5I): 2. The benzene solution of halide and catalyst (1%) was added all at once to the ethereal Grignard reagent at 0°C. The mixture was worked up as in the general procedure. Concentrations of Grignard reagent and iodobenzene were 0.4 and 0.8 mol/l respectively.
b) Determined by GLPC.
c) Based on the C_6H_5I used.

far better yields were obtained from a combination of mono-Grignard reagent and dihalide than from that of di-Grignard reagent and monohalide (Table IX and VI).

In the attempted cross-coupling of arylmagnesium halide (Ar^1MgX) and aryl iodide (Ar^2I), the formation of Ar^1–Ar^1 by the homo-coupling of Ar^1MgX was observed as a usual side reaction.[8] Besides this, small amounts of Ar^1H and Ar^2H were also formed in some cases. From the viewpoint of polyphenyl synthesis, such a combination of the reactants seems preferable in that the product of cross-coupling is easily separable from that of Grignard homo-coupling.

Scope and Limitations of the Cross-coupling

The foregoing results clarified that the Kharash-type Grignard cross-coupling reaction catalyzed by $Ni(acac)_2$ is widely applicable to the syntheses of a variety of polyphenyls with only a few limitations.

Thus, the attempted coupling of aryl Grignard reagent (Ar^1MgBr, two equivalents) with aryl or arylene iodide (Ar^2I or I·Aryn·I) in the presence of a catalytic amount of $Ni(acac)_2$ (0.01—1.0%) in an ether or ether–benzene solution proceeded highly selectively and almost quantitatively within a few hours under mild conditions. Because the usual by-product, Ar^1–Ar^1, was generally separable with ease by recrystallization or by column chromatography, the coupling reaction made possible the synthesis of polyphenyls in high purity. The use of aryl bromide instead of iodide, however, required an impractically prolonged reaction time.

In coupling reactions involving sterically crowded geometry in the reactants, better yields could be obtained by using the crowded moiety as Ar^2I than as Ar^1MgBr. However, coupling reactions in which the iodide involved highly crowded geometry were less successful, *e.g.*, coupling of C_6H_5MgBr with 1,2,3-$I_3C_6H_3$ gave a rather poor yield of 1,2,3-$(C_6H_5)_3C_6H_3$ together with appreciable amounts of undesired partially coupled products.

In addition to the present C_{ar}–C_{ar} bond formation, cross-coupling reactions of aryl and heteroaryl or of two heteroaryl moieties catalyzed by a variety of Ni(II) complexes are now being investigated to extend the scope of this useful synthetic method.

Experimental

Instruments——The melting points were determined with a Mettler FP-51 or FP-52 apparatus, except for those above 300°C, which were determined with a Shimadzu DSC-30M differential scanning calorimeter. The ultraviolet (UV) spectra were measured on a Shimadzu MPS-50L spectrophotometer, the infrared (IR) spectra on a Leitz III-G spectrophotometer, and the proton magnetic resonance (^{1}H-NMR) spectra on a Varian CFT-20 spectrometer at 80 MHz, using tetramethylsilane (TMS) as an internal standard. The mass spectra (MS) were recorded on a Hitachi RMU-6E mass spectrometer. Quantitative GLPC was performed on a Shimadzu GC-5APTF gas chromatograph using a 1 m × 3 mmϕ glass column 3% Dexil 300GC on Chromosorb W AW-DMCS.

Materials——2-Bromobiphenyl,[2d] 2-, 3-, and 4-iodobiphenyl,[2a] 4-iodo-p-terphenyl,[2d] and 2′-iodo-m-terphenyl[5b] were prepared as reported previously. 4-Bromo- and 2-chlorobiphenyl were prepared by the

Sandmeyer reaction of the corresponding amines.

4-Bromobiphenyl: Leaves, mp 89—89.8°C (lit.[9] mp 89°C).

2-Chlorobiphenyl: Prisms, bp 150—155°C (10 mmHg), mp 34°C (lit.[9] mp 34°C).

1,2,3-Triiodobenzene was prepared by the direct iodination of *p*-nitroaniline, conversion of amino group by iodine, and reduction ($SnCl_2$), followed by deamination; colorless prisms, mp 115.8°C (lit.[10] mp 110—113°C). *Anal.* Calcd for $C_6H_3I_3$: C, 15.81; H, 0.66. Found: C, 15.99; H, 0.52.

o-, *m*-, and *p*-Quaterphenyl used as authentic samples were obtained in the previous work.[2a] 4,4′-Dimethylbiphenyl and 4-methyl-*o*-terphenyl were prepared by the coupling reaction of *p*-tolylmagnesium bromide with *p*-iodotoluene and with 2-iodobiphenyl, respectively, catalyzed by $Ni(acac)_2$.

4,4′-Dimethylbiphenyl: Colorless plates from ethanol, mp 119—120°C (lit.[11] mp 121°C). IR (CS_2) cm^{-1}: 720 vw; 803 s, 835 m (γ_{C-H}, *p*); 2862 w, 2934 m (ν_{C-H}, CH_3); 3035 m, 3060 m (ν_{C-H}, *p*).[12] UV $\lambda_{max}^{cyclohexane}$ nm (ε): 201 (56400), 254 (20600). ^{1}H-NMR ($CDCl_3$) δ: 2.38 (6H, s, CH_3), 7.21 and 7.48 (8H, q, J=8.1 Hz, C_6H_4).

4-Methyl-*o*-terphenyl: Colorless prisms from methanol, mp 74—75°C (lit.[13] no mp given). IR (CS_2) cm^{-1}: 699 s (γ_{C-C}); 717 w; 742 s, 752 s, 761 s (γ_{C-H}, M, *o*); 774 m (γ_{C-H}, *o*); 823 s (γ_{C-H}, *p*); 913 (γ_{C-H}, M); 2868 w, 2938 w (ν_{C-H}, CH_3); 3036 m, 3068 m (ν_{C-H}, M, *o*, *p*). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 200 (61600), 235 (28600), 251 (sh) (13200). ^{1}H-NMR ($CDCl_3$) δ: 2.29 (3H, s, CH_3), 7.01 (4H, s, *p*-C_6H_4), 7.18 (5H, s, C_6H_5), 7.39 (4H, s, *o*-C_6H_4).

1,2,3-Triphenylbenzene was prepared by the Ullmann reaction of 2′-iodo-*m*-terphenyl and a large excess of iodobenzene, and used as an authentic sample. 1,2,3-Triphenylbenzene: Colorless needles, mp 156—157°C (lit.[10] mp 156—157°C). IR (KBr) cm^{-1}: 679 w; 701 vs (γ_{C-C}); 745 s, 755 vs, 761 vs, 768 vs, 775 vs (γ_{C-H}, M); 808 w, 818 m (γ_{C-H}, as); 848 w, 854 w, 908 w. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 186 (69000), 196 (62600), 242 (33800). ^{1}H-NMR ($CDCl_3$) δ: 6.75—7.03 (5H, m, 2-C_6H_5), 7.07—7.14 (10H, m, 1-, 3-C_6H_5), 7.43 (3H, s, C_6H_3). *Anal.* Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.00. MS *m/e*: 306 (M^+).

The following materials were obtained commercially. Bromobenzene, iodobenzene, *p*-bromotoluene, and *p*-iodotoluene were purified by distillation before use. Biphenyl, 4-chlorobiphenyl, *p*-dichloro-, *p*-dibromo-, and *p*-diiodobenzene, *o*-, *m*-, and *p*-terphenyl were purified by recrystallization. Diethyl ether, benzene, and tetrahydrofuran (THF) were distilled and dried over sodium wire. 4-Methylbiphenyl and bis (acetylacetonato)-nickel(II) were used without further purification.

General Procedure for Grignard Cross-coupling——Magnesium turnings were placed in a four-necked round-bottomed flask equipped with a reflux condenser. To the flask was added *ca.* 30% of an ethereal solution of aryl halide (concentration, 0.8—1.0 mol/l) under a nitrogen atmosphere, and the mixture was stirred and heated, if necessary, to initiate the reaction. The remaining aryl halide solution was added dropwise just rapidly enough to maintain a gentle reflux. After a further 0.5 h of heating, the resulting solution was cooled to 0°C. To this Grignard reagent, a mixture of aromatic halide (0.3—0.5 mol/l) and a catalyst in ether or benzene was added all at once. The whole was stirred for 1 h at 0°C, then refluxed for 3 h. The mixture was hydrolyzed with dilute hydrochloric acid and then extracted with benzene. The organic layer was separated, washed with dilute hydrochloric acid, sodium carbonate solution, sodium thiosulfate solution, and finally with water, then dried. To the whole (or an aliquot), a known quantity of *m*-terphenyl or an appropriate internal standard calibrated against pure authentic samples was added, and the mixture was subjected to GLPC for determination of the products and starting materials.

Coupling Reaction of Phenylmagnesium Iodide with 2-Iodobiphenyl——A mixture of 2-iodobiphenyl (4 mmol) and a catalyst (1%) in ether was added all at once to an ethereal solution of phenylmagnesium iodide (8 mmol). The mixture was worked up as described in the general procedure. Reaction products were separated into three fractions by chromatography on alumina, with cyclohexane as the eluent. The fractions afforded *o*-terphenyl and two by-products, which were identified by means of mixed-melting-point measurements and spectral comparisons with corresponding authentic samples.

Biphenyl: Leaves, mp 69°C, 0.15 g (24%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 248 nm (18500). ^{1}H-NMR ($CDCl_3$) δ: 7.16—7.77 (10H, m, C_6H_5).

o-Terphenyl: Needles, mp 56°C (lit.[14] mp 56—57°C), 0.46 g (50%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 233 (29100), 251 (sh) (13300). ^{1}H-NMR ($CDCl_3$) δ: 7.16 (10H, s, C_6H_5), 7.40 (4H, s, C_6H_4).

o-Quaterphenyl: Cubes, mp 118°C (lit.[15] mp 118°C), 0.01 g (2%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 230 (34100), 245 (sh) (25600).

Coupling Reaction of *m*-Terphenyl-2′-ylmagnesium Iodide with 2′-Iodo-*m*-terphenyl——Magnesium turnings (0.15 g, 6 mg-atom) were added to a hot saturated solution of about half the total amount of 2′-iodo-*m*-terphenyl (2.14 g, 6 mmol) in an ether–benzene (2: 1) mixture, and the mixture was heated gently to initiate the reaction. The remaining halide solution was added slowly and the mixture was refluxed for 3 h to dissolve the magnesium turnings. A mixture of 2′-iodo-*m*-terphenyl (0.71 g, 2 mmol) and a catalyst (0.015 g, 0.06 mmol) in benzene was added all at once to the Grignard reagent thus prepared, and the resulting mixture was worked up as described in the general procedure. After hydrolysis of the mixture, the resulting solid was filtered off. The filtrate was extracted repeatedly with benzene. The combined organic layer was washed with water, then concentrated to one-third of the initial volume. A crystalline solid which separated out on standing overnight was filtered off. The solvent was evaporated off from the filtrate, and

the resulting residue was subjected to chromatography on alumina with a C–B (9: 1) mixture to give *m*-terphenyl. The combined solid was recrystallized from benzene to afford 2,6,2′,6′-tetraphenylbiphenyl.

2,6,2′,6′-Tetraphenylbiphenyl: Colorless cubes from benzene, mp 396°C, 1.40 g (77%, based on the reactants used). IR (KBr) cm^{-1}: 677 w; 697 vs (γ_{C-C}); 711 (sh) m; 745 s, 760 vs, 776 m (γ_{C-H}, M); 812 m (γ_{C-H}, as); 828 w, 838 w, 905 w. UV $\lambda_{max}^{cyclohexane}$ nm (ε): 188 (87100), 254 (50100). ^{1}H-NMR ($CDCl_3$) δ: 6.57—7.35 (26H, m, all protons). *Anal.* Calcd for $C_{36}H_{26}$: C, 94.28; H, 5.72. Found: C, 94.47; H, 5.78. MS *m/e*: 458 (M^+).

m-Terphenyl: Colorless needles, mp 86.2°C (mixed mp 86.2—86.5°C), 0.31 g (17%). UV $\lambda_{max}^{cyclohexane}$ nm (ε): 247 (39100).

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References and Notes

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