sealed with a rubber septum, and irradiated in a Rayonet photoreactor (Model PR-100), provided with a merry-go-round, at 350 nm for 6 h. The solvent was rotoevaporated (ca. 15 °C at 20 Torr) and the product confirmed as bisepoxide **3c** by ^{1}H NMR, IR, and TLC (silica gel, $CH_2Cl_2/n\text{-}C_5H_{12}$ as eluant), formed in 57% yield. Control experiments showed that **2c** was photostable at 295–300 nm.

Methanolysis of Endoperoxide 2c. A solution of 2 mmol of **2c** in 10 mL of MeOH was allowed to stand at room temperature (ca. 30 min) and monitored by ^{1}H NMR. After 90 min the endoperoxide **2c** was completely transformed into a complex mixture of products. Rotoevaporation (ca. 25 °C at 15 Torr) of the MeOH and by silica gel chromatography at 25 °C, eluting with $CHCl_3$, the individual products were isolated and purified.

As first eluate, the *cis,cis*-**4c** and *trans,trans*-**4c** dienes were obtained in 8 and 2% yields, respectively, as confirmed by ^{1}H NMR and IR. A control experiment showed that *cis,cis*-**4c** isomerized into *trans,trans*-**4c**. As second eluate, 9% tropone was obtained.

As third eluate, the ketol **7c** was isolated[4a] in 57% yield, pale yellow liquid, which on attempted distillation at 110 °C (bath temperature) and 1 Torr partially dehydrated into tropone. The spectral data are: ^{1}H NMR ($CDCl_3$, Me_4Si, ppm) δ 2.5–3.25 (2 H, multiplet, J_{AB} = 15.67 Hz), 3.5 (1 H, multiplet, exchanged with D_2O), 4.3–4.7 (1 H, multiplet), and 5.4–6.6 (4 H, multiplet); IR ($CHCl_3$, cm^{-1}) 3590, 3360 (OH), 3010 (olefinic C—H), 2990 (aliphatic C—H), 1650 (C=O), 1635 (C=C), 1575 (CH_2 bending); MS (70 eV) *m/e* 124. Catalytic reduction of ketol **7c** over Pd/C (10%) in MeOH afforded the known[5] 3-hydroxycycloheptanone, colorless liquid, bp 90 °C at 1 Torr.

On the silica gel column, the ketol **7c** partially dehydrated to form tropone.

Triphenylphosphine Deoxygenations of Endoperoxides 2. A 10-mL, one-necked, round-bottomed flask, provided with a magnetic spinbar, was charged with 0.5 mmol of endoperoxide **2** in 5 mL of $CHCl_3$. While stirring magnetically, 0.5 mmol of triphenylphosphine in 2 mL of $CHCl_3$ was added dropwise and allowed to stir 30 min at room temperature. The solvent was rotoevaporated (ca. 25 °C at 15 Torr), the residue was triturated with 2 mL of cold ether, the solid triphenylphosphine oxide removed by filtration, the solvent rotoevaporated, and the product bulb-to-bulb distilled at 50 °C and 0.1 Torr.

Endoperoxide 2a. Deoxygenation of **2a** at 80 °C afforded a mixture of epoxydiene **7a**, its valence isomer **7a'**, and epoxydiene **7b** in 57% total yield, confirmed by ^{1}H NMR and IR which were identical with the authentic compounds.[10]

Endoperoxide 2b. The ene-epoxide **4b** was obtained in 69% yield at 0 °C, colorless liquid, satisfactory elemental composition by high resolution mass spectrometry. The spectral data are: ^{1}H NMR (CCl_4, Me_4Si, ppm), for numbering refer to eq 2, $\delta_{6_{endo}}$ 0.6–0.9 (1 H, multiplet), $\delta_{6_{exo},7}$ 0.9–1.4 (2 H, multiplet), δ_5 1.5–1.9 (1 H, multiplet), δ_3 2.6–2.9 (1 H, multiplet), δ_4 3.4–3.6 (1 H, multiplet), δ_2 5.2–5.5 (1 H, multiplet), and δ_1 5.7–6.0 (1 H, multiplet), $J_{1,3} = 1.30$, $J_{4,5} = 1.75$, $J_{2,3} = 3.66$, $J_{1,7} = 3.77$, $J_{3,4} = 4.50$, and $J_{12} = 9.66$ Hz; IR (CCl_4, cm^{-1}) 3010 (olefinic C—H), 3040 (cyclopropyl C—H), 2970 (aliphatic C—H), 1665 (C=C).

Endoperoxide 2c. At 0 °C a complex reaction mixture was obtained, whose NMR clearly showed the presence of cycloheptatriene epoxide **7b**, prepared by peracetic acid epoxidation of cycloheptatriene.[10b]

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Mechanism of Biaryl Synthesis with Nickel Complexes

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Abstract: The mechanism of the nickel-catalyzed coupling of aryl halides to afford biaryls is examined by focusing on the reactions of arylnickel(II) halide as the important organometallic intermediate. A variety of triethylphosphinenickel(II) complexes, *trans*-$ArNiX(PEt_3)_2$ (**1**), are synthesized and found to yield biaryls only upon treatment with aryl halide (ArX). Biaryl formation is shown to involve a radical-chain process in which paramagnetic nickel(I) and arylnickel(III) species are reactive intermediates. The propagation steps include the oxidative addition of ArX to nickel(I) to produce the reactive arylnickel(III) species, which undergoes aryl transfer with **1** to afford a diarylnickel(III) intermediate, followed by reductive elimination of biaryl and the regeneration of nickel(I). This series of chain reactions provides an efficient mechanism for the cross coupling of **1** and ArX selectively to ArAr, except for a competition from a halogen exchange process which, in effect, scrambles aryl groups between **1** and an arylnickel(III) species. The initiation of the catalytic cycle is associated with electron transfer from **1** to ArX, and it can be manipulated by a rational choice of initiators and inhibitors. In the course of biaryl formation, the triethylphosphine ligand reacts with excess ArX to produce arylphosphonium salts, $ArPEt_3^+$, by a second catalytic process induced by the nickel(I) intermediate. The phosphine levels in the reaction are critical to initiation and inhibition of both of these catalytic or chain processes, which are discussed in relation to nickel ligation.

Introduction

Synthetic procedures for the preparation of biaryls by the classical Ullmann reaction[1] have, in recent years, been supplanted by the use of zerovalent nickel to effect the reductive coupling of aryl halides under homogeneous conditions.

$$2ArX \xrightarrow{+2e} ArAr + 2X^-$$

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The original method discovered by Semmelhack and co-workers,[2] utilizing the isolable albeit air-sensitive bis(1,5-cyclooctadiene)nickel(0), has been modified by Kende et al.[3] with an in situ generation of the nickel(0) species from nickel(II) precursors with zinc dust. Although both procedures employ stoichiometric amounts of nickel, Kumada and co-workers[4] have recently reported that aryl coupling can be carried out with catalytic amounts (~10%) of nickel(II), with zinc powder as the ultimate reductant. The method is also applicable to the coupling of the α,β-unsaturated alkenyl halides.[5,6]

It is generally agreed and reasonable to formulate the coupling reaction as proceeding via an organonickel(II) intermediate formed by oxidative addition of the organic halide to nickel(0) species,[7-10] e.g.

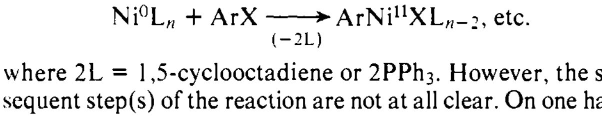
$$\mathrm{Ni^0L_{\mathit{n}} + ArX \xrightarrow[(-2L)]{} ArNi^{II}XL_{\mathit{n}-2}}, \text{ etc.}$$

where 2L = 1,5-cyclooctadiene or $2PPh_3$. However, the subsequent step(s) of the reaction are not at all clear. On one hand, a second oxidative addition of aryl halide followed by reductive elimination of biaryl from a diarylnickel(IV) species has been proposed.[2] Alternatively, a case can be presented for the reductive coupling to proceed via a diarylnickel(II) species formed by trans arylation between two arylnickel(II) halides.[11] Simple homolysis followed by dimerization of aryl radicals also cannot be entirely discounted on the basis of the evidence at hand.[12]

Since arylnickel(II) halides are isolable in pure crystalline form,[8,13] the most direct attack on this mechanistic problem is to determine how these complexes react. This approach is facilitated by the ready characterization of a variety of diamagnetic organonickel intermediates directly by ^{1}H and ^{31}P NMR spectroscopy, particularly in hydrocarbon media.[14]

Results

The arylnickel(II) halides used in this study can be readily prepared by the oxidative addition of aryl halides to tetrakis(triethylphosphine)nickel(0) or by metathesis of dihalobis(triethylphosphine)nickel(II), i.e.,[8,13] eq 1. The four-coordinate



$$\mathrm{Ni^0(PEt_3)_4 + ArX \xrightarrow[(-2PEt_3)]{} Ar\overset{\substack{PEt_3\\|}}{\underset{\substack{|\\PEt_3}}{Ni^{II}}}X \xleftarrow[-(MgX_2)]{} X_2Ni^{II}(PEt_3)_2 + ArMgX} \quad (1)$$

adduct which is isolated as a brown, crystalline solid shows only a single resonance in the ^{31}P NMR spectrum due to the trans configuration of the pair of phosphine ligands.[13] These arylnickel(II) halides are soluble in a variety of nonpolar organic solvents. When pure, they are stable at elevated temperatures for prolonged periods, but decompose readily in the presence of aryl halides. For example, *trans-o*-tolylbromobis(triethylphosphine)nickel(II) [hereafter designated as *o*-tolylnickel(II) bromide] underwent no perceptible decomposition in cyclohexane or benzene solution, when heated in a sealed, evacuated tube for 20 h at 70 °C. However, in the presence of tolyl bromide, the characteristic brown color gradually disappeared on heating for a few hours. The rate accelerated with increasing concentrations of tolyl bromide.

I. Products and Stoichiometry. The induced decomposition of *o*-tolylnickel(II) bromide by *o*-tolyl bromide produced a colorless solution containing 1 equiv of bi-*o*-tolyl, together with a deep blue oil consisting of the paramagnetic arylphosphonium tetrabromonickelate(II) salt, $(o\text{-}CH_3C_6H_4PEt_3)_2NiBr_4$. Similar results were obtained with phenyl, chlorophenyl, anisyl, and tolyl bromides and iodides. In each case, the biaryl fraction was analyzed by quantitative gas–liquid chromatography and compared to authentic samples (see Experimental Section). The paramagnetic tetrabromo- and tetraiodonickelate salts were readily characterized by their distinctive colors (blue and red) and absorption spectra (λ_{max} 755 and 510 nm, respectively).[15] The arylphosphonium ions were prepared independently by the alkylation of the corresponding aryldiethylphosphine with ethyl bromide and analyzed by their characteristic NMR spectra in aqueous solutions. Together with the analysis of the unreacted aryl bromide, the overall stoichiometry for the induced decomposition of arylnickel(II) bromide is given as

$$\mathrm{ArNiBrL_2 + 3ArBr \rightarrow ArAr + (ArL)_2NiBr_4} \quad (2)$$

where Ar = $o\text{-}CH_3C_6H_4$ and L = PEt_3. The reduced arenes (ArH) are not formed in any significant amounts under these reaction conditions.

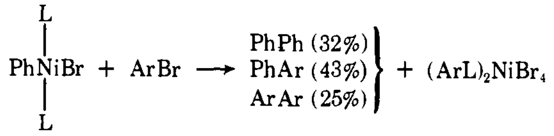
For the most part, nonpolar organic solvents such as benzene, toluene, and hexane were found to be the most suitable media for our studies. In solvents such as nitromethane, the arylnickel(II) complex afforded high yields of homocoupled biaryl, e.g.

$$\mathrm{PhNiBrL_2 \xrightarrow[CH_3NO_2]{} PhPh}, \text{ etc.} \quad (3)$$

without consuming aryl halide. In halogenated solvents such as methylene chloride, low yields of homocoupled biaryls were also formed, but the remaining products were not examined.

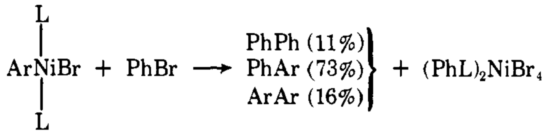
II. The Identity of Aryl Groups in the Formation of Biaryls and Phosphonium Salts. According to the stoichiometry in eq 2, the aryl groups are converted to two unique products—biaryls and arylphosphonium salt. Two questions arise immediately: (1) what is the source of biaryl, and (2) how is it related to the formation of arylphosphonium salt? To answer these questions, one of the aromatic rings in eq 2 was labeled with a substituent to distinguish it from the other. Under these circumstances, the *specificity* of the reaction is measured by the yield of the cross-coupled biaryl (**Ar**Ar) relative to that of either of the dimers ($\mathbf{Ar}_2$ and Ar_2) resulting from the homocoupling of the aryl groups derived from **Ar**$NiXL_2$ or ArX. Methyl and methoxy substituents, particularly in the ortho position, served as useful labels since they enabled us to follow the course of reaction directly by their characteristic chemical shifts in the ^{1}H NMR spectra. [In order to emphasize the distinction between the aryl groups in eq 2, the arylnickel(II) complex will be designated hereafter in boldface type (**Ar**-$NiBrL_2$) and the aryl halide in ordinary type (ArBr).]

A. Scrambling of Aryl Groups in the Biaryls. The reaction of phenylnickel(II) halide with another aryl halide leads to extensive scrambling of the phenyl groups in the biaryl fraction, as shown by the use of an *o*-methoxy group as the label (Ar = $o\text{-}CH_3OC_6H_4$), i.e., eq 4. Although extensive, the scrambling



$$\mathrm{Ph\overset{\substack{L\\|}}{\underset{\substack{|\\L}}{Ni}}Br + ArBr \longrightarrow \left.\begin{matrix} PhPh\ (32\%) \\ PhAr\ (43\%) \\ ArAr\ (25\%) \end{matrix}\right\} + (ArL)_2NiBr_4} \quad (4)$$

is not complete since reversing the label does not quite produce the equivalent results (eq 5). Indeed, the trend in Table I is for



$$\mathrm{Ar\overset{\substack{L\\|}}{\underset{\substack{|\\L}}{Ni}}Br + PhBr \longrightarrow \left.\begin{matrix} PhPh\ (11\%) \\ PhAr\ (73\%) \\ ArAr\ (16\%) \end{matrix}\right\} + (PhL)_2NiBr_4} \quad (5)$$

more scrambling to occur with increasing reactivity of the arylnickel(II) complexes.

B. Origin of Arylphosphonium Salts. The aryl group in the phosphonium salt is derived exclusively from the aryl halide,

Table I. Scrambling of Aryl Groups in the Reaction between Arylhalonickel(II) Halide and Aryl Halide[a]

ArNi(PEt$_3$)$_2$X (mmol)		ArX	(mmol)	solvent	Ar$_2$, mmol	ArAr, mmol	Ar$_2$, mmol	Σ biaryls mmol	Σ biaryls %[c]	ΣAr[d] mmol	ΣAr/ ArNiX
				General							
C_6H_5-	-Br (0.4)	none		cyclohexane	0.057	0	0	0.057	14	0.114	0.29
C_6H_5-	-Br (0.4)	C_6H_5Br	(4.0)	cyclohexane	0.41	0	0	0.41	100	0.82	2.05
C_6H_5-	-Br (0.4)	*o*-ClC_6H_4Br	(4.0)	cyclohexane	0.155	0.037	*b*	0.192	48	0.35	0.88
				Effect of Aryl Group							
C_6H_5-	-Br (0.4)	*o*-$MeOC_6H_4Br$	(2.0)	cyclohexane	0.122	0.166	0.098	0.386	97	0.41	1.02
C_6H_5-	-Br (0.4)	*o*-$MeOC_6H_4Br$	(4.0)	cyclohexane	0.116	0.150	0.070	0.336	84	0.38	0.95
o-$MeOC_6H_4$-	-Br (0.4)	C_6H_5Br	(2.0)	cyclohexane	0.036	0.238	0.051	0.325	81	0.31	0.78
o-$MeOC_6H_4$-	-Br (0.4)	C_6H_5Br	(4.0)	cyclohexane	0.033	0.233	0.054	0.320	80	0.29	0.73
				Effect of Halide							
o-$MeOC_6H_4$-	-Br (0.04)	C_6H_5Br	(0.4)	benzene	0.006	0.024	0.005	0.036	90	0.036	0.90
o-$MeOC_6H_4$-	-Br (0.04)	C_6H_5I	(0.4)	benzene	0.010	0.016	0.007	0.033	83	0.036	0.90
o-$MeOC_6H_4$-	-I (0.04)	C_6H_5Br	(0.4)	benzene	0.008	0.020	0.004	0.032	80	0.036	0.90
o-$MeOC_6H_4$-	-I (0.04)	C_6H_5I	(0.4)	benzene	0.012	0.014	0.008	0.034	85	0.038	0.95
				Effect of Solvent							
o-$MeOC_6H_4$-	-Br (0.108)	C_6H_5Br	(0.54)	THF	0.013	0.075	0.007	0.095	88	0.101	0.94
o-$MeOC_6H_4$-	-Br (0.135)	C_6H_5Br	(0.675)	cumene	0.011	0.055	0.026	0.092	68	0.077	0.57
C_6H_5-	-Br (0.58)	C_6H_5Br	(2.9)	CH_3NO_2	0.28	0	0	0.28	48	0.56	0.96
C_6H_5-	-Br (0.25)	C_6H_5Br	(2.5)	CH_2Cl_2	0.022	0	0	0.022	9	0.044	0.18

[a] Reactions were carried out at 70 °C in a sealed tube for 20-36 h. [b] Not analyzed. [c] Based on ArNi(PEt$_3$)$_2$X used, i.e., 100(Σ biaryls)/(ArNi(PEt$_3$)$_2$X). [d] Total Ar groups (from ArNiL$_2$X) which are present as biaryls.

Table II. Formation of Arylphosphonium Salts from Arylnickel(II) Halides and Aryl Halides[a]

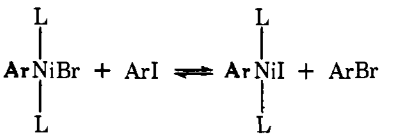
ArNiBr(PEt$_3$)$_2$	(M)	ArX	(M)	(ArPEt$_3$)$_2$NiBr$_4$ Ar	(M)	%[b]
Ar = *o*-$CH_3OC_6H_4$						
	(0.080)	*o*-$CH_3OC_6H_4Br$	(1.6)	*o*-$CH_3OC_6H_4$	(0.16)	100
	(0.080)	*o*-$CH_3C_6H_4Br$	(1.6)	*o*-$CH_3C_6H_4$	(0.16)	100
	(0.080)	C_6H_5Br	(0.36)	C_6H_5	(0.16)	100
Ar = *p*-$Me_2NC_6H_4$						
	(0.054)	*p*-$MeO_2CC_6H_4I$	(0.26)	*p*-$Me_2OCC_6H_4$	(0.11)	100

[a] In benzene solution at 70 °C. [b] Yield based on ArNiBr(PEt$_3$)$_2$.

independent of the presence of ortho substituents, as listed in Table II. In order to show that the absence of aryl scrambling in the phosphonium product did not arise from a mass action effect, the reaction was also carried out with only a slight excess of aryl halide. Although the rate of decomposition was slow, no scrambling of the aryl groups in the phosphonium product was observed.

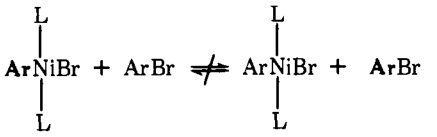
It is noteworthy that the aryl group originally attached to nickel is always converted in high yields to biaryls, and none of it is scrambled into the arylphosphonium moiety. These results clearly indicate that the arylphosphonium salt is formed in a separate process from that of biaryls.

C. Halogen Exchange between Arylnickel Halide and Aryl Halide. The extent of aryl scrambling during biaryl formation is also dependent on the halide—the specificity decreasing from the bromo (69%) to the iodo (41%) derivatives in Table I. A close examination of the results shows that, when the halogens associated with the reactants are different, the specificity follows that of the aryl halide. Thus, the extent of biaryl scrambling from an arylnickel(II) bromide with iodobenzene is more akin to that obtained from arylnickel(II) iodide and iodobenzene, rather than that from arylnickel(II) bromide and bromobenzene. This pattern evolves from a third reaction extant in this system, viz., the facile *halogen exchange* between arylnickel(II) halides and aryl halides, i.e., eq 6. Indeed, halogen exchange as described in eq 6 occurs more readily than either phosphonium or biaryl formation, since it can be observed separately as a prior reaction. For example, the ^{1}H NMR spectrum of *o*-anisylnickel(II) bromide is readily distinguished from that of *o*-anisylnickel(II) iodide by the sharp singlet resonances of the methoxy groups at 3.30 and 3.40 ppm, respectively. If a benzene solution of *o*-anisylnickel(II) bromide is warmed in the presence of iodobenzene, the bromine-iodine exchange is observed by the clear-cut, progressive shift in the proton resonance from 3.30 to 3.40 ppm. The reverse occurs with *o*-anisylnickel(II) iodide and bromobenzene. In both cases, the halogen-exchanged aryl halide can also be isolated without contamination by either biaryls or phosphonium salts.[16] Halogen exchange is also manifested in the identity of the tetrahalonickelate products, in which the reaction of arylnickel(II) bromides with excess aryl iodides always produces tetraiodonickelate and not bromotriiodonickelate(II).



$$\mathrm{Ar}\overset{\mathrm{L}}{\underset{\mathrm{L}}{\mathrm{Ni}}}\mathrm{Br} + \mathrm{ArI} \rightleftharpoons \mathrm{Ar}\overset{\mathrm{L}}{\underset{\mathrm{L}}{\mathrm{Ni}}}\mathrm{I} + \mathrm{ArBr} \qquad (6)$$

The ready halogen exchange in eq 6 is to be distinguished from an alternative process involving *aryl exchange*, i.e., eq 7, in which an aryl group bonded to nickel(II) is converted to aryl halide. The extensive material balance observed in these systems precludes the occurrence of such a preequilibrium exchange process. Furthermore, the aryl exchange in eq 7 can



$$\mathrm{Ar}\overset{\mathrm{L}}{\underset{\mathrm{L}}{\mathrm{Ni}}}\mathrm{Br} + \mathrm{ArBr} \not\rightleftharpoons \mathrm{Ar}\overset{\mathrm{L}}{\underset{\mathrm{L}}{\mathrm{Ni}}}\mathrm{Br} + \mathrm{ArBr} \qquad (7)$$

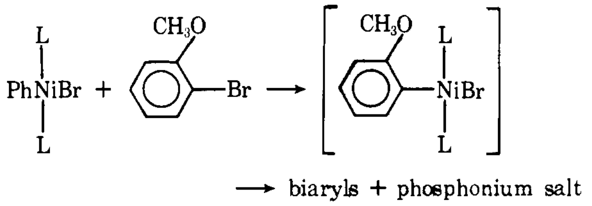
Table III. Induction Periods Observed during the Reaction of Arylnickel(II) Halide with Aryl Halides

$ArNi(PEt_3)_2X$[a]		ArX[b]		temp, °C	additives	induction period,[c] min
o-$CH_3OC_6H_4$-	-Br	20	o-$CH_3C_6H_4Br$	80	0	130
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5Br	80	0	21
o-$CH_3OC_6H_4$-	-Br	40	C_6H_5Br	80	0	6
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5I	70	0	5
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5I	60	0	20
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5I	55	0	40
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5I	55	PEt_3 (0.2%)[d]	63
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5I	55	$NiBr_2$	2
o-$CH_3OC_6H_4$-	-Br	20	C_6H_5I	55	MeOTf	9
o-$CH_3C_6H_4$-	-Cl	20	C_6H_5Br	80	0	80
o-$CH_3C_6H_4$-	-Br	20	C_6H_5Br	80	0	20
o-$CH_3C_6H_4$-	-I	20	C_6H_5Br	80	0	2
o-$CH_3C_6H_4$-	-Br	20	C_6H_5I	80	0	4
o-$CH_3C_6H_4$-	-Br	20	C_6H_5Br	80	$NiBr_2$	2

[a] An 0.08 M solution in benzene. [b] Numbers refer to equivalents of aryl halide used relative to each arylnickel(II) halide. [c] Induction period observed for degassed, sealed-tube reactions. [d] 0.2% of the total amount of arylhalonickel(II) complex.

be independently tested by carrying out the reaction with an excess of ArBr to allow ArBr, if formed, to be diluted sufficiently and survive intact. However, under no circumstances was the exchanged aryl bromide ever detected in these systems.

D. Arylnickel(II) Species from Aryl Halides as Intermediates. Although the aryl ligand on nickel is not exchanged with halide as in eq 7, the aryl halide is converted to an arylnickel(II) species in the course of reaction. Such a process can be observed directly during the reaction of phenylnickel(II) bromide with o-anisyl bromide by the examination of the ^1H NMR spectrum. Thus, the disappearance of o-anisyl bromide (δ 3.03) coincided with the buildup of o-anisylnickel(II) bromide (δ 3.30) to a maximum of about 20% of the phenylnickel(II) bromide initially present, and it gradually disappeared as the reaction proceeded to completion, i.e., eq 8.



→ biaryls + phosphonium salt (8)

In a similar manner, a maximum of approximately 10% of o-anisylnickel(II) bromide was observed during the reaction of o-tolylnickel(II) bromide and o-anisyl bromide. However, the reverse reaction between o-anisylnickel(II) bromide and o-tolyl bromide produced less than 1% o-tolylnickel(II) bromide. Qualitatively, the trend in reactivity of arylnickel(II) bromides appears to be $C_6H_5 > o\text{-}CH_3C_6H_4 > o\text{-}CH_3OC_6H_4$. This order is consistent with the observation that the amount of the new arylnickel species observed is minor whenever it is more reactive than the reactant ($ArNiXL_2$). Irrespective of such a trend, however, it is important to emphasize that this *aryl* transfer *occurs without the concomitant* exchange *of the aryl ligand on nickel,* as represented in eq 7.

III. Rates of Decomposition of Arylnickel(II) Halides Induced by Aryl Halides. The kinetic behavior of the decomposition shows two distinct and unique phases: (A) an induction period followed by (B) a rapid second-order reaction, as described separately below.

A. Promotion and Removal of the Induction Period. When a clear, homogeneous, brown solution of arylnickel(II) halide and aryl halide in benzene is heated at 70 °C, there is no apparent change for variable lengths of time, depending on the aryl halide, the arylnickel(II) complex, the temperature, and the purity of the reactants. During this quiescent period, there is also no change in the ^1H NMR spectrum of the solution. As the heating is continued, the solution gradually becomes opalescent, and changes in the NMR spectrum are clearly discernible.[17] The induction periods for the various halides are listed in Table III.

The induction period could be deliberately lengthened by adding less than 0.2% of triethylphosphine. The presence of large amounts of phosphine inhibited the reaction completely. Control experiments showed that triethylphosphine did not separately react with either arylnickel(II) halide or aryl halide to any detectable extent under these reaction conditions.

Conversely, the induction period could be shortened considerably by adding small amounts of either nickel bromide (heterogeneous) or methyl trifluoromethanesulfonate.[18] It is striking that, as chemically dissimilar as nickel bromide and methyl trifluoromethanesulfonate are, they both effectively serve a common function in this system. Indeed, nickel bromide is so insoluble in benzene that the amount actually in solution could not be measured. Nonetheless, even under these conditions, it can coordinate with triethylphosphine:

$$NiBr_2 + 2PEt_3 \rightarrow NiBr_2(PEt_3)_2 \qquad (9)$$

In a similar vein, methyl trifluoromethanesulfonate readily alkylates triethylphosphine:

$$CH_3OSO_2CF_3 + PEt_3 \rightarrow CH_3PEt_3{}^+CF_3SO_3{}^- \qquad (10)$$

Thus, these reactions are effective in the removal of free triethylphosphine extant in solution, and both can be considered as "phosphine traps".

B. Kinetics. Following the induction period, the decomposition of the arylnickel(II) complex in Figure 1 proceeded with pseudo-first-order kinetics:

$$-\frac{d[ArNiXL_2]}{dt} = k_{obsd}[ArNiXL_2] \qquad (11)$$

where $k_{obsd} = k_2[ArX]$. Significantly, the apparent rate constant of $k_{obsd} = 1.23 \times 10^{-3}\ s^{-1}$ was the same as that obtained from the phosphine-inhibited reaction with $k_{obsd} = 1.18 \times 10^{-3}\ s^{-1}$. Furthermore, the same rate constant was observed in those reactions promoted by nickel bromide and by methyl triflate.[19] One can conclude from these results that these additives, independent of whether they shorten or extend the induction periods, are not directly involved in decomposition itself.

The rate constants of decomposition of o-anisylnickel(II) bromide in the presence of various substituted phenyl bromides are listed in Table IV. The listed values of k_2 are indicated to only two significant figures since they were obtained from only those parts of the kinetic plots after the (variable) induction

Table IV. Kinetics of the Reaction of Arylnickel(II) Halide and Aryl Bromide in Benzene Solution at 80 °C

o-MeOC$_6$H$_4$NiBr, M	ArBr	(M)	$t_{1/2}$, s	k_{obsd}, 10^3 s^{-1}	k_2, 10^4 s^{-1} M^{-1}
0.08	p-MeOC$_6$H$_4$Br	(1.6)	1760	0.39	2.5
0.08	p-CH$_3$C$_6$H$_4$Br	(1.6)	2100	0.33	2.1
0.08	C$_6$H$_5$Br	(1.6)	1260	0.55	3.4
0.08	C$_6$H$_5$Br	(2.4)	840	0.83	3.5
0.08	C$_6$H$_5$Br	(3.2)	600	1.15	3.6
0.08	p-ClC$_6$H$_4$Br	(1.6)	960	0.72	4.5
0.08	p-CH$_3$COC$_6$H$_4$Br	(1.2)	570	1.21	10.1

Table V. Relative Rates of Arylphosphonium Salt Formation[a]

RC$_6$H$_4$X		RC$_6$H$_4$X/ C$_6$H$_5$X	[RC$_6$H$_4$PEt$_3$$^+$][b]/ [C$_6H_5PEt_3$$^+$]	$r_{\mathrm{RC_6H_4PEt_3^+}}/r_{\mathrm{C_6H_5PEt_3^+}}$		σ
p-Me$_2$N	Br	1.0	7.04	7.04	(0.85)[c]	−0.60
p-MeO	Br	1.0	1.52	1.52	(0.18)	−0.27
p-CH$_3$	Br	0.50	0.58	1.16	(0.06)	−0.17
		1.0	1.20	1.20	(0.08)	
		1.5	2.08	1.04	(0.02)	
m-CH$_3$	Br	1.0	1.18	1.18	(0.07)	−0.069
p-Cl	Br	0.67	0.15	0.22	(−0.66)	+0.23
p-MeO	I	1.0	1.76	1.76	(0.24)	−0.27
p-CH$_3$	I	1.0	1.70	1.70	(0.23)	−0.17
m-CH$_3$	I	1.0	1.48	1.48	(0.17)	−0.069
p-Cl	I	0.67	0.62	0.93	(−0.03)	+0.23
m-MeOOC	I	0.50	0.30	0.60	(−0.22)	+0.32
p-MeOOC	I	0.50	0.26	0.52	(−0.28)	+0.46

[a] Decomposition of 0.06 M o-tolylnickel(II) halide with 40-fold excess of aryl halides carried out in benzene at 80 °C for 20 h. [b] Product analyzed by ^{31}P NMR in acetone/H$_2$O mixture. [c] Rate relative to hydrogen; logarithm in parentheses.

periods were complete.[19] Electron-withdrawing substituents enhanced the rate of decomposition, whereas electron-releasing substituents retarded the rate; although the effect is not large, it corresponded roughly to a Hammett ρ value of one (vide infra). The effect of an ortho substituent is to diminish the rate of decomposition whether it is located on the arylnickel(II) complex (where C$_6$H$_5$NiBr > o-CH$_3$OC$_6$H$_4$NiBr) or on the aryl halide (where C$_6$H$_5$I > C$_6$H$_5$Br > o-CH$_3$OC$_6$H$_4$Br).

The kinetics of the formation of arylphosphonium salts was determined by a competition method in which a limited amount of o-tolylnickel(II) halide was treated with a mixture consisting of a pair of aryl halides (C$_6$H$_5$X and RC$_6$H$_5$X) in large excess. The effects of para (R) substituents were determined relative to hydrogen from the quantitative analysis of the mixture of the arylphosphonium salts [C$_6$H$_5$PEt$_3$$^+$ and p-RC$_6$H$_4$PEt$_3$$^+$] utilizing their characteristic ^{31}P NMR spectra as described in the Experimental Section.

The rate of formation of arylphosphonium salt is first order in aryl halide (see Table V), and it is facilitated by electron-releasing substituents. The Hammett correlation affords $\rho = -1.8$ for aryl bromides and $\rho = -0.8$ for aryl iodides.

IV. Probes for Chain Reactions and Radical Intermediates. The dual observations of induction periods and aryl scrambling are symptomatic of radical chain reactions and aryl radicals as intermediates, as described below.

A. Inhibition of Radical Chain Processes. The participation of radical chain processes was examined with three types of inhibitors: (1) nitroaromatics and quinones, (2) oxygen, and (3) stable radicals.

(1) **Nitroaromatics and quinones** are known to be effective suppressors of chain reactions proceeding via radical-anion intermediates.[20] Their inhibitory effects were studied under a standard set of conditions employing o-tolylnickel(II) bromide with phenyl bromide in the presence of 5% additive. Chloranil, which is a powerful electron acceptor, reacted with the arylnickel(II) complex upon mixing. However, subsequent to its immediate consumption, the usual coupling reaction proceeded unabated. 1,4-Benzoquinone, which is a weaker electron acceptor, also reacted with arylnickel(II) bromide, but at considerably slower rates. The weakest acceptor, duroquinone, strongly retarded the rate of loss of arylnickel(II) complex. However, the coupling reaction proceeded after prolonged heating.

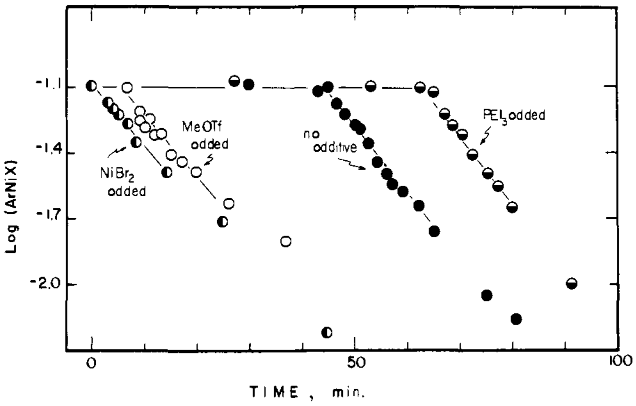


Figure 1. Effects of additives on the induction periods and rates of reaction of 0.08 M o-anisylnickel(II) bromide and 1.6 M iodobenzene in benzene solution at 55 °C: ◐, NiBr$_2$; ○, methyl triflate; ⊖, 0.2% PEt$_3$; ●, none.

Nitrobenzene and p-dinitrobenzene both completely inhibited the coupling reaction. Strong retardation by 5% duroquinone and complete inhibition by 5% p-dinitrobenzene were also observed even in the presence of nickel bromide which was deliberately added to reduce the induction period. Thus, the inhibitory nature of quinones and nitroaromatics appears to differ from that effected by triethylphosphine. (The difference will be elaborated later.)

(2) **Oxygen** is selective in its behavior toward arylnickel(II) halides. Those with ortho substituents are rather stable in air,[10b,21] but phenylnickel(II) bromide is air sensitive. The latter in the solid state shows no apparent signs of reaction with

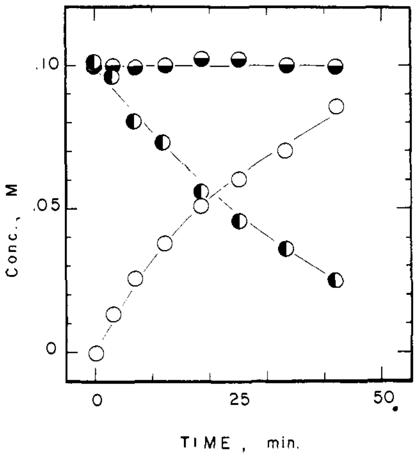


Figure 2. Decomposition of *p*-tolylazotriphenylmethane (◐) in the presence of *o*-anisylnickel(II) bromide (◓) and 5 equiv of 1,4-dihydrobenzene in benzene solution at 60 °C, and the production of toluene (○).

Table VI. Oxygen as an Inhibitor[a]

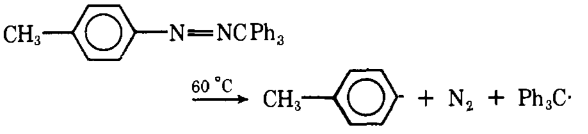
$PhNiBrL_2$, mmol	PhBr, mmol	O_2, mmol	Ph_2, mmol	recovered PhBr, mmol
0.245	0	0.245	0	0
0.245	2.45	0.245	0	1.87
0.090	0.90	0.045	0	0.83
0.090	0.90	0.018	0	0.80[b]
0.090	0.90	0.009	0	0.79

[a] In cyclohexane at 70 °C for 24 h. [b] Analysis of the residue showed the presence of $PhPEt_3^+$ salts.

air if kept at −20 °C for several days. Nonetheless, treatment of this exposed complex to bromobenzene under the usual reaction conditions afforded no biphenyl. Similarly, the addition of small amounts of oxygen completely inhibited the normal coupling reaction in Table VI. A colloidal, light green suspension, probably nickel oxide, was observed but not examined further.

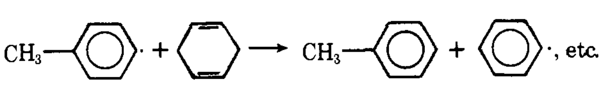
(3) **Stable radicals** such as diphenylpicrylhydrazyl (DPPH) and galvinoxyl, in amounts less than 5%, were ineffective in the prevention of aryl coupling or scrambling. When the amount of DPPH was increased to 65% in Table VII, no coupling was observed. Under these conditions, however, it is possible for a direct reaction between arylnickel(II) halide and DPPH to occur, which obscures its inhibitory effect.

B. Aryl Radicals as Possible Intermediates. The thermal decomposition of *p*-tolylazotriphenylmethane (TATM) generates free *p*-tolyl radicals at 60 °C in benzene solution with a half-life of approximately 18 min[22] (eq 12). The *p*-tolyl



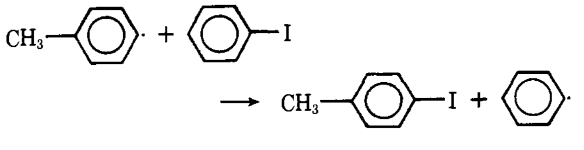
(12)

radical generated in this manner can be effectively trapped with 1,4-dihydrobenzene to afford toluene[23] (eq 13), as shown



, etc. (13)

in Figure 2. *p*-Tolyl radicals are also effectively trapped by iodobenzene (eq 14).[24-26] The reactions in eq 13 and 14 thus



(14)

constitute a convenient and unequivocal test for aryl radicals as reactive intermediates.

The presence of *o*-anisylnickel(II) bromide had no effect on either the rate of decomposition of *p*-tolylazotriphenylmethane or the production of toluene. This series of experiments proves that 1,4-dihydrobenzene is capable of effectively trapping *p*-tolyl radicals even in the presence of the *o*-anisylnickel(II) complex. Since the addition of 5 equiv of 1,4-dihydrobenzene to the reaction of *o*-anisylnickel(II) bromide and iodobenzene did not affect either the biaryl coupling or the aryl scrambling process, *o*-anisyl radicals are clearly not intermediates in either.[27]

In another test for aryl radicals, the *p*-tolylazotriphenylmethane and 1,4-dihydrobenzene were added together to a system consisting of *o*-anisylnickel(II) bromide and iodobenzene. (The latter was chosen to expedite the coupling reaction so that it would match the rate of thermolysis of TATM.) In the first set of reactions, no attempt was made to reduce the induction period inherent in the coupling reaction of the arylnickel(II) complex. Consequently, the spontaneous decomposition of *p*-tolylazotriphenylmethane occurred prior to the commencement of the coupling reaction. (This experiment also establishes that the induction period is not related to the presence or absence of aryl radicals.) In the second set of experiments, nickel bromide was added to reduce the induction period to approximately 1 min so that the reaction of *o*-anisylnickel(II) iodide coincided with the thermolysis of the azo compound. The results in Table VIII show that all the free *p*-tolyl radicals generated from the decomposition of TATM[28,29] can be quantitatively accounted for as either toluene or *p*-tolyl iodide. Therefore, free aryl radicals cannot be intermediates in either process which leads to biaryl coupling or to aryl scrambling.

Discussion

The stoichiometry for the formation of biaryls and arylphosphonium salts in eq 2 can be represented by three separate transformations:

$$ArNiBrL_2 + ArBr \rightarrow ArAr + NiBr_2L_2 \qquad (15)$$

$$NiBr_2L_2 + 2ArBr \rightarrow 2ArL^+Br^- + NiBr_2 \qquad (16)$$

$$NiBr_2 + 2Br^- \rightarrow NiBr_4^{2-} \qquad (17)$$

where L = PEt_3. From a mechanistic point of view, biaryl and arylphosphonium salts are largely derived from separate processes since scrambling is observed in the biaryls, whereas $ArPEt_3^+$ is formed specifically from the aryl halide. However, the two processes are intimately related—they both take place simultaneously, and only immediately after the cessation of the induction period. Indeed, the observations of aryl scrambling and an induction period together provide rare insight into the mechanism of biaryl formation, and they allow us to focus on the delineation of this problem first. The mechanism of the accompanying formation of arylphosphonium salts should then evolve naturally. For brevity of presentation, we have omitted the phosphine ligands in the discussion which follows immediately. The importance of phosphine ligation is elaborated later.

I. Mechanism of Biaryl Formation. The most straightforward formulation of biaryl formation from arylnickel(II) halides involves reductive elimination from a diarylnickel(II) intermediate followed by the reoxidation of nickel(0) species by oxidative addition of aryl halide. The first step in such a process is an exchange of aryl ligands between a pair of arylnickel(II) halides as shown in Scheme I. (The formal oxidation

Table VII. Stable Radicals as Inhibitors[a]

$PhNiBrL_2$, mmol	ArBr,[b] mmol	additive	(%)	biaryl products, mmol Ph_2	PhAr	Ar_2	ArBr recovered, mmol	coupling, %[c]
0.250	1.25	DPPH	(65)	0	0	0	0.850	0
0.236	1.18	DPPH	(4.7)	0.034	0.075	0.039	0.542	63
0.236	1.18	galvinoxyl	(3.3)	0.058	0.082	0.029	0.401	70

[a] In cyclohexane at 70 °C for 40 h. [b] $o\text{-}CH_3OC_6H_4Br$. [c] Based on $PhNiBrL_2$.

Table VIII. Competitive Trapping of *p*-Tolyl Radicals with 1,4-Dihydrobenzene and Iodobenzene[a]

TATM, mmol	1,4-dihydrobenzene, mmol	ArNiBr,[b] mmol	C_6H_5I, mmol	additive	products, mmol $CH_3C_6H_5$	$CH_3C_6H_4I$	$\Sigma Ar\cdot$[c] %
0.095	0.95	0.071	0.71	0	0.039	0.021	63
0.076	0.76	0.65	0.65	$NiBr_2$	0.032	0.017	64

[a] In 1.0 mL of benzene at 60 °C for 5 h. [b] $o\text{-}CH_3OC_6H_4NiBr(PEt_3)_2$. [c] Based on TATM; remainder represents cage reactions.

Scheme I. Reductive Elimination from Diarylnickel(II) as an Intermediate for Biaryls

$$2ArNi^{II}X \xrightarrow{(i)} ArNi^{II}Ar + NiX_2 \tag{18}$$

$$ArNi^{II}Ar \xrightarrow{(ii)} Ar_2 + Ni^0 \tag{19}$$

$$Ni^0 + ArX \xrightarrow{(iii)} ArNi^{II}X, \text{etc.} \tag{20}$$

states are indicated for nickel only to emphasize the redox changes.)

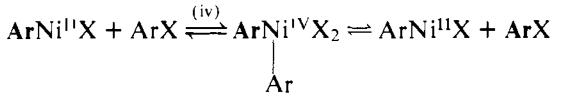
Indeed there is ample evidence for each of these steps occurring individually, i.e., (1) ligand exchange in eq 18,[11] (2) reductive coupling in eq 19,[30] and (3) oxidative addition in eq 20[13] are all well-known transformations. In order to include the important role played by aryl halide in promoting the reaction of arylnickel halides, step iii in Scheme I must be rate limiting, and aryl exchange in step i as well as reductive coupling in step ii, relatively fast. However, such a mechanism would require the arylnickel(II) halide itself to undergo decomposition to biaryl and nickel(0), which of course it does not under these conditions.

An alternative formulation based on the same basic notions involves interconversion of nickel(II) and nickel(IV) intermediates.[2] For example, oxidative addition of aryl halide to arylnickel(II) halide is now included as the rate-limiting activation process in Scheme II, and the reversible formation of the diarylnickel(IV) intermediate would account for the observed aryl scrambling.

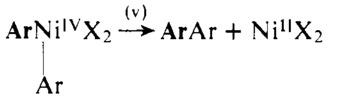
Indeed, it has been suggested on quasi-theoretical grounds that associative processes through 18-electron intermediates are favored by reductive elimination from 16-electron diarylnickel(II) complexes.[30] Reductive elimination of diaryl nickel(IV) intermediates to biaryls has also been proposed in the reaction of bis(cyclooctadiene)nickel(0) with 2 mol of aryl halide.[2] However, the absence of aryl exchange of the type described in eq 7 militates against this mechanism.

Aryl transfer to nickel from aryl halide in eq 8 is a most intriguing observation since it occurs in the absence of the reverse process (i.e., aryl exchange in eq 7). Such a transformation most likely requires the aryl halide to be transformed into a new, quite reactive species which is able to exchange aryl groups with arylnickel(II) halide on its way to biaryl products. The properties of the aryl radical conform to this picture, and it is included in Scheme III.

Scheme II. Reversible Oxidative Addition to Diarylnickel(IV) Intermediates Leading to Biaryls and Aryl Scrambling

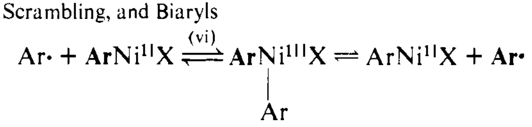


$$ArNi^{II}X + ArX \overset{(iv)}{\rightleftharpoons} \underset{\substack{|\\ Ar}}{ArNi^{IV}X_2} \rightleftharpoons ArNi^{II}X + ArX \tag{21}$$

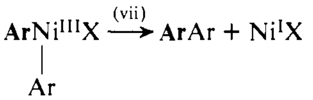


$$\underset{\substack{|\\ Ar}}{ArNi^{IV}X_2} \xrightarrow{(v)} ArAr + Ni^{II}X_2 \tag{22}$$

Scheme III. Aryl Radicals and Arylnickel(III) Leading to Aryl Transfer, Aryl Scrambling, and Biaryls



$$Ar\cdot + ArNi^{II}X \overset{(vi)}{\rightleftharpoons} \underset{\substack{|\\ Ar}}{ArNi^{III}X} \rightleftharpoons ArNi^{II}X + Ar\cdot \tag{23}$$



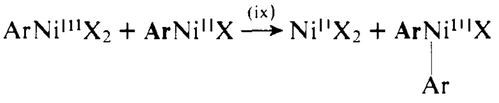
$$\underset{\substack{|\\ Ar}}{ArNi^{III}X} \xrightarrow{(vii)} ArAr + Ni^{I}X \tag{24}$$

Indeed, there is electrochemical evidence for the facile reductive coupling of diarylnickel(III) species, as in step vii.[31] Similarly, the oxidative addition of radicals to metal centers is known.[32] Step vi, expected to be highly reversible, accounts for both aryl scrambling as well as aryl transfer, without invoking aryl exchange. However, the carefully designed experiments described in Table VIII rigorously preclude aryl radicals as intermediates.

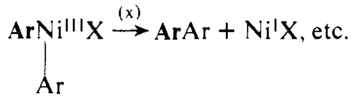
In the absence of aryl radicals as viable intermediates, we turn to other reactive intermediates which could promote aryl scrambling and aryl exchange with the initial arylnickel(II) halide. The rather selective inhibition by electron acceptors such as quinones and nitroaromatics suggests that ion radicals such as nickel(I) and nickel(III) are intermediates, reminiscent of a similar observation in the alkylation of π-allylnickel(II) halides with alkyl and vinylic halides.[33] Such paramagnetic species as arylnickel(III) species, for which there is recent independent evidence,[34] are included as key reactive intermediates in the propagation steps for the chain process shown in Scheme IV.

Scheme IV. Arylnickel(I,III) Species as Intermediates in the Radical Chain Mechanism

$$Ni^{I}X + ArX \xrightarrow{(viii)} ArNi^{III}X_2 \tag{25}$$



$$ArNi^{III}X_2 + ArNi^{II}X \xrightarrow{(ix)} Ni^{II}X_2 + \underset{\substack{|\\ Ar}}{ArNi^{III}X} \tag{26}$$



$$\underset{\substack{|\\ Ar}}{ArNi^{III}X} \xrightarrow{(x)} ArAr + Ni^{I}X, \text{etc.} \tag{27}$$

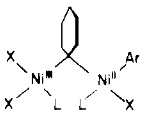
According to Scheme IV, biaryls result in step x from the reductive elimination of a metastable diarylnickel(III) species, which is formed by aryl transfer in step ix. Oxidative addition of aryl halide to nickel(I) in step viii completes the cycle. Indeed, the formulation of nickel(I) and arylnickel(III) species in a chain process provides a consistent basis for explaining all the diverse phenomena observed in this system. Each of these facets will be described separately.

1. Scrambling of Aryl Groups. Ligand Exchange Process. The aryl halide enters the cycle via oxidative addition to nickel(I) halide in step viii. The resultant arylnickel(III) dihalide is to be distinguished from the reactant, arylnickel(II) halide, insofar as it contains an additional halogen *atom.* Since such a paramagnetic species is expected to be labile,[35] it is susceptible to transfer of an aryl ligand as in step ix. Alternatively, transfer of halogen as depicted below

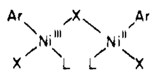
$$\mathrm{ArNi^{III}X_2} + \mathbf{ArNi^{II}X} \rightarrow \mathrm{ArNi^{II}X} + \mathbf{ArNi^{III}X_2} \quad (28)$$

is tantamount to aryl transfer, although it occurs without actual rupture of the **Ar**–Ni bond. Furthermore, halogen transfer in eq 28 scrambles aryl groups between nickel(II) and nickel(III) without causing a simultaneous aryl exchange in eq 7.

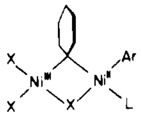
Aryl transfer and halogen transfer in eq 26 and 28, respectively, are formally considered to be electron-transfer reactions between nickel(II) and nickel(III) centers. As such, they are to be included in the well-known class of ligand-transfer processes[36] in which there are established examples of halo and aryl groups as bridging ligands.[37,38] The transition state (or intermediate) for such an inner-sphere process can be depicted as the singly bridged **2a** and **2b** or the doubly bridged **3**. Although aryl radicals and halogen atoms are not explicitly included as reactive intermediates in such a formulation, their effectiveness as bridging ligands is reflected in the facility with which they are transferred. Viewed in this way, cross coupling and scrambling in biaryl formation actually represent competing processes for aryl and halogen transfer in eq 26 and 28, respectively. Indeed the available data can be interpreted in this regard. Thus, the observation that the extent of aryl scrambling decreases in the order I > Br is consistent with their relative abilities to serve as bridging ligands.[37,39] Similarly, a more facile aryl transfer would lead to biaryls with higher specificity for cross coupling and less aryl scrambling in those systems employing a single halogen. Judging from the conjugate pairs of reactions in eq 4 and 5, the presence of an *o*-methoxy substituent retards aryl transfer since more scrambling occurs in the reaction of *o*-anisyl bromide with phenylnickel(II) than with phenyl bromide and *o*-anisylnickel(II).



2a



2b



3

An inner-sphere complex or transition state as depicted in **2** and **3** requires coordinative unsaturation at a nickel center. Indeed, the extremely high susceptibility of biaryl coupling to the presence of triethylphosphine suggests that its coordination as in **2** or **3** (where L = PEt_3) may influence not only the extent of scrambling but also biaryl formation. Its relationship to the formation of arylphosphonium salts is discussed in the next section.

2. The Initiation Process. According to Scheme IV, an arylnickel(III) species is responsible for the initiation of the catalytic cycle. Such a paramagnetic species may be formed directly from the diamagnetic reactants by an intermolecular electron-transfer process, since it can be shown independently that the arylnickel(II) halide is oxidized and the aryl halide is reduced in 1-equiv transformations,[40] as described below.

(a) The oxidation of arylnickel(II) halides is shown by the electrochemical studies at platinum electrodes. The process is a one-electron oxidation:

$$\mathrm{ArNi^{II}X} \xrightarrow{-e} \mathrm{ArNi^{III}X} \quad (29)$$

although the anodic wave in the cyclic voltammogram is irreversible even at sweep rates greater than 1 V s^{-1}.[41] The latter is consistent with electron transfer followed by a rapid chemical reaction (see Experimental Section). Arylnickel(II) halide is also readily oxidized by a variety of 1-equiv oxidants such as hexachloroiridate(IV), cerium(IV), and cobalt(III) trifluoroacetates.[42] If the reaction of $o\text{-}CH_3C_6H_4NiBr(PEt_3)_2$ is carried out at −50 °C, the absorption spectrum of a new species, stable at this temperature and absorbing at λ_{max} 410 nm, can be observed independent of whether Na_2IrCl_6, $Ce(TFA)_4$, or $CuBr_2$ is employed as the oxidant. The same reactions carried out directly in the cavity of an ESR spectrometer afforded an intense spectrum with $g = 2.196$[34] immediately upon mixing. We ascribe these spectral changes to the same paramagnetic arylnickel(III) species in eq 29 formed by anodic oxidation.

(b) The electrochemical reduction of aryl halides proceeds by a similar EC process in which electron transfer is followed by a rapid, spontaneous fragmentation of the anion radical:[43]

$$\mathrm{ArX} \xrightarrow{+e} \mathrm{ArX^{-}\cdot} \rightarrow \mathrm{Ar\cdot} + \mathrm{X^-} \quad (30)$$

The electrochemical irreversibility of the electron-transfer step precludes a determination of the reduction potential of aryl halides.[44] Polarographic studies have established, however, that the ease of reduction follows the order ArI > ArBr > ArCl with Hammett ρ values of +0.26, +0.56, and +0.71, respectively.[45] The lifetime of the chlorobenzene anion radical has been estimated to be 10^{-7} s, but it is strongly dependent on the presence of polar substituents.[46]

The ease of intermolecular electron transfer between arylnickel(II) halide with various aryl halides

$$\mathrm{ArNi^{II}X} + \mathrm{ArX} \rightarrow \mathbf{ArNi^{III}X} + \mathrm{ArX^{-}\cdot}, \text{ etc.} \quad (31)$$

should follow the trend in their reduction potentials, i.e., ArI > ArBr > ArCl. Indeed, induction periods which follow the order ArI < ArBr < ArCl in Table III parallel the expected relative rates of electron transfer in eq 31. However, the magnitude of the driving force for electron transfer is not expected to be large, since neither is an exceptional electron donor or acceptor, as reductants and oxidants go.[47] As a result, electron transfer is likely to be an inner-sphere process, as shown recently for a related example in Scheme V, involving the mechanism of oxidative addition of aryl halides to nickel(0) complexes.[48]

The rate-limiting electron-transfer step in eq 33 is subject to phosphine retardation due to the preequilibrium dissociation in eq 32. By analogy, electron transfer from arylnickel(II) halide is expected to proceed via a similar coordinatively unsaturated species (Scheme VI).

Such a mechanism provides a ready explanation for the unusual and marked dependence of the induction period on the availability of phosphine.

3. Oxidative Addition of Aryl Halides to Nickel(I) during the Propagation Cycle. According to Scheme IV, the aryl halide

Scheme V

$$(Et_3P)_4Ni \underset{}{\overset{K_1}{\rightleftharpoons}} (Et_3P)_3Ni + PEt_3 \quad (32)$$

$$(Et_3P)_3Ni + ArX \xrightarrow{k_{et}} (Et_3P)_3Ni^I + ArX^{-}\cdot, \text{ etc.} \quad (33)$$

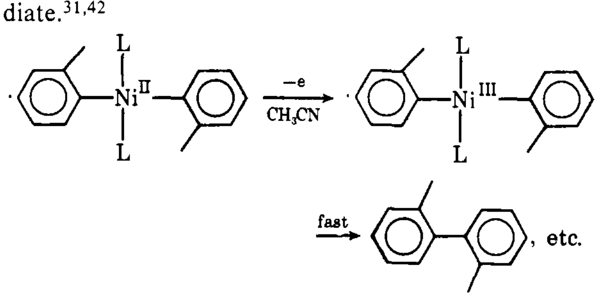
Scheme VI

$$\mathrm{ArNiX(PEt_3)_2 \overset{K_1'}{\rightleftharpoons} ArNiX(PEt_3) + PEt_3} \qquad (34)$$

$$\mathrm{ArNiX(PEt_3) + ArX \xrightarrow{k'_{et}} ArNi^{III}X(PEt_3) + ArX^{-}\cdot}, \text{ etc.} \qquad (35)$$

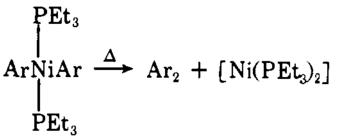
enters the propagation cycle by effecting oxidative addition to nickel(I) species in step viii (see eq 25). Indeed, the positive Hammett ρ value of about one in Figure 3 accords with electron accession to the metal center generally required for such an oxidative addition process.[32] It is noteworthy, however, that the magnitude of ρ in this example is substantially less than $\rho = 5.4$ for oxidative addition to nickel(0) in eq 33.[48]

4. Reductive Coupling of Arylnickel(III) Intermediates during the Propagation Cycle. The efficiency of the sequence of propagation steps in Scheme IV also depends critically on the rate of reductive elimination of biaryl in step x (eq 27). In accord with this expectation, the anodic oxidation of the diarylnickel(II) complex, $(o\text{-}\mathrm{CH_3C_6H_4})_2\mathrm{Ni(PEt_3)_2}$, affords high yields of biaryl, presumably via a diarylnickel(III) intermediate.[31,42]



, etc. (36)

The much slower thermal decomposition of diarylnickel(II) also affords biaryl in essentially quantitative yields. Reductive coupling probably obtains, as qualitatively indicated by the



$$\mathrm{Ar\overset{PEt_3}{\underset{PEt_3}{Ni}}Ar \xrightarrow{\Delta} Ar_2 + [Ni(PEt_3)_2]} \qquad (37)$$

change in color of the solution from yellow to deep brown, suggestive of the presence of unsaturated nickel(0) species.[49] Crossover experiments in Table IX indicate that the elimination process is intramolecular. Thermolysis as described in eq 37, however, is too slow to account for biaryl formation in this system. As expected, addition of bromobenzene considerably enhances the rate of coupling biaryl formation, and it is accompanied by aryl scrambling in basic accord with the mechanism in Scheme IV.

5. Inhibition of the Chain Process. The effectiveness of quinones and nitroaromatics as inhibitors is most easily reconciled with the oxidation of nickel(I) species in Scheme IV, since these compounds are known to be effective one-electron acceptors.[19,20] The less efficient inhibition by the stable radicals DPPH and galvinoxyl may be related to the slower rates of oxidation of nickel(I).

Oxygen is a more complex inhibitor since the results in Table IV indicate that arylnickel(II) halide as well as aryl halide is consumed during the induction period. A complex series of reactions involving autoxidation of phenylnickel(II) halide and further reaction of peroxynickel species is likely to be involved.

II. Comments on the Formation of Arylphosphonium Salts. The formation of arylphosphonium salts from aryl halides as described by the stoichiometry

$$\mathrm{ArX + PEt_3 \rightarrow ArPEt_3{}^{+}X^{-}} \qquad (38)$$

does not occur under the usual reaction conditions.[50] However, this phosphine arylation is induced by zerovalent nickel(0) complexes, and a catalytic mechanism involving sequential oxidative addition–reductive elimination steps has been speculatively proposed,[51] e.g., Scheme VII.

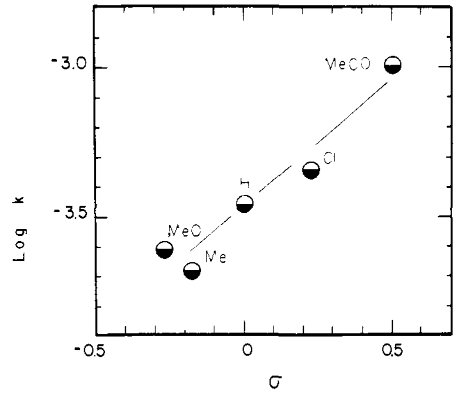


Figure 3. Hammett correlation of the rates of reaction of o-anisylnickel(II) bromide with para-substituted bromobenzenes in benzene solution at 80 °C.

Table IX. Thermal Reductive Elimination of Diarylnickel(II) Complexes[a]

$\mathrm{Ph_2Ni(PEt_3)_2}$, 10^2 mmol	$\mathrm{Ar_2Ni(PEt_3)_2}$,[b] 10^2 mmol	biaryl, 10^2 mmol		
		PhPh	PhAr	$\mathrm{Ar_2}$
6.0	0	4.5	0	0
0	6.0	0	0	6.0
6.0	6.0	6.0	0	6.0
0	6.0[c]	3.0	0.5	5.0

[a] In benzene solution at 80 °C for 20 h. [b] Ar = $o\text{-}\mathrm{CH_3OC_6H_4}$. [c] In the presence of 0.3 mmol of bromobenzene at 70 °C for 20 h.

Although reductive elimination of arylphosphonium salts from aryl(phosphine)platinum(IV) complexes has been reported,[52] it only occurs at elevated temperatures and requires polar solvents. However, more to the point, the arylnickel(II) halide employed in this study is thermally stable in the absence of aryl halide, and it cannot be involved as in Scheme VII.[53,54]

The simultaneity of the processes leading to biaryls and arylphosphonium salts, both with regard to radical chain initiation and inhibition, strongly suggests that the same paramagnetic arylnickel(III) and/or nickel(I) species are involved as intermediates in these transformations. Both of these possibilities will be discussed briefly, since there are mechanistic ambiguities in each.

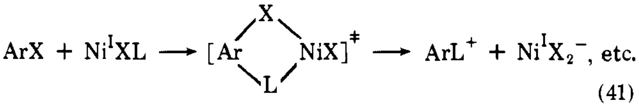
1. Nickel(I) Catalysis. One of the most direct formulations for arylphosphonium salt involves nickel(I) catalysis in a direct displacement on aryl halide by a coordinated phosphine. Such a nickel(I) assistance could involve a four-center transition state or intermediate, e.g., Scheme VIII, similar to that proposed for a variety of aromatic substitutions promoted by copper(I) complexes.[55] Scheme VIII readily accommodates the formation of arylphosphonium salt specifically from the aryl halide, without aryl scrambling taking place with the extant arylnickel(II) halide.

Scheme VII

$$\mathrm{(Ph_3P)_3Ni^0 + ArX \rightarrow ArNi^{II}X(PPh_3)_2 + PPh_3} \qquad (39)$$

$$\mathrm{ArNi^{II}X(PPh_3)_2 + 2Ph_3P \rightarrow ArPPh_3{}^{+}X^{-} + (Ph_3P)_3Ni^0}, \text{ etc.} \qquad (40)$$

Scheme VIII



$$\mathrm{ArX + Ni^{I}XL \longrightarrow [Ar\overset{X}{\underset{L}{\diamond}}NiX]^{\ddagger} \longrightarrow ArL^{+} + Ni^{I}X_2{}^{-}}, \text{ etc.} \qquad (41)$$

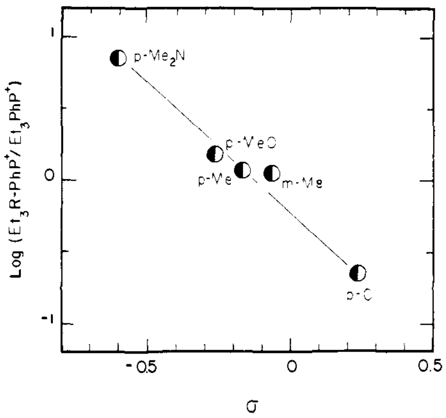


Figure 4. Hammett correlation of the relative rates of formation of arylphosphonium salts from RC_6H_4Br and C_6H_5Br during the decomposition of *o*-tolylnickel(II) bromide in benzene at 80 °C.

Table X. Phosphonium Salt Formation from Aryl Halide and Nickel(I) Complex[a]

$NiBr(PEt_3)_3$, mmol	ArX	(mmol)	$ArPEt_3^+$	(mmol)
0.10	C_6H_5Br	(1.0)	$C_6H_5PEt_3^+$	(0.18)
0.10	C_6H_5I	(1.0)	$C_6H_5PEt_3^+$	(0.19)
0.10	*o*-$CH_3OC_6H_4I$	(1.0)	*o*-$CH_3OC_6H_4PEt_3^+$	(0.22)

[a] Carried out in THF at 70 °C for 20 h in a sealed tube.

Nickel(I) catalysis in Scheme VIII can be examined directly since halo(phosphine)nickel(I) can be prepared independently by the synproportionation reaction[56]

$$Ni^0(PEt_3)_4 + Br_2Ni^{II}(PEt_3)_2 \rightarrow 2BrNi^I(PEt_3)_3 \quad (42)$$

Indeed, when this bromonickel(I) complex is treated with aryl halides, the arylphosphonium salt, $ArPEt_3^+$, is formed in high yields as shown in Table X.

In the formation of arylphosphonium salts, the effects of polar substituents on the reactivity of bromobenzene are reflected in a Hammett ρ value of -1.8 shown in Figure 4. The negative value of ρ suggests that the phosphine moiety is involved in an electrophilic attack on the aromatic nucleus in the transition state for arylphosphonium formation since such a process would be aided by electron release by nuclear substituents. This conclusion is readily accommodated by the cyclic transition state in Scheme VI, in which part of the driving force is derived from the expansion of the coordination sphere around the positive phosphorus center[57] as a result of nucleophilic attack by the ipso carbon center.

2. Nickel(I) and Arylnickel(III) Intermediates. The opposite signs of the ρ values for oxidative addition and arylphosphonium formation in Figures 3 and 4, respectively, strongly suggest that different mechanisms are involved in these processes, in accord with Schemes IV and VIII. However, Scheme VIII does not consider the ready reductive elimination of arylphosphonium salts which is known to occur from aryl(phosphine)nickel(III) species,[42] Since the latter are also included as intermediates in Scheme IV for biaryl formation, an alternative process for arylphosphonium formation must be considered, i.e., Scheme IX.

Scheme IX

$$Ni^IXL + ArX \rightarrow ArNi^{III}X_2L \quad (43)$$

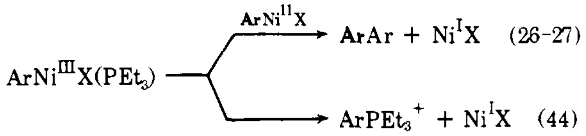
$$ArNi^{III}X_2L \rightarrow ArL^+X^- + Ni^IX \quad (44)$$

$$Ni^IX + L \rightarrow Ni^IXL, \text{etc.} \quad (45)$$

According to this mechanism, arylphosphonium salt arises from reductive elimination of a metastable aryl(phosphine)nickel(III) species formed by oxidative addition of aryl halide to phosphinenickel(I). Indeed, aryl(phosphine)nickel(III) generated independently by either an electrochemical or chemical oxidation of arylnickel(II) halide (see eq 29) affords excellent yields of arylphosphonium salt.[42]

$$ArNi^{II}X(PEt_3)_2 \xrightarrow{-e} ArNi^{III}X(PEt_3)_2^+ \xrightarrow{\text{fast}} ArPEt_3^+ + [Ni^IX] \quad (46)$$

However, in order to accommodate the negative ρ value described by Figure 4, Scheme IX must be modified so that reductive elimination in eq 44 is rate limiting and oxidative addition in eq 43 is reversible. Furthermore, a more serious problem arises from the postulation of Scheme IX, since both nickel(I) and arylnickel(III) species now become intermediates common with those in biaryl formation according to Scheme IV. These catalytic cycles become intertwined as they share a common arylnickel(III) intermediate, which is competitively partitioned between biaryl and arylphosphonium salt. Thus, the route to biaryls according to Scheme IV occurs via a prior aryl transfer to arylnickel(II) halide followed by reductive elimination, whereas the formation of arylphosphonium salt according to Scheme IX involves a direct, unimolecular process, i.e., eq 26-27 and 44. However, it is difficult to account for the specificity in arylphosphonium formation by this competition, since halogen exchange in eq 28 scrambles aryl groups between arylnickel(II) halide and the arylnickel(III) intermediate derived from the aryl halide.[58] Possibly, the extent of phosphine ligation may control the relative rates of these processes sufficiently to eliminate crossover processes (vide infra).



$$ArNi^{III}X(PEt_3) \xrightarrow{ArNi^{II}X} ArAr + Ni^IX \quad (26\text{-}27)$$

$$ArNi^{III}X(PEt_3) \longrightarrow ArPEt_3^+ + Ni^IX \quad (44)$$

3. The Role of Phosphine. In actuality, the problem is more complex than this, since the biaryl cycle is interlocked to the arylphosphonium cycle. Without the latter available to scavenge phosphine, the formation of biaryl as described in eq 15 is self-inhibited owing to the simultaneous release of phosphine. Conversely, in the absence of biaryl formation, insufficient phosphine would be available to fuel the arylphosphonium cycle. Indeed, it is probably the latter which curtails the induction period in absence of agents such as $NiBr_2$ or methyl trifluoromethanesulfonate to scavenge triethylphosphine.

The phosphine level in the reaction also controls the biaryl formation to the extent that it affects aryl transfer and halide exchange as described by structures **2** and **3.** We think that the ultimate resolution of the mechanistic conundrum posed by Schemes VIII and IX will rely upon a quantitative assessment of phosphine ligation in nickel(I) and arylnickel(III) intermediates, as well as in arylnickel(III) halide during the course of reaction. This problem is, no doubt, related to the dual role played by triethylphosphine in the initiation and inhibition of the system.

Summary and Conclusion

Aryl coupling proceeds from arylnickel(II) halides and aryl halides by a chain process involving nickel(I) and arylnickel(III) intermediates. The catalytic cycle in Scheme IV would lead specifically to cross-coupled biaryls, except for a halogen exchange process in eq 28 which, in effect, scrambles aryl groups in the reactant arylnickel(II) halide and the arylnickel(III) intermediate without actually reversibly cleaving any aryl-nickel bonds. The accompanying formation of arylphosphonium salts also derives from a catalytic process involving arylnickel(III) and/or nickel(I) intermediates. The two systems are *interdependent* in that arylphosphonium formation removes triethylphosphine, which is an inhibitor in the biaryl formation. Conversely, in the course of biaryl formation, phosphine is released to fuel the formation of arylphosphonium salt. We conclude on the basis of these studies that phosphine serves no useful function in the catalytic process for biaryl formation except possibly to provide for high selectivity and turnover numbers by stabilizing any nickel(0) or arylnickel(II) intermediates. These and other mechanistic insights provide a basis for the development of optimum, catalytic procedures for biaryl synthesis.[59]

Experimental Section

All reactions and manipulations of air-sensitive nickel complexes were carried out under an argon atmosphere using Schlenk equipment and standard bench-top techniques.[60] Melting points were determined in sealed capillary tubes in vacuo and are uncorrected. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind. Proton magnetic resonance spectra were obtained on a Varian T-60 spectrometer using tetramethylsilane as an internal standard, or otherwise as specified. The ^{31}P NMR spectra were recorded at 40.4 MHz on a Varian XL-100 NMR spectrometer, employing 85% H_3PO_4 as an external standard. The ultraviolet-visible absorption spectra were recorded on Cary 14 or Beckman DBG spectrophotometers. A Beckman GC-5 gas chromatograph was used for the analysis of arenes and biaryls.

Materials. Solvents and reagents used in this study were commercial reagent grade materials, repurified by standard methods. Tetrahydrofuran, diethyl ether, and hydrocarbon solvents were purified by distillation from sodium benzophenone ketyl under argon prior to use. Acetonitrile was distilled from P_2O_5.

The aryl halides, bromobenzene, iodobenzene, *p*-bromotoluene, *p*-iodotoluene, *m*-bromotoluene, *o*-bromotoluene, *p*-bromoanisole, *o*-bromoanisole, and *p*-bromoacetophenone, were obtained commercially and purified according to standard methods.[61] The following aryl iodides were synthesized from the corresponding diazonium salts and potassium iodide: *p*-iodoanisole, *m*-iodotoluene, and *p*-chloroiodobenzene. The esters, methyl *p*-bromobenzoate, methyl *p*-iodobenzoate, methyl *m*-bromobenzoate, and methyl *m*-iodobenzoate, were obtained by the esterification of the corresponding acids with boron trifluoride-methanol.[62] The *o*-chlorodiphenyl was synthesized from *o*-aminobiphenyl by the Sandmeyer reaction. *o*-Methoxybiphenyl was obtained from the nickel-catalyzed cross coupling of *o*-anisylmagnesium bromide and bromobenzene.[63] It contained less than 1% bi-*o*-anisyl. The bi-*o*-anisyl was synthesized by the Ullmann coupling of *o*-anisyl iodide with copper.[64] Phenyltriethylphosphonium bromide was prepared from phenyldiethylphosphine and ethyl bromide, mp 185-186 °C (lit. 187 °C).[65] *p*-Tolylazotriphenylmethane was prepared according to Wang's procedure.[22] Diphenylmethane and 1,4-dihydrobenzene, obtained from Aldrich Chemical Co., were redistilled before use.

Triethylphosphine was purchased from Pressure Chemical Co. and used without further purification. *trans*-Dibromobis(triethylphosphine)nickel(II) was prepared by the procedure described by Jensen and Nygaard.[66] Tetrakis(triethylphosphine)nickel(0) was prepared from bis(1,5-cyclooctadiene)nickel(0) according to Schunn.[67]

Preparation of Arylnickel Complexes. *trans-o*-Tolylbromobis(triethylphosphine)nickel(II) and *trans*-phenylbromobis(triethylphosphine)nickel(II) were synthesized from *trans*-dibromobis(triethylphosphine)nickel(II) as described earlier.[13]

***trans*-Diphenylbis(triethylphosphine)nickel(II)** was synthesized according to the procedure described by Chatt and Shaw,[21] mp 128-134 °C (lit. 125-130 °C).

***trans-o*-Anisylbromobis(triethylphosphine)nickel(II)** was prepared by a similar procedure. To a stirred ethereal solution of 6.0 g (13.2 mmol) of *trans*-dibromobis(triethylphosphine)nickel(II) at −10 °C was added a solution of *o*-anisylmagnesium bromide prepared from 3.5 g (18.7 mmol) of *o*-anisyl bromide, 1.0 g (41 mmol) of magnesium, and 2.0 g (10.6 mmol) of 1,2-dibromoethane in 30 mL of ether. After 10 min, the reaction mixture was cooled further and a solution of 5% aqueous HBr added. Extraction, followed by washing, drying, and evaporation of the solvent, gave a dark brown solid residue which included some starting material. The product was recrystallized from hot hexane several times, yielding 1.0 g of brown crystals, mp 108-110 °C. The ^1H NMR spectrum in C_6D_6 consisted of a singlet (δ 3.30, 3 H) for the methoxy group and unresolved multiplets (δ 6.22, 6.81, 4 H) for the aromatic protons, in addition to multiplets (between δ 0.65 and 1.65, 30 H) for the ethyl groups. Anal. Calcd for $C_{19}H_{37}OP_2BrNi$: C, 47.34; H, 7.74; P, 12.85. Found: C, 47.57; H, 7.84; P, 12.67

***trans-o*-Anisyliodobis(triethylphosphine)nickel(II).** A mixture of *trans-o*-anisylbromobis(triethylphosphine)nickel(II) (0.5 g, 1.0 mmol) and 4.0 g of sodium iodide (3.3 mmol) was dissolved in 30 mL of acetone. After the mixture was stirred for 5 min, the acetone was removed in vacuo. Water (40 mL) was added and the mixture stirred for 10 min. Filtration of the mixture afforded an insoluble residue which was dissolved in a mixture of benzene and hexane and then dried with $MgSO_4$. The solvent was removed and the residue recrystallized from hexane to afford 0.23 g (42% yield) of brown crystals, mp 136-138 °C. The ^1H NMR spectrum of this material in benzene consisted of a singlet (δ 3.40, 3 H) for the methoxy group and multiplets (between δ 0.65 and 1.65, 30 H) for the ethyl groups. The resonance due to aromatic protons was not observed owing to a large solvent (benzene) absorption.

***trans-p-N,N*-Dimethylaminophenylbromobis(triethylphosphine)nickel(II).** A solution of *p-N,N*-dimethylaminophenyl bromide (0.16 g, 0.8 mmol) in 20 mL of hexane was added to a solution of $Ni(PEt_3)_4$ (0.4 g, 0.75 mmol) in 20 mL of hexane. The solution was stirred overnight during which time the color changed from purple-red to yellow-brown. The solvent was recovered in vacuo and the residue recrystallized from cold hexane to afford yellow-brown crystals of 0.25 g of *trans-p-N,N*-dimethylaminophenylbromobis(triethylphosphine)nickel(II) (67% yield), mp 160-165 °C dec. The ^1H NMR spectrum in C_6D_6 consisted of a singlet (δ 2.70, 6 H) due to the dimethylamino group and an unresolved multiplet (δ 6.70, 7.25, 4 H) due to aromatic protons, in addition to multiplets (between δ 0.74 and 1.80, 30 H) for ethyl groups.

***trans*-Di-*o*-anisylbis(triethylphosphine)nickel(II).** *o*-Bromoanisole (4.0 g, 21.4 mmol) and *n*-butyllithium (20 mL of a 1.25 M solution in hexane) were mixed in 30 mL of hexane. The resulting *o*-anisyllithium precipitate was removed by filtration through a sintered glass filter. The solid *o*-anisyllithium was washed several times with hexane and redissolved in 25 mL of THF. The solution of *o*-anisyllithium was then added to *trans*-dibromobis(triethylphosphine)nickel(II) (4.5 g, 9.9 mmol) dissolved in 30 mL of degassed, anhydrous ether under argon with the aid of a hypodermic syringe. The reaction mixture was stirred for 15 min and 100 mL of water added. The organic layer, as well as insoluble residue, was collected, and the ether removed in vacuo. The residue was then recrystallized twice from hexane to afford 0.8 g of light yellow crystals, mp 134-135 °C. The ^1H NMR spectrum in acetone-d_6 consisted of a singlet (δ 3.77, 6 H) due to the methoxy group and unresolved multiplets for aromatic protons (δ 6.47, 3 H; 7.27, 1 H). The resonances due to the ethyl groups consisted of multiplets (between δ 0.87 and 1.17, 30 H). Anal. Calcd for $C_{26}H_{44}O_2P_2Ni$: C, 61.32; H, 8.71; P, 12.16. Found: C, 61.94; H, 9.01; P, 12.33.

Reaction of Arylnickel(II) Halides with Aryl Halides Product Analysis. Reaction of *trans*-Arylhalobis(triethylphosphine)nickel(II) with Aryl Halide. A typical procedure was carried out as follows. *trans*-Phenylbromobis(triethylphosphine)nickel(II) (0.36 g, 0.81 mmol) was weighed into a small Schlenk tube and 2.1 mL of freshly degassed dry benzene added. A 1-mL aliquot of this solution was transferred with the aid of a hypodermic syringe to a Pyrex glass tube under argon. A calculated amount of *o*-anisyl bromide (1.4 g, 7.7 mmol) was added, and the glass tube degassed by three freeze-pump-thaw cycles and finally sealed in vacuo. The tube was heated in a constant-temperature oil bath regulated at 70 ± 1 °C for 20 h. At the end of this period, a clear solution containing a deep blue, oily precipitate was observed. The tube was opened, and the clear solution separated from the blue precipitate. An internal standard (*o*-bromotoluene) was added, and the contents of the solution were analyzed by gas-liquid chromatography using a 10-ft 15% Apiezon L column at 240 °C. Since the remaining tetrahedral tetrabromonickelate salts are paramagnetic, the NMR spectra were broadened in nonaqueous media. To obviate this difficulty, the blue, oily precipitate was washed with hexane several times and dried. It was then dissolved in 1 mL of D_2O. Methanol (20 μL) was added as an internal reference to the D_2O

Table XI. ^{1}H NMR Spectra of Aryltriethylphosphonium Salts[a]

$ArPEt_3^+X^-$	substituent $-CH_3$	aromatic protons	PEt_3[d]				
			CH_3[b]	CH_2[c]	$J_{H\text{-}PCH_3}$	$J_{H\text{-}PCH_2}$	$J_{H\text{-}H}$
$(C_6H_5PEt_3)Br$		7.4-7.9	1.05	2.41	19	13	7
$(C_6H_5PEt_3)_2NiBr_4$		7.4-7.9	1.10	2.48	19	13	7
$(o\text{-}CH_3C_6H_4PEt_3)_2NiBr_4$	2.52	7.2-7.8	1.12	2.55	19	12	7
$(o\text{-}CH_3OC_6H_4PEt_3)_2NiBr_4$	3.85	7.0-7.9	1.01	2.41	19	13	7
$[p\text{-}(CH_3)_2NC_6H_4PEt_3]_2NiBr_4$	2.96	6.8-7.8	1.11	2.38	19	13	7
$(p\text{-}CH_3O_2CC_6H_4PEt_3)_2NiBr_4$	3.87	7.6-8.3	1.07	2.52	20	13	7

[a] Spectra taken in D_2O at room temperature; chemical shift in δ relative to a residual resonance of D_2O at δ 4.61. [b] Doublet of triplets. [c] Doublet of quartets. [d] Coupling constants in hertz.

solution, and the NMR spectrum recorded. The amount of the *o*-anisyltriethylphosphonium salt was calculated from the integrated peak areas of the methoxy protons relative to the methyl protons of methanol. The spectral data for several aryltriethylphosphonium salts are listed in Table XI.

Reaction of *trans-p-N,N*-Dimethylaminophenylbromonickel(II) Complex with Methyl *p*-Iodobenzoate. The *trans-p-N,N*-dimethylaminophenylbromonickel(II) complex (27 mg, 0.054 mmol) and methyl *p*-iodobenzoate (69 mg, 0.26 mmol) were mixed in 1 mL of degassed, dry benzene. The solution was transferred into a 5-mm Pyrex glass tube with the aid of a hypodermic syringe and degassed by three freeze-pump-thaw cycles. The tube was sealed in vacuo and heated at 80 °C in a thermostated oil bath for 10 h. The tube was opened, and the red, oily residue washed with hexane several times and then dried. The red phosphonium salt was dissolved in D_2O and its NMR spectrum recorded. The single, sharp ^{31}P NMR resonance at 36.3 ppm showed that the *p*-carbomethoxyphenyltriethylphosphonium ion was the only salt formed in this reaction. This conclusion was confirmed by the examination of the ^{1}H NMR spectrum, which showed a singlet at δ 3.87 corresponding to the carbomethoxy group present in the phosphonium salt (Table XI).

Induction Period. A procedure similar to that described above was followed. *trans*-Arylhalobis(triethylphosphine)nickel(II) was weighed into a small Schlenk tube, and measured amounts of degassed solvent and aryl halide were added. Aliquots of this solution were transferred with the aid of a hypodermic syringe into several Pyrex tubes under argon. Various amounts of the additives listed in Table III were added. The tubes were then degassed by three successive freeze-pump-thaw cycles and sealed in vacuo. After the tubes were heated in a constant-temperature oil bath, the yellow solutions remained clear throughout the induction period. However, they each developed a distinct cloudiness at the end of the induction period. The time required for the observation of the first hint of cloudiness was arbitrarily taken as denoting the induction period.

Halide Exchange. *trans-o*-Anisylbromobis(triethylphosphine)nickel(II) complex (0.35 g, 0.72 mmol) and iodobenzene (2.9 g, 14.2 mmol) were dissolved in 8.4 mL of benzene contained in a small Schlenk tube under argon. The solution was degassed by successive freeze-pump-thaw cycles, and the tube heated in a constant-temperature oil bath maintained at 55 °C. No change was apparent during the induction period. After 40 min, cloudiness began to develop. The tube was heated for an additional 2 min after the first sign of cloudiness was noted. The tube was then cooled to room temperature. The entire volatile fraction was removed by vacuum transfer into another receiving flask. Analysis of the volatile fraction by gas chromatography indicated the presence of 0.9 g (79%) of bromobenzene. The brown residue was recrystallized from hexane and shown to consist of *trans-o*-anisyliodobis(triethylphosphine)nickel(II) complex, 0.34 g (89%), mp 136-138 °C.

Kinetics of the Biaryl Coupling. The rate of the reaction was followed by monitoring the arylhalonickel(II) complex by means of its NMR spectral change. A typical procedure is as follows. *trans-o*-Anisylbromobis(triethylphosphine)nickel(II) (50 mg, 0.105 mmol), bromobenzene (330 mg, 2.1 mmol), and diphenylmethane (17.5 mg, 0.105 mmol, as an internal reference) were dissolved in 1.1 mL of dry benzene. The solution was transferred to an NMR tube with the aid of a hypodermic syringe and degassed via three freeze-pump-thaw cycles. The tube was then sealed in vacuo and placed into an 80 °C oil bath upside down. At prescribed time intervals, the tube was removed from the oil bath, cooled, and centrifuged until all the insoluble, oily precipitate was concentrated at the top of the tube. The NMR spectrum of the reinverted tube was recorded. The disappearance of the methoxy resonance at δ 3.30 of the anisylnickel complex was measured relative to the methylene resonance of the internal reference at δ 3.59.

Effect of Additives. A. Oxygen. *trans*-Phenylbromobis(triethylphosphine)nickel(II) (122 mg, 0.27 mmol) and bromobenzene (424 mg, 2.7 mmol) were mixed with 6 mL of cyclohexane under argon in a small Schlenk tube. The solution was divided into three equal aliquots, and each was placed into a small Schlenk tube with the aid of a hypodermic syringe. Each Schlenk tube was capped with an air-tight rubber septum, and the calculated amount of oxygen introduced with the aid of a gas-tight hypodermic syringe. The tubes were heated at 70 °C in a constant-temperature oil bath for 24 h. The yellow color faded and dirty-appearing precipitate developed during the course of the heating. The liquid content was analyzed by gas-liquid chromatography, but no coupled biaryl was detected.

B. Phosphine, Quinones, and Nitroaromatics. The progress of the reaction in the presence of these additives was monitored by the NMR spectral change in a similar manner as described above. *trans-o*-Tolylbromobis(triethylphosphine)nickel(II) (135 mg, 0.29 mmol) and bromobenzene (910 mg, 5.8 mmol) were mixed in 3 mL of dry benzene. Aliquots of this solution were transferred into several NMR tubes under argon. The calculated amount of various additives was added. The solution was then degassed via three freeze-pump-thaw cycles, and the tube sealed in vacuo. The tube was heated in a constant-temperature oil bath maintained at 80 °C. The progress of the reaction was monitored by following the changes in the ^{1}H NMR spectrum. In the presence of 5 mol % nitrobenzene or *p*-dinitrobenzene, the NMR spectrum of *trans-o*-tolylbromobis(triethylphosphine)nickel(II) remained unchanged throughout the whole heating period (24 h). The control experiment without any inhibitor added showed an induction period of 22 min and the reaction was essentially complete in 3 h, as evident from the complete disappearance of the NMR absorption of the methyl resonance at δ 2.80 and the ethyl resonance due to the triethylphosphine at δ 0.7-1.6. The reaction with 5% duroquinone added showed an induction period of about 4 h, followed by a much slower coupling reaction for the next 20 h.

In another experiment, the small Schlenk tube containing a stock solution of the *trans-o*-tolylbromonickel(II) complex and bromobenzene was first heated in the 80 °C oil bath until the induction period was just complete, as indicated by the first hint of cloudiness. The tube was removed from the bath, cooled, and centrifuged to clarify the solution. Aliquots of this solution were then transferred into several NMR tubes under argon with the aid of hypodermic syringes. The calculated amounts of various additives were added, and the tubes degassed by repeated freeze-pump-thaw cycles and sealed in vacuo prior to heating. Inhibition and retardation similar to those observed with *p*-dinitrobenzene and duroquinone as described above were observed.

Test for Aryl Radicals. A. Generation and Trapping of Aryl Radicals. *p*-Tolylazotriphenylmethane (104 mg, 0.28 mmol), 1,4-dihydrobenzene (115 mg, 1.4 mmol), and diphenylmethane (48 mg, 0.28 mmol, as an internal reference) were dissolved in 2.7 mL of benzene. A 1-mL aliquot of this solution was transferred into an NMR tube. The tube was degassed by three freeze-pump-thaw cycles and sealed in vacuo. Another tube was prepared in a similar manner but containing *trans-o*-anisylbromobis(triethylphosphine)nickel(II) (22 mg, 0.046 mmol). The two tubes were heated in a constant-temperature oil bath maintained at 60 °C. The *p*-tolylazotriphenylmethane upon decomposition produced *p*-tolyl radicals which were trapped by 1,4-dihydrobenzene to afford toluene. The rate of the reaction was

Table XII. ^{31}P Chemical Shifts of Aryltriethylphosphonium Salts in D_2O-Acetone[a]

σ	$RC_6H_4PEt_3^+$	^{31}P chemical shift,[b] ppm
−0.60	*p*-Me_2N	33.05
−0.27	*p*-MeO	34.15
−0.17	*p*-CH_3	34.48
0	H	35.00
0.23	*p*-Cl	35.62
0.32	*m*-MeOOC	35.78
0.46	*p*-MeOOC	36.30

[a] Tetraiodonickelate as counterion, at room temperature. [b] Downfield relative to H_3PO_4.

monitored by the disappearance of the *p*-tolylazotriphenylmethane resonance and the appearance of toluene resonance (δ 2.37) in the ^1H NMR spectrum. The presence of added *trans*-*o*-anisylbromobis(triethylphosphine)nickel(II) had no effect on this reaction.

B. Generation of Tolyl Radicals and Trapping of Other Radicals during the Coupling Reaction. *p*-Tolylazotriphenylmethane (22 mg, 0.095 mmol), 1,4-dihydrobenzene (76 mg, 0.95 mmol), *trans*-*o*-anisylbromobis(triethylphosphine)nickel(II) (34 mg, 0.071 mmol), iodobenzene (145 mg, 0.71 mmol), and diphenylmethane (12 mg, 0.07 mmol, as an internal reference) were all dissolved in 0.8 mL of benzene. The solution was degassed by three freeze-pump-thaw cycles and sealed in an NMR tube in vacuo. A similar tube which also contained $NiBr_2$ was prepared. The two tubes were heated in a 60 °C bath, and the course of the reaction followed by monitoring the changes in the ^1H NMR spectrum. The tube without added $NiBr_2$ showed no unusual reaction other than the decomposition of *p*-tolylazotriphenylmethane and the production of toluene. On the other hand, the tube with added $NiBr_2$ showed both the decomposition of *p*-tolylazotriphenylmethane as well as the coupling reaction between *trans*-*o*-anisylbromonickel(II) and iodobenzene. After completion, both tubes were opened and the liquid contents analyzed by gas-liquid chromatography, as described above.

Kinetics of the Formation of Phosphonium Salt. A 1-mL aliquot of a stock solution of 0.06 M *trans*-*o*-tolylbromobis(triethylphosphine)nickel(II) in benzene was transferred to a 5-mm Pyrex tube with the aid of a hypodermic syringe. A substituted aryl iodide in 15-20-fold excess, together with a 15-20-fold excess of the reference iodobenzene, was added. The solution was degassed by successive freeze-pump-thaw cycles and sealed in vacuo. After 20 h of heating in an 80 °C oil bath, the reactions were complete, as evidenced by the formation of a clear solution together with a red, oily residue. After separation of the solution, the red residue was washed with benzene and dried. The red solid was completely dissolved in D_2O. The ^1H NMR and ^{31}P NMR spectra were taken. For some phosphonium salts which are not very soluble in water, a mixture of acetone and water was used as solvent. The relative yields of the two phosphonium salts were calculated from the intensities of the phosphorus resonances in the ^{31}P NMR spectrum. The ^{31}P chemical shifts for various substituted aryltriethylphosphonium salts listed in Table XII correlate linearly with the Hammett σ constants as shown in Figure 5.

Electrochemical Studies of Arylhalo(phosphine)nickel(II) Complexes. The anodic oxidation of *trans*-*o*-tolylhalobis(triethylphosphine)nickel(II) complexes was examined by cyclic voltammetry (CV) and controlled potential oxidation in acetonitrile, THF, and acetone solutions with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. The CV of *trans*-*o*-tolylbromobis(triethylphosphine)nickel(II) showed one irreversible anodic wave at +0.57 vs. SCE in acetone. In the less polar THF solution, the peak was shifted to +0.90 V. The anodic wave was irreversible even at −55 °C with a scan rate of 1 V s^{-1}. However, a small reduction peak, observed at −0.8 V in THF solution at low temperature, is associated with the anodic wave since it was not observed without proceeding through a prior anodic cycle. The CV of *o*-tolylchlorobis(triethylphosphine)nickel(II) showed a similar anodic wave at +0.68 V vs. SCE in acetonitrile solution. A controlled potential oxidation of *o*-tolylchloronickel(II) complex in acetonitrile at 0.8-1.1 V consumes 2 electrons overall (by coulometry). A quantitative yield of the corresponding *o*-tolyltriethylphosphonium salt was obtained, as determined from the ^{31}P NMR analysis of the resulting solution. Since a paramagnetic intermediate was observed in the corresponding chemical oxidation of the arylnickel(II) complex at low temperature,[42] the anodic reaction is also presumed to produce an arylnickel(III) complex as an intermediate by a one-electron process. If so, the facile oxidation of the nickel(I) intermediate resulting from the decomposition of the arylnickel(III) intermediate (compare eq 48) would consume an additional electron. Indeed, the CV of authentic $NiCl(PEt_3)_3$ in THF showed an irreversible anodic wave at −0.15 V vs. SCE, which is roughly 1 V less than that required to oxidize arylnickel(II) halides.

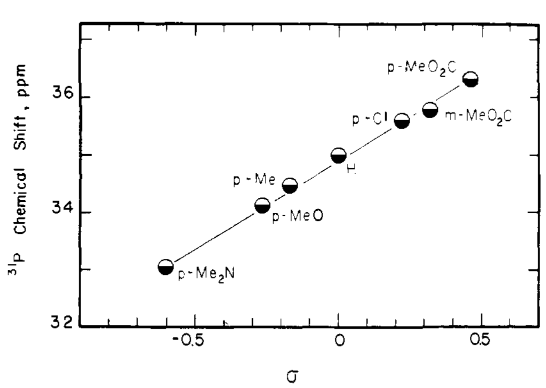


Figure 5. Hammett correlation of the ^{31}P NMR chemical shifts of ring-substituted phenyltriethylphosphonium salts in aqueous acetone.

Reductive Elimination of Diarylnickel(II) Complex. A typical procedure for the reaction is as follows. *trans*-Diphenylbis(triethylphosphine)nickel(II) (0.1 g, 0.22 mmol) was weighed into a small Schlenk tube under argon, and the solvent benzene (3.7 mL) added. A 1-mL aliquot of this solution was transferred into a Pyrex glass tube under argon with the aid of a hypodermic syringe. The tube was degassed by several freeze-pump-thaw cycles and sealed in vacuo. After heating in a constant-temperature oil bath maintained at 80 °C for 20 h, the tube was opened and allowed to stand in air for 15 min. During this time the nickel(0) product was autoxidized, and a green precipitate was formed. The filtered solution was analyzed by gas-liquid chromatography using a 10-ft 15% Apiezon L column at 240 °C.

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(53) Furthermore the cis isomer is not a viable intermediate either, since facile phosphine exchange indicates that cis–trans isomerization is likely to be too rapid in these square-planar arylnickel(II) halides.[13]

(54) Under drastic thermal conditions, the decomposition of arylnickel(II) halides does afford biaryls and nickel(I) species.[12]

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(57) (a) From arguments based on dipole moment, X-ray photoelectron spectroscopic, and electrochemical measurements, it has been deduced that the coordinated phosphine has a formal positive charge distribution; for example, in dichlorobis(triethylphosphine)nickel(II) it is Cl(-0.3 e) and P(+0.3 e). See J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 2392 (1975). (b) A similar transition state (or intermediate) involving a five-coordinate phosphorus moiety has been proposed in oxygen atom transfers between nitro compounds and phosphinenickel(0) complexes to afford phosphine oxides and the corresponding nitroso compounds, i.e.

$$RNO_2 + (Et_3P)_4Ni \xrightarrow[-PEt_3]{} Et_3PO + (RNO)Ni(PEt_3)_2$$

(R. S. Berman and J. K. Kochi, *Inorg. Chem.*, in press).

(58) Even if reductive elimination in eq 51 were faster than aryl transfer, scrambling in the phosphonium salt would result from reductive elimination subsequent to the halogen exchange in eq 20, which accompanies the biaryl formation. Conversely, if reductive elimination were slower than halogen exchange, the interconversion of arylnickel(II) and arylnickel(III) would eventually lead to scrambling in arylphosphonium salt.

(59) Studies in progress.

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