(63) H. Hartmann, C. Beermann, and H. Czempik, *Z. Anorg. Allg. Chem.*, **287**, 261 (1956).

(64) A second possibility, that the acetylene is activated by intermolecular coordination to a second palladium atom has been suggested by a referee. The infrared active stretching mode $\nu(C{\equiv}C)$ is a sensitive probe of acetylene coordination in Pd(II), Pt(II), Pd(0), and Pt(0) complexes.[65] We have found no infrared evidence for metal–acetylene π-interactions either in the solid state or in solution in a variety of organic solvents for any of the complexes $PdCl_2(Ph_2PC{\equiv}CR)_2$ (R = CF_3, Ph, Et, *i*-Pr, *t*-Bu). While we cannot completely rule out this possibility, our results can be adequately explained without invoking such interactions.

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Mechanistic Studies of Nickel Catalysis in the Cross Coupling of Aryl Halides with Alkylmetals. The Role of Arylalkylnickel(II) Species as Intermediates

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Abstract: The cross coupling of bromobenzene and *o*-bromotoluene with methyllithium and methylmagnesium bromide to produce toluene and *o*-xylene, respectively, is used for the mechanistic study of nickel catalysis. The synthesis, characterization, and reactions of arylmethylnickel(II) compounds (I) as reaction intermediates provide a rational basis for examining individual steps in the catalytic cycle. It is shown that I is formed rapidly under reaction conditions from either nickel(II) or nickel(0) as potential precursors. The subsequent reductive elimination of I does afford the requisite arene products by an intramolecular route, but it proceeds too slowly for the catalytic process to be effective. The rate is enhanced by aryl bromide and by methyllithium or methylmagnesium bromide and even more strikingly by molecular oxygen. A mechanism is proposed in which reductive elimination is promoted by prior electron transfer from I and the corresponding nickelate species to the aryl bromide. The stereochemical features inherent in reductive eliminations of *trans*-arylmethylnickel(II) compounds are discussed.

The formation of carbon–carbon bonds is one of the most important operations in organic synthesis, and it is represented by the coupling of organometallic reagents R–m including alkyllithium and Grignard reagents, with organic derivatives R–X such as alkyl halides among others.

$$R{-}m + R'{-}X \xrightarrow{[M]} R{-}R' + m{-}X \qquad (1)$$

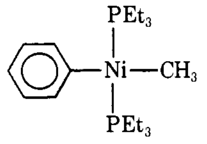
Transition metal complexes are particularly effective catalysts in the cross coupling reaction depicted in eq 1.[1-4] However, the role played by the metal has not been clearly delineated in most cases. It has been generally and presumptively assumed that the catalyst undergoes a series of two-electron oxidation and reduction cycles via a dialkylmetal intermediate.[5] Thus, a species such as I has been presented without direct proof as an intermediate in the nickel catalyzed coupling of Grignard reagents and aryl halides as outlined in eq 2 and 3.[1,7]

$$\underset{\text{I}}{L_2Ni(Ar)R} + Ar{-}X \longrightarrow \underset{\text{II}}{L_2Ni(Ar)X} + Ar{-}R \qquad (2)$$

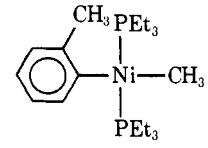
$$\text{II} + R{-}MgX \longrightarrow MgX_2 + \text{I, etc.} \qquad (3)$$

Indeed, recent studies by Parshall have shown that nickel(0) complexes can be used in the synthesis of I via a two-step sequence involving oxidative addition of aryl halide followed by metathesis with methyllithium.[8] He also observed qualitatively the reductive elimination of the fluorophenylmethylnickel species I (L = triethylphosphine) to fluorotoluene.

The sequence of reactions 2 and 3 constitutes a potentially attractive catalytic scheme for the cross coupling process and obviously merits further attention. We feel that the mechanism of the formation and decomposition of the arylmethylnickel species I is central to the understanding of the catalytic cycle. In this report we describe the isolation and decomposition of two series of arylnickel complexes using the phenyl and *o*-tolyl moieties. The *o*-tolyl group allowed the relevant arylnickel complexes to be isolated and well characterized due to the stabilization known to be imparted by the presence of *o*-methyl groups.[6,9] Factors involved in the reductive elimination of methyl and aryl ligands from I have provided interesting insight into the mechanism of the nickel catalyzed cross coupling reaction.



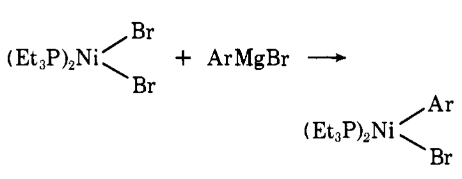
Ia



Ib

Results

Synthesis and Characterization of Arylmethylbis(triethylphosphine)nickel(II) Complexes. The nickel(II) complexes II, *trans*-arylbromobis(triethylphosphine)nickel, were synthesized by the reaction of dibromobis(triethylphosphine)nickel with the aryl Grignard reagent according to eq 3

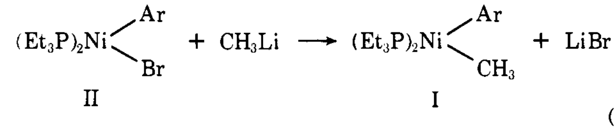


$$(Et_3P)_2NiBr_2 + ArMgBr \longrightarrow (Et_3P)_2Ni(Ar)Br + MgBr_2 \qquad (3)$$

IIa, Ar = C_6H_5
b, Ar = o-$C_6H_4CH_3$

since the replacement of the second bromide is much slower than the first.[9,10] Thus, immediately upon the addition of the Grignard reagent to $(Et_3P)_2NiBr_2$ dissolved in benzene, the solution turned from purple to yellow-brown, and II could be isolated as a crystalline compound. The *o*-tolyl derivative IIb is stable in air, but the phenyl compound IIa is slowly autoxidized to an unidentified green solid.

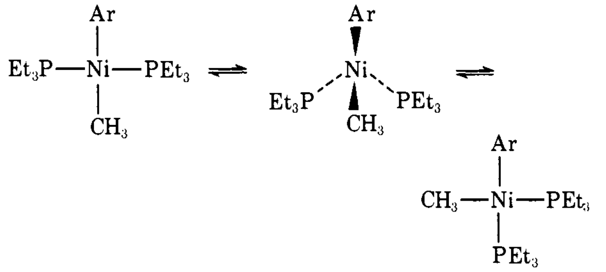
Conversion of II to the methylaryl derivative I was achieved by careful metathesis with methyllithium at low temperatures.[11]



$$\underset{\text{II}}{(Et_3P)_2Ni{<}^{Ar}_{Br}} + CH_3Li \longrightarrow \underset{\text{I}}{(Et_3P)_2Ni{<}^{Ar}_{CH_3}} + LiBr \quad (4)$$

Both bromoaryl species IIa and IIb are slightly soluble in diethyl ether at −40°C, but the reaction rapidly become homogeneous upon the addition of methyllithium at this temperature. The *o*-tolyl derivative Ib can be readily isolated from the reaction mixture as a yellow air-sensitive compound and recrystallized from hexane as brown sharp-melting prisms. On the other hand, compound Ia ($Ar = C_6H_5$) easily reacts with excess methyllithium to form a highly air-sensitive nickelate complex. The attendant purple color is reminiscent of the color of triethylphosphinenickel(0) (vide infra). In order to facilitate the isolation of Ia, it was necessary to add chlorotrimethylsilane to the cold reaction mixture first to destroy[12] any excess methyllithium. (In the absence of this treatment, pure Ia could not be isolated.) The marked difference between the behavior of the phenyl and the *o*-tolyl derivatives of II toward oxygen and of I to methyllithium suggests that the presence of an ortho substituent discourages additional coordination to nickel, consistent with other observations.[6,9]

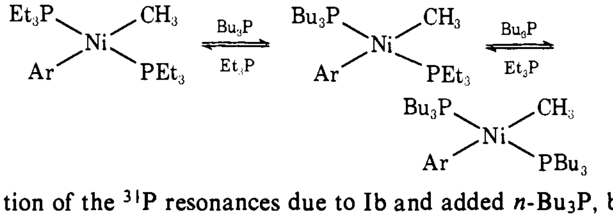
Generally, four-coordinate complexes of nickel(II), such as the arylmethyl derivatives I examined here, have a square-planar configuration.[6,13] The stereochemistries of both Ia and Ib are characterized as the trans isomers by their proton NMR spectra, which show the $Ni\text{-}CH_3$ resonances as 1:2:1 triplets. There is no evidence for the cis isomer. The sharp unbroadened lines also suggest no rapid exchange with paramagnetic tetrahedral species.[14]



(5)

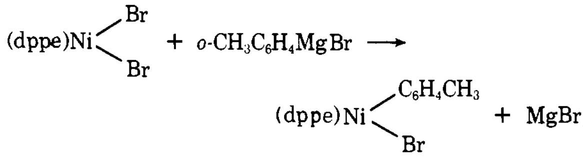
The ^{31}P NMR spectra of both Ia and Ib showed single sharp resonances at δ 122 ppm upfield relative to an external trimethyl phosphite standard, which supports the proton NMR results that both phosphorus ligands are equivalently associated in a trans arrangement about nickel. Temperature-dependent changes in the ^{31}P spectra were examined in benzene solutions (sealed tube) at 33, 51, 68 and 85°C. No significant change in the chemical shift, line width, or line intensity was observed in this temperature range. On prolonged warming of either Ia or Ib, two broad lines began to appear at δ 120 and 135 ppm. The latter were ascribed to the irreversible formation of triethylphosphinenickel(0) species formed by reductive elimination since they both persisted on recooling the solution and the same resonances were observed when either Ia or Ib was completely decomposed (vide infra). We conclude from these studies that there are no significant amounts of either the cis isomer or the tetrahedral species, separately or in exchange with Ia or Ib.

The exchange of the phosphorus ligands in Ib can be induced by added phosphine. The process, however, is slow on the NMR time scale. Thus, the ^{31}P spectrum obtained soon after the addition of tri-*n*-butylphosphine consists simply of the separate resonances of Ib and free ligand [$n\text{-}Bu_3P$, δ 172 ppm]. On standing, the resonance due to free Et_3P (δ 159 ppm) gradually appears, together with those associated with the completely exchanged bis(tri-*n*-butylphosphine) derivative [^{31}P, δ 129 ppm, singlet] and the half-exchanged mono(tri-*n*-butylphosphine) derivative [^{31}P, δ 121, δ' 130 ppm, $J_{P-P'} = 287$ Hz] of Ib. There is a concomitant diminution of the ^{31}P resonances due to Ib and added $n\text{-}Bu_3P$, but no perceptible broadening of any of the lines occurs throughout the course of these changes in the spectrum. On raising the temperature of the solution, only the lines due to free Et_3P and $n\text{-}Bu_3P$ are broadened; those lines due to the three *o*-tolylmethyl derivatives described in eq 6 remain unbroadened up to 85°C. We attribute this selective broadening to exchange of the free ligands with adventitious nickel(0) species [known to be formed thermally from Ib (vide infra)] and observed previously with other phosphinenickel(0) complexes.[15]



(6)

Attempts were made to synthesize analogs to Ia and Ib, in which the methyl and aryl groups were constrained to a cis stereochemistry using bis(diphenylphosphino)ethane (dppe) as a bidentate ligand. Thus, *cis*-bromo-*o*-tolyl(dppe)nickel(II) could be prepared from the known dibromide (eq 7).[16] However, addition of methyllithium to a suspension of the bromotolyl nickel complex in ether at −40°C, followed by careful work-up, did not yield the expected *cis*-methyltolyl(dppe)nickel(II). Examination of the mother liquors revealed the presence of substantial amounts of toluene and *o*-xylene. Further studies with the more soluble bis(diethylphosphino)ethanenickel(II) complexes are in progress.



$$(dppe)Ni{<}^{Br}_{Br} + o\text{-}CH_3C_6H_4MgBr \longrightarrow (dppe)Ni{<}^{C_6H_4CH_3}_{Br} + MgBr_2 \quad (7)$$

Decomposition of *trans*-Arylmethylbis(triethylphosphine)nickel(II). I. Reductive Elimination by Thermolysis. A. Products and Stoichiometry. The thermal decompositions of Ia and Ib were carried out in decalin or *n*-heptane solution at 80° in sealed evacuated tubes. As the reaction progressed, the clear yellow-brown solution turned progressively purple but remained homogeneous. After completion, the contents were exposed to air and filtered, and an aliquot was quantitatively analyzed by gas chromatography for the aromatic compounds shown in Table I. The remaining solution was distilled, and the arenes were isolated by preparative gas chromatography and identified by their mass spectrum. An alternative work-up procedure, in which the tubes were opened in an argon atmosphere and the arenes separated directly by vacuum transfer, afforded similar results.

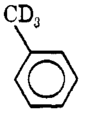
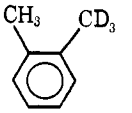
The results in Table I show that the cross-coupled arene

Table I. Arenes Formed from the Reductive Elimination of *trans*-Arylmethylbis(triethylphosphine)nickel(II)[a]

Ar–Ni(PEt$_3$)$_2$–R		Arenes, mmol			Material balance, %
		C_6H_6	$C_6H_5CH_3$	o-$(CH_3)_2$-C_6H_4	
C_6H_5	CH_3	0.06	0.39	0	86
C_6H_5	CD_3	0.05	0.39[b]	0	85
o-$C_6H_4CH_3$	CH_3	0	0.03	0.44	88
o-$C_6H_4CH_3$	CD_3	0	0.04	0.35[c]	78
C_6H_5 o-$C_6H_4CH_3$	CH_3 CH_3	0.05	0.43	0.39	87
C_6H_5 o-$C_6H_4CH_3$	CH_3 CD_3	0.09	0.50[d]	0.37[d]	96
C_6H_5 o-$C_6H_4CH_3$	CD_3 CH_3	0.05	0.46[d]	0.43[d]	94

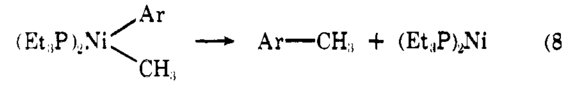
[a] In 2.0 ml of decalin solution containing 0.50 mmol of arylmethylnickel compound at 80 °C for 9 hr. [b] $C_6H_5CD_3$. [c] o-$(CD_3)C_6H_4CH_3$. [d] See Table II.

Table II. Scrambling of Methyl Groups during Reductive Elimination of Ia,b by Isotopic Labeling[a]

Ar–Ni(PEt$_3$)$_2$–R			
o-$C_6H_4CH_3$ C_6H_5	CH_3 CD_3	>95%	<2%
o-$C_6H_4CH_3$ C_6H_5	CD_3 CH_3	<1%	>90%

[a] From the decomposition of a mixture of Ia and Ib (0.5 mmol each) in 2 ml of decalin at 80 °C for 9 hr.

Ar-CH$_3$ was formed in >80% yields during the decomposition of either Ia or Ib according to the stoichiometry in eq 8.



$$(Et_3P)_2Ni\begin{matrix}Ar\\CH_3\end{matrix} \longrightarrow Ar{-}CH_3 + (Et_3P)_2Ni \qquad (8)$$

Small but significant amounts of reduced product Ar-H were also produced during thermolysis. Biaryls, if present, were formed in less than 5% yields.

Isotopic labeling experiments were carried out to demonstrate the intramolecular nature of the reduction. Thus, trideuteriomethyl derivatives of Ia and Ib were synthesized using trideuteriomethyllithium in the metathesis reaction (eq 4), and thermolysis afforded α,α,α-trideuteriotoluene and α,α,α-trideuterio-o-xylene, respectively (Table I). High isotopic purity of each was indicated by a comparison of the mass spectra with the parent protio compounds. However, the complexity of overlapping ions precluded a quantitative analysis. Mixtures of Ia and Ib, in which one component was labeled, afforded similar overall yields of arenes on thermolysis. Isotopic scrambling in the arenes isolated from the mixture was determined from a comparison of the mass spectra of labeled and unlabeled toluene and o-xylene. The results summarized in Table II indicate no significant amounts of crossover products.

The presence of a reduced triethylphosphinenickel species was apparent from the intense visible absorption at 498 nm which compares with λ_{max} of 503 nm reported for tris(triethylphosphine)nickel(0).[15] However, the two species may not be precisely the same due to the insufficiency of phosphine ligand in the former. Furthermore, disproportionation is unlikely since there was no visual evidence for a nickel mirror.

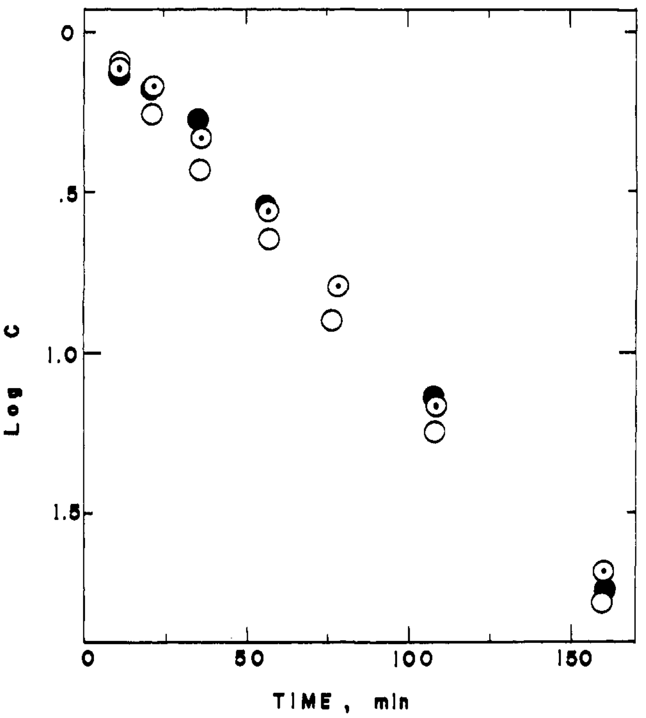
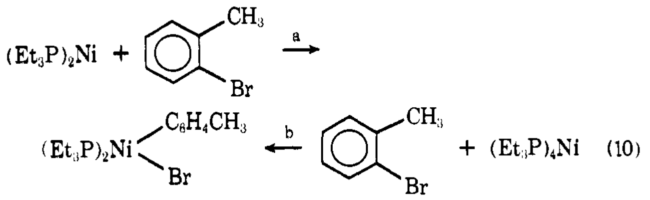


Figure 1. Decomposition of 0.5 *M* *trans*-o-tolymethylbis(triethylphosphine)nickel(II) in benzene at 80°. Rates of disappearance of Ni-CH$_3$ (●) and o-CH$_3$C$_6$H$_4$-Ni (⊙), with simultaneous appearance of o-(CH$_3$)$_2$C$_6$H$_4$ (○) relative to β-methoxynaphthalene as internal standard by proton NMR.

$$3(Et_3P)_2Ni \rightleftharpoons 2(Et_3P)_3Ni + Ni \qquad (9)$$

The bis(triethylphosphine)nickel(0) species demanded by the stoichiometry is highly unsaturated coordinatively, being generated in the singular absence of suitable ligands (such as decalin and low concentrations of arenes). The presence of triethylphosphinenickel(0) species can be shown indirectly by the isolation of bromo o-tolyl oxidative adduct on the addition of o-bromotoluene in eq 10a. This adduct is



identical with IIb [*trans*-o-tolylbromobis(triethylphosphine)nickel(II)] previously formed by metathesis in eq 3. It is also the same as that prepared from o-bromotoluene and tetrakis(triethylphosphine)nickel(0) by the procedure in eq 10b.[17]

B. Kinetics. The rates of reductive elimination of Ia and Ib were measured in benzene solutions by monitoring the change in the ^{1}H NMR spectrum in the presence of an internal standard. The rate of disappearance of Ia or Ib (followed by the Ni-CH$_3$ and o-CH$_3$ resonance)[18] coincided with the rate of appearance of the methylarene product. Variations in the concentrations showed that the kinetics obeyed a first-order dependence on Ia and Ib in the range between 0.02 and 0.2 *M*. A typical kinetic plot is shown in Figure 1, and the first-order rate constants are listed in Table III. Interestingly, the rate of reductive elimination of the phenyl derivative Ia is not much faster than that of the o-tolyl analog Ib at 80°C. The similarity in rates suggests that the transition state for reductive elimination is not

Table III. Kinetics of Reductive Elimination of Ia and Ib

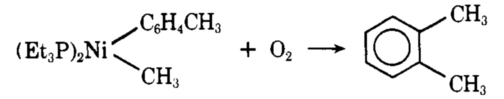
$[(Et_3P)_2Ni(CH_3)Ar]$, *M*	Solv[a]	*T*, °C	[Add],[b] *M*	First-order rate constant, min^{-1} Reactant Ni–CH_3	Reactant *o*-CH_3	Product *o*-CH_3
			Ar = *o*-$C_6H_4CH_3$			
0.50	C_6H_6	60		0.00089	0.00087	0.00086
0.50	C_6H_6	70		0.0019	0.0018	0.0017
0.50	C_6H_6	80		0.011	0.011	0.011
0.25	C_6H_6	80	0.12P	0.0096	0.0097	0.010
0.25	C_6H_6	80	0.25P	0.0083	0.0079	0.0082
0.25	C_6H_6	80	0.50P	0.0068	0.0071	0.0070
0.25	C_6H_{14}	80		0.0034	0.0038	*c*
0.25	Bu_2O	80		0.0047	0.0045	*c*
0.25	Dec	80		0.0033	*c*	0.0037
0.25	DME	80		0.0067	*c*	0.0072
			Ar = C_6H_5			
0.22	C_6H_6	80		0.016		0.013

[a] Solvent; C_6H_{14} = *n*-hexane, Bu_2O = di-*n*-butyl ether, Dec = decalin, DME = 1,2 dimethoxyethane. [b] Additive; P = triethylphosphine. [c] Not determined; proton nmr resonance obscured by solvent.

highly affected by the configuration of the *o*-methyl substituent. The activation parameters for reductive elimination of Ib are: $\Delta H^{\ddagger}$ = 29 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 15 eu. Added triethylphosphine retards the decomposition of Ib, but the rate still follows first-order kinetics. The reaction is also slower in decalin, *n*-hexane, and di-*n*-butyl ether solvents.

II. Reductive Elimination Induced by Molecular Oxygen. The arylmethylnickel complexes Ia and Ib are highly sensitive to oxygen, which causes solutions to turn immediately from yellow to black (the intensity of which deepens with increasing amounts of oxygen). The nickel products were not identified, but the presence of paramagnetic species is indicated by the broadened NMR spectra. The darkened solutions revert to yellow when acetic acid is added.

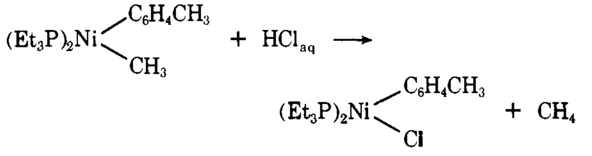
o-Xylene as well as small amounts of toluene are formed when solutions of *o*-tolyl compound Ib in decalin are exposed to varying amounts of oxygen given in Table IV. The reaction



(11)

occurs rapidly at room temperature. Reductive elimination of *o*-xylene induced by oxygen is not catalytic since the yields increase with added oxygen. Furthermore, the stoichiometric relationship between Ib, oxygen, and *o*-xylene is not clear since relatively more Ib disappears at the lower oxygen levels. Although the reaction merits further study, it is readily apparent from these studies that oxygen can rather effectively induce reductive elimination. The reasonable yields of cross-coupled arene obtained under these conditions suggest a concerted pathway for reductive elimination which does not involve free radicals.

The unreacted arylmethylnickel complex is most conveniently assayed by determining the amount of methane liberated on acidic hydrolysis. Thus, addition of aqueous hydrochloric acid to a solution of Ib in tetrahydrofuran afforded methane in quantitative yields according to eq 12.

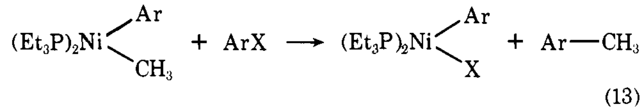


$$(Et_3P)_2Ni\left\langle\begin{matrix}C_6H_4CH_3\\CH_3\end{matrix}\right. + HCl_{aq} \longrightarrow (Et_3P)_2Ni\left\langle\begin{matrix}C_6H_4CH_3\\Cl\end{matrix}\right. + CH_4 \quad (12)$$

The nickel(II) species on recovery showed visible and proton NMR spectra which were the same as those of IIb (λ_{max} 412 nm; *o*-CH_3, δ 2.80).

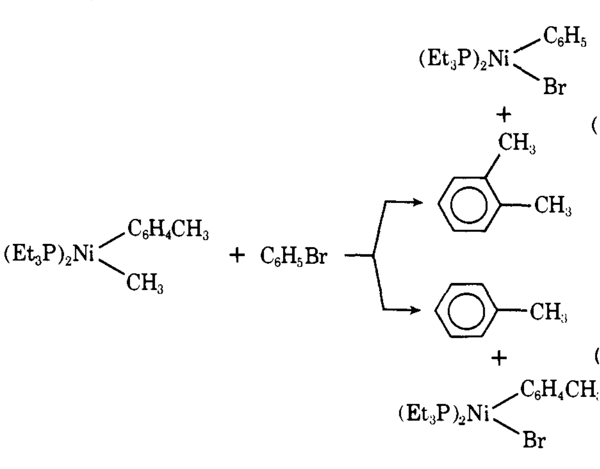
III. Reductive Elimination Induced by Aryl Bromide. The reductive elimination of arylmethylnickel compounds Ia and Ib can be induced by aryl bromides. Thus, a 0.5 *M* solution of the *o*-tolyl compound Ib in ether decomposed about six times faster in the presence of 1.4 *M* bromobenzene (Table V).

The persistence of the yellow-brown color until the end of the decomposition indicates that the metal remains as nickel(II). No doubt any nickel(0) species formed by reductive elimination is rapidly reoxidized to nickel(II) (compare eq 10a), leading to the overall stoichiometry in eq 13. The



$$(Et_3P)_2Ni\left\langle\begin{matrix}Ar\\CH_3\end{matrix}\right. + ArX \longrightarrow (Et_3P)_2Ni\left\langle\begin{matrix}Ar\\X\end{matrix}\right. + Ar{-}CH_3 \quad (13)$$

reaction, however, does not simply consist of the reductive elimination of aryl and methyl followed by oxidative addition of aryl bromide to nickel(0). For example, if bromobenzene is used to induce the reductive elimination of the *o*-tolylmethylnickel compound Ib, appreciable amounts of toluene (40%) are formed in addition to *o*-xylene (60%) (see eq 14a and 14b). The aryl groups are obviously scrambled during the reductive elimination of I induced by aryl bromide.



(14a)

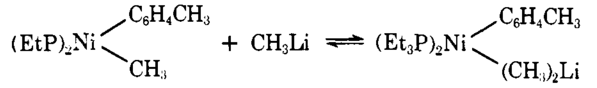
(14b)

IV. Formation of Nickelate(II) Species and Their Role in Reductive Elimination. A. Exchange Studies. The addition of an ethereal solution of methyllithium to a solution of the *o*-tolylmethylnickel compound Ib at −70°C affords a highly air-sensitive precipitate, which we ascribe to the nickelate species III in eq 15.[19] The complex

Table IV. Reductive Elimination of Ib Induced by Molecular Oxygen[a]

Oxygen, mmol	O_2/Ib	*o*-Xylene, mmol	Toluene, mmol	Acetolysis[b] CH_4, mmol
0		0.014	0.004	0.31
0.084	0.28	0.022	0.021	0.26
0.16	0.53	0.045	0.023	0.12
0.23	0.77	0.058	0.018	0.11
0.34	1.13	0.084	0.022	*c*
0.63	2.1	0.13	0.027	0.084
∞[c]		0.16	0.013	0.010
∞		0.17	0.020	0.010

[a] Each sample contained 0.30 ± .03 mmol of Ib in 1 ml of decalin at room temperature. [b] Unreacted Ib measured by acetolysis (see text). [c] Exposure to air.



$$(EtP)_2Ni(C_6H_4CH_3)(CH_3) + CH_3Li \rightleftharpoons (Et_3P)_2Ni(C_6H_4CH_3)(CH_3)_2Li \quad (15)$$

III

redissolves upon the addition of an equivalent of trimethylchlorosilane at the same temperature due to the facile destruction of methyllithium (eq 16)[7] and reversion to Ib.

$$CH_3Li + (CH_3)_3SiCl \xrightarrow{\text{fast}} (CH_3)_4Si + LiCl \quad (16)$$

Support for such a reversibility is obtained from exchange studies with isotopically labeled compounds. When the trideuteriomethylnickel compound Ib was exposed to methyllithium for 30 min at −70°C under conditions in eq 15 and then worked up, the reisolated Ib was found to have lost 35% of its CD_3 label (by mass spectral analysis of *o*-xylene formed in reductive elimination). A similar exchange carried out at −30°C afforded the same results. Repetition of these series of experiments with the trideuteriomethylnickel analog Ia was much more difficult to carry out quantitatively due to the enhanced susceptibility of the nickelate intermediate to decomposition. Thus, Ia could not be reisolated in pure form, but qualitative analysis indicated extensive exchange had also occurred.

B. Rate Studies. The formation of nickelate species from Ia and Ib in the presence of methyllithium is also indicated by their enhanced rates of decomposition. Thus, a 0.05 *M* solution of Ib in ether decomposes approximately ten times faster in the presence of 0.15 *M* methyllithium to produce *o*-xylene and toluene as listed in Table V. A similar result is obtained with methylmagnesium bromide and also for the phenyl analog Ia.

Comparisons with the Catalytic System. The nickel catalyzed cross coupling of aryl bromides and methyllithium or methylmagnesium bromide in diethyl ether solution was studied at partial conversions. The results in Table VI were obtained with dibromobis(triethylphosphine)nickel(II) as the catalyst precursor. It is interesting to note that relatively large amounts of reduction product ArH are formed in diethyl ether compared with the stoichiometric studies carried out in decalin solutions.

Discussion

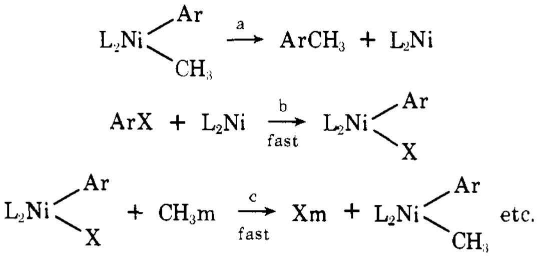
For the study of nickel catalysis in the cross coupling reaction, we employed as a model the system consisting of aryl bromides and methyllithium or methylmagnesium bromide

$$Ar{-}Br + CH_3{-}m \xrightarrow{(Et_3P)_2NiBr_2} Ar{-}CH_3 + m{-}Br \quad (17)$$

where m = Li or MgX.

Although the triethylphosphine complexes of nickel(II) may not necessarily represent optimum examples of catalysts,[1,7] they allow us access to the key intermediate, viz., the arylmethylnickel complexes such as Ia and Ib. Any catalytic cycle which is developed around this intermediate must depend on the availability of pathways for its rapid formation and facile decomposition.[20] The most straightforward formulation simply consists of a sequence of steps involving (a) reductive elimination followed by (b) oxidative addition and (c) metathesis as shown in Scheme I (L = triethylphosphine).

Scheme I

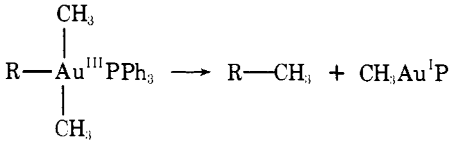


$$L_2Ni(Ar)(CH_3) \xrightarrow{a} ArCH_3 + L_2Ni \quad (8)$$

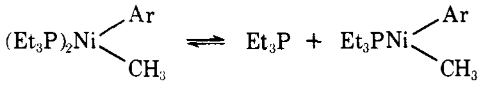
$$ArX + L_2Ni \xrightarrow[\text{fast}]{b} L_2Ni(Ar)(X) \quad (10)$$

$$L_2Ni(Ar)(X) + CH_3m \xrightarrow[\text{fast}]{c} Xm + L_2Ni(Ar)(CH_3) \quad \text{etc.} \quad (4)$$

Indeed, each step in this catalytic cycle can be documented separately. We have shown that reductive elimination in step a proceeds to a nickel(0) species which can undergo rapid oxidative addition in step b as does the metathesis in step c. Similar observations have been made qualitatively by Parshall and others.[8,17] There are, however, two serious points to be raised on this simple mechanism. Most importantly, we find that the rate of reductive elimination in step a is too slow to allow for a catalytic process. Secondly, arylmethylbis(triethylphosphine)nickel(II) complexes Ia and Ib exist exclusively in the trans configuration. Oxidative addition to nickel(0) species in step b also affords only the trans adducts.[22b] Our demonstration of the *intra*molecular route for reductive elimination of Ia and Ib demands that it proceeds in a concerted fashion via a transition state in which the aryl and methyl groups are juxtaposed. Thus, a cis square planar or tetrahedral geometry for reductive elimination would be similar to that previously shown for the somewhat analogous example of the trialkylgold(III) complexes in eq 18.[21] Since we could find no evidence of the isomerization of the trans to either a cis isomer or a tetrahedral species even at 80°C, we tentatively conclude that reductive elimination of Ia and Ib does not proceed via these stereoisomeric forms. In such an event, reductive elimination can proceed directly from the *trans* complex via a tetrahedral-like transition state. On the other hand, retardation of reductive elimination by added triethylphosphine suggests that it proceeds by a prior dissociation such as that shown in eq 19 since no five-coordinate nickel species can be detected[22a] in the ^{31}P NMR spectrum to account quantitatively for the reduction in rate. The three-coordinate intermediate in eq 19 would then allow for greater mobility of the groups from which reductive elimination could proceed.[21,22] Rearrangement followed by a very rapid reductive elimination of the cis isomer is also a possibility. However, our unsuccessful attempts to synthesize *cis*-arylmethylnickel(II) complexes still leaves open the question of re-



$$R{-}Au^{III}(CH_3)_2PPh_3 \longrightarrow R{-}CH_3 + CH_3Au^{I}PPh_3 \quad (18)$$



$$(Et_3P)_2Ni(Ar)(CH_3) \rightleftharpoons Et_3P + Et_3PNi(Ar)(CH_3) \quad (19)$$

Table V. Reductive Elimination of Arylmethylnickel(II) Complexes by Aryl Bromide and Methyllithium[a]

$\left[(EtP)_2Ni\begin{smallmatrix}Ar\\CH_3\end{smallmatrix}\right]$, *M*	Y–C_6H_4Br,[b] mmol	CH_3m,[c] mmol	Product, mmol		Conv,[d] %
			$ArCH_3$	ArH	
		Ar = *o*-$C_6H_4CH_3$			
0.50	0	0	<0.005	0.02	4
0.50	0	1.5 L	0.24	0.08	64
0.50	0	1.5 M	0.18	0.08	52
0.50	1.4 H	0	0.09	0.06	30
		Ar = C_6H_5			
0.25	0	0	0.04	*e*	
0.25	0	0.60 M	0.07	*e*	
0.25	0.75 H	0	0.05	*e*	

[a] In 10 ml of diethyl ether refluxed for 3 hr. [b] H = C_6H_5Br. [c] L = CH_3Li, M = CH_3MgBr. [d] Based on $L_2Ni(Ar)CH_3$. [e] Not analyzed.

Table VI. Nickel Catalyzed Cross Coupling of Aryl Bromide and Methyllithium or Grignard Reagent

$(Et_3P)_2NiBr_2$, mmol	YC_6H_4Br,[b] mmol	CH_3m;[c] mmol	Products, mmol		Mat[d] Bal, %	Conv,[e] %	Cat[f] Eff
			$ArCH_3$	ArH			
0	0.96 H	1.2 L	0.02	<0.001	95	2	
0.05	1.0 H	1.2 L	0.16	0.32	84	46	9.6
0.05	1.0 H	1.2 M[g]	0.42	*h*			
0.05	1.1 C	1.2 L	0.15	0.45	95	54	11

[a] In 10 ml of diethyl ether refluxed for 3 hr. [b] H = C_6H_5Br, C = *o*-$C_6H_4CH_3$. [c] L = CH_3Li, M = CH_3MgBr. [d] Based on recovered ArBr. [e] Based on ArBr. [f] Catalytic efficiency to aryl products based on L_2NiBr_2 employed. [g] Contains 1 ml of THF. [h] Benzene obscured by THF.

ductive elimination from such stereoisomers. The results we obtained in studies with the bidentate diphosphine ligand (dppe), though qualitatively in this direction, unfortunately lack definitiveness as yet.

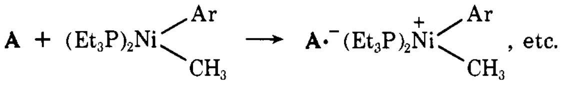
The foregoing discussion indicates that other considerations must be invoked in order to allow for the facile expulsion of aryl and methyl groups from Ia and Ib necessary for a catalytic cycle. Indeed, the observation that oxygen induces the rapid reductive elimination of Ia and Ib provides the key to this understanding. In order to develop this thesis, we present first the autoxidation of organometals within the general context of electron transfer processes.

The rapid reaction of a variety of organometallic complexes with molecular oxygen proceeds from a prior electron transfer step such as eq 20

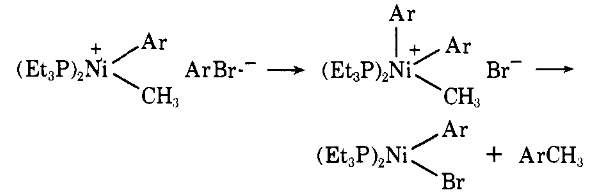
$$O_2 + [R{-}M] \longrightarrow O_2\cdot + [R{-}M]^{\cdot+}, \text{ etc.} \qquad (20)$$

in which oxygen acts as an electron acceptor. This process is important independently of whether the subsequent steps in autoxidation involve a stoichiometric or a radical chain process.[23] Similarly, organic alides such as aryl bromides are also known to be acceptors in electron transfer processes.[23-25] Furthermore, organometals being generally electron-rich species are capable of acting as donors in a number of electron transfer reactions.[26] The enhanced lability of the resultant cation radical toward reductive elimination has been discussed recently with regard to some main group as well as transition metalloorganic complexes.[27]

As structurally different as they are, nonetheless oxygen and aryl bromides bear interesting resemblances in that their interaction with arylmethylnickel compounds Ia and Ib both lead to the elimination of aryl and methyl groups. For purposes of further discussion, we propose a charge transfer interaction common to both, in which reactions are promoted by a prior electron transfer from I to oxygen or aryl bromide acting as electron acceptors (**A**). A concerted process for reductive elimination from the nickel(III) species[13] in eq 21 is indicated by the reasonable yields of $ArCH_3$ obtainable even when **A** is oxygen. Moreover, the partial scrambling observed when **A** is aryl bromide (and the aryl groups on the nickel compound I and the aryl bromide are different) suggests that the ion pair in eq 21 may be intimately associated. According to this formulation, the scrambling of the aryl groups in the cross coupled product must occur after electron transfer since the recovered aryl bromide is not exchanged. Several possibilities can be envisaged, including irreversible collapse to a five-coordinate intermediate[28] such as:



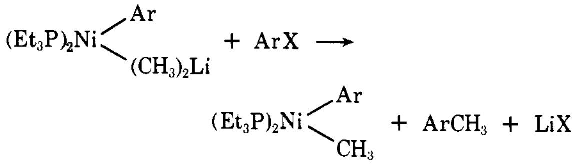
$$\mathbf{A} + (Et_3P)_2Ni\begin{smallmatrix}Ar\\CH_3\end{smallmatrix} \longrightarrow \mathbf{A}\cdot^{-}(Et_3P)_2\overset{+}{Ni}\begin{smallmatrix}Ar\\CH_3\end{smallmatrix}, \text{ etc.} \qquad (21)$$



$$(Et_3P)_2\overset{+}{Ni}\begin{smallmatrix}Ar\\CH_3\end{smallmatrix}\ ArBr\cdot^{-} \longrightarrow (Et_3P)_2\overset{Ar}{\overset{|}{\overset{+}{Ni}}}\begin{smallmatrix}Ar\\CH_3\end{smallmatrix}\ Br^{-} \longrightarrow (Et_3P)_2Ni\begin{smallmatrix}Ar\\Br\end{smallmatrix} + ArCH_3 \qquad (22)$$

followed by the elimination of the aryl and methyl groups in a subsequent step.

We have also observed that the sensitivity of arylmethylnickel compounds Ia and Ib to oxygen is greatly enhanced by the addition of methyllithium. Under these conditions, the presence of Ia and Ib as nickelate complexes III (eq 15) is indicated by isotopic exchange studies. These anionic nickel complexes should be even better donors than their neutral counterparts I,[29] and they are thus expected also to show enhanced reactivity to aryl bromides in those interactions proceeding by electron transfer. Reductive eliminations similar to those presented for I can be formulated as:



$$(Et_3P)_2Ni\begin{smallmatrix}Ar\\(CH_3)_2Li\end{smallmatrix} + ArX \longrightarrow (Et_3P)_2Ni\begin{smallmatrix}Ar\\CH_3\end{smallmatrix} + ArCH_3 + LiX \qquad (23)$$

The Catalytic Cycle. The various stoichiometric reactions of the arylmethylnickel compounds of Ia and Ib leading to reductive elimination can be assembled as components of a

Scheme II

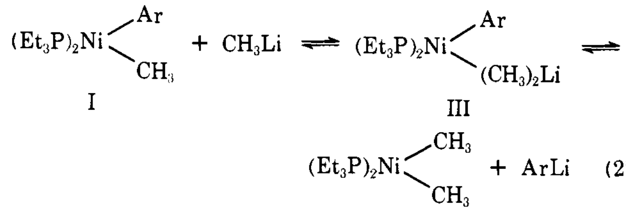
$$L_2Ni(Ar)CH_3 + ArX \xrightarrow{slow} [L_2Ni(Ar)CH_3^{+}\ ArX\cdot^{-}] \quad (24)$$

$$L_2Ni(Ar)CH_3^{+} \xrightarrow{fast} L_2Ni^{+} + ArCH_3 \quad (25)$$

$$L_2Ni^{+} + ArX\cdot^{-} \xrightarrow{fast} L_2NiArX \quad (26)$$

catalytic cycle in the cross coupling process. Scheme II is consistent with the facts in hand, including the products, stoichiometry, kinetics, and exchange and scrambling experiments. Scheme II is presented stepwise only to emphasize the mechanistic factors brought out by the study of Ia and Ib. Thus, it is probable the eq 24-26 occur in one to two steps such as eq 22, or in rapid succession before any of the intermediates diffuse apart.[30] Furthermore, Scheme II is obviously incomplete without considering the nickelate species III as participating in reactions such as eq 23 which are mechanistically equivalent to the rate-limiting step shown by I in eq 24 of the catalytic cycle.

Finally, there are several mechanistic points yet to be clarified. For example, the origin of side products such as reduced arene is unclear. Preliminary results suggest that the arene arises from an arylmethyl exchange process such as



$$\underset{I}{(Et_3P)_2Ni(Ar)(CH_3)} + CH_3Li \rightleftharpoons \underset{III}{(Et_3P)_2Ni(Ar)(CH_3)_2Li} \rightleftharpoons (Et_3P)_2Ni(CH_3)_2 + ArLi \quad (27)$$

since deuteriolysis of the reaction mixture leads partly to deuterated arene. It does not appear, however, that all of the hydrogen is derived from protonolysis, and it is possible that some other source such as that from the methyl group may be involved. Moreover, it is not known how the scrambling of aryl groups occurs during the reaction of I and the nickelate species III with aryl bromide in reactions 22 and 23, respectively. The effect of the homologation of the alkyl group, particularly to moieties containing β-hydrogens remains to be explored. Nonetheless, the principal features of the catalytic cycle in the cross coupling reaction appear to be resolved by these studies, and further work will hopefully provide additional insight into the mechanistic details of the catalysis.

Experimental Section

***trans*-Bromo-*o*-tolyl-bis(triethylphosphine)nickel (IIb).** An ethereal solution of *o*-tolylmagnesium bromide was prepared by the entrainment method from 3.35 g of *o*-bromotoluene (20 mmol), 2.3 g of ethylene bromide (12 mmol), and 2.0 g of magnesium turnings (83 mmol). The solution was cooled in an ice bath and a benzene solution of 6.0 g (12.5 mmol) of dibromobis(triethylphosphine)-nickel(II) added. After 10 min, the reaction was cooled further, and a solution of 10% HBr was added. Extraction, followed by washing, drying, and evaporation of the solvent, gave a yellow oil which afforded 4.1 g (67% yield) of material melting at 102-103°C dec after recrystallization from ethanol.[9a] The infrared spectrum in fluorolube showed bands at 3020, 2955, 2860, 1575, 1450, 1410, 1035, 1020, 1005, 765, 745, 720, 715, 635 cm^{-1}. The proton NMR spectrum consisted of a *o*-CH_3 singlet (3 H, δ 2.80 ppm) and unresolved multiplets for aromatic protons at δ 6.75 (3 H) and δ 7.25 (1 H), in addition to the ethyl multiplets between δ 0.7 and 1.6. The ^{31}P NMR spectrum consisted of a sharp singlet at δ 130 ppm (relative to external trimethyl phosphite).

Anal. Calcd for $C_{19}H_{37}NiP_2Br$: C, 48.96; H, 8.00; P, 13.29. Found: C, 48.7; H, 8.1; P, 13.1.

***trans*-Bromophenylbis(triethylphosphine)nickel (IIa).** The procedure was similar to that employed for the *o*-tolyl analog except that anaerobic conditions were maintained throughout: yield 85%; mp 82-83°C dec. The infrared spectrum was similar to the *o*-tolyl analog. The proton NMR spectrum showed two broad aromatic resonances at δ 6.90 (3 H) and 7.40 (2 H) in addition to those due to triethylphosphine. The ^{31}P consisted of a single sharp resonance at δ 129 (external TMP).

Anal. Calcd for $C_{18}H_{35}NiP_2Br$: C, 47.82; H, 7.81; P, 13.71. Found: C 47.6; H, 7.5; P, 14.0.

***cis*-Bromo-*o*-tolylbis(diphenylphosphino)ethanenickel(II).** The synthetic procedure was similar to that employed for the bis(triethylphosphine) compound: yield 10%; mp 200-201°C dec after recrystallization from benzene-ethanol. Poor yields were mainly due to the insolubility of (dppe)$NiBr_2$[14a] recovered in 50%.

Anal. Calcd for $C_{33}H_{31}NiP_2Br$: C, 63.09; H, 4.97; P, 9.86. Found: C, 63.0; H, 5.0; P, 9.8.

***trans*-Methyl-*o*-tolyl-bis(triethylphosphine)nickel (Ib).** To an ethereal solution of 1.0 g (2.15 mmol) of *trans*-bromo-*o*-tolylbis-(triethylphosphine)nickel(II) at −40°C was added a 1.5 *M* solution (3.0 mmol) of methyllithium under a positive pressure of argon. The solvent was removed on a vacuum line after stirring the solution for 60 min at this temperature. The dry pale yellow powder was dissolved in hexane and the solution filtered in a glovebox. A yellow amorphous powder separated on cooling the solution to −78°C, yield 0.65 g (79%). Recrystallization afforded prismoidal brown crystals melting at 72-73°C dec. The infrared spectrum consisted of bands at 3020, 2950, 2900, 2860, 1570, 1450, 1410, 1035, 1020, 1005, 840, 760, 735, 716 and 640 cm^{-1}. The proton NMR spectrum consisted of a single sharp resonance at $\delta - 0.72$ (3 H, triplet, $J_{P-H} = 12$ Hz) and *o*-CH_3) δ 2.52 singlet (3 H) and two aromatic resonances at δ 7.25 (1 H) and 6.65 (3 H). The ^{31}P NMR spectrum consisted of a single sharp resonance at δ 122 ppm (external TMP).

Anal. Calcd for $C_{20}H_{40}NiP_2$: C, 59.87; H, 10.05; P, 15.44. Found: C, 59.6; H, 10.2; P, 15.5.

***trans*-Methylphenylbis(triethylphosphine)nickel(Ia).** To an ethereal solution of 4.0 g (9 mmol) of *trans*-bromophenylbis(triethylphosphine)nickel(II) at 0°C. was added 7.3 ml of 1.8 *M* methyllithium in ether. The solution was stirred for 30 min, always maintaining the temperature below −30°. Trimethylchlorosilane (2.5 ml, 20 mmol) was added and the solvent vacuum transferred from the reaction vessel immersed in an ice bath. The solution was concentrated until approximately 10 ml remained, whereupon the solution was recooled to −78°C and the excess ethereal solution removed with a hypodermic syringe. The remaining brown-yellow solid was subjected to high vacuum, and the resulting solid was redissolved in hexane at room temperature. The solution was filtered, the volume reduced by evaporation on a vacuum line, and the solution recooled to −78°C. The yellow solid was collected and recrystallized several times from hexane to afford yellow-brown crystals, which are highly air sensitive: yield 1.35 g (39%); mp 71.5-72°C dec. The infrared spectrum is similar to that of the *o*-tolyl analog. The proton NMR spectrum consisted of: ($NiCH_3$) δ −0.76 (3 H, triplet $J_{P-H} = 12$ Hz) and unresolved aromatic at 7.40 (2 H) and 6.90 (3 H). The ^{31}P NMR spectrum consisted of a single sharp resonance at δ 122 ppm (external TMP).

Anal. Calcd for $C_{19}H_{38}NiP_2$: C, 58.94; H, 9.89; P, 16.00. Found: C, 58.7; H, 9.6; P, 15.8.

Solvents were commercial reagent grade materials, repurified by standard methods, redistilled and or degassed on a vacuum line before use in kinetic experiments. Methyllithium was from the Foote Chemical Co. and the concentration determined by double titration and GLC methods.[21a] All manipulations of air-sensitive compounds were carried out in a glovebox filled with recirculated argon or on a vacuum line. The visible absorption spectra were recorded on a Cary 15 or a Beckman DBG spectrometer. A Perkin-Elmer 221 and Varian EM360 spectrometers were used for infrared and proton NMR spectra, respectively. The ^{31}P NMR spectra were recorded in 5 mm (o.d.) tubes at 40.5 MHz using Fourier transform techniques on a Varian XL100 instrument. Mass spectra were obtained on a Varian MAT CH7 or a -1 M59 spectrometer at 70 eV.

Kinetic Experiments. In a glovebox, 0.40 g (1 mmol) of nickel complex Ib was weighed into 2 ml of benzene and 0.18 g of methyl β-naphthyl ether added. A 0.35-ml aliquot was added to a 5-mm NMR tube fitted with a joint and vacuum stopcock. After removal from the glovebox, the tubes were degassed by repeated freeze-pump-thaw cycles on a vacuum line and sealed in vacuo. The NMR spectrum was recorded before the tube was placed in a thermostated bath. During the course of the reaction, the orange-brown solution turned to a purple solution with no evidence of a suspended solid or plated metal mirror. The rate was followed by examining the Ni–CH_3 triplet (δ −0.72) and the *o*-CH_3 group on Ar–Ni (δ 2.52), as well as the disappearance of the *o*-dimethyl singlets (δ 2.09) of *o*-xylene relative to the internal standard (δ 3.21) methyl β-naphthyl ether.

Labeling Studies. Methyllithium-d_3 was prepared from CD_3I obtained via dimethyl sulfoxide.[33] The methyliodide contained 70% d_3 and 30% d_2 enrichment. *trans*-Methyl-d_3-arylbis(triethylphosphine)nickel(II) compounds were synthesized by the procedures used for Ia and Ib with trideuteriomethyllithium. The compounds were decomposed in decalin solutions at 80° for 12 hr. After work-up, the toluene and xylene were separated by preparative gas chromatography. The principal ions in the mass spectra are for *o*-$CD_3(CH_3)C_6H_4$: *m/e* 109 (rel intensity 100), 108 (29), 107 (9.5), 106 (2.9), 105 (3.9), 104 (0.8), 94 (72); 93 (26), 92 (33). 91 (67). For *o*-$(CH_3)_2C_6H_4$:[34] 106 (57), 105 (24), 92 (7.5), 91 (100). For $C_6H_4CD_3$: 95 (100), 94 (94), 93 (50), 92 (1.9), 91 (1.6). For $C_6H_4CH_3$:[34] 92 (78), 91 (100), 90 (9). The mass spectra obtained from the arenes isolated from the mixed decomposition of CH_3–C_6H_5 and CD_3–$CH_3C_6H_4$ nickel complexes are: (toluene) 95 (0.9), 94 (0.6), 93 (5.0), 92 (75), 91 (100), 90 (2.8), 63 (7.2); *o*-xylene 109 (72) 108 (20), 107 (4.5), 106 (17), 105 (7.5), 94 (53), 93 (14), 92 (34), 91 (100). The mass spectra obtained of the arenes isolated from the mixed decomposition of CD_3–C_6H_5 and CH_3–$CH_3C_6H_4$-nickel complexes are: (toluene) 95 (100), 94 (92), 93 (49), 92 (7.8), 91 (11); (*o*-xylene) 109 (0.5), 107 (4.1), 105 (55), 105 (20), 95 (2.4), 94 (2.3), 93 (1.3), 92 (7.3), 91 (100).

Oxidative Additions with Phosphinenickel(0) Complexes. A solution 0.45 g of Ib in *n*-heptane was decomposed thermally. The visible absorption spectrum showed a new maximum at 498 nm. The solvent and xylene were removed in vacuo and 1.8 g of *o*-bromotoluene in hexane added. IIb was isolated in 22% yield mp 102–103°C.[9]

Bis(triphenylphosphine)bis(diphenylphosphino)ethanenickel(0) (IV). To a benzene solution of 4.0 g (8 mmol) of dichlorobis(diphenylphosphino)ethanenickel(II) and 4.2 g (16 mmol) of triphenylphosphine at 2°C was added 20 ml of a 1.2 *M* solution of *n*-butyllithium in hexane. Butane, 1-butene, and octane were formed as the solution was stirred for 18 hr in an ice bath and then filtered. Vacuum evaporation of the solution left a brown solid to which hexane was added by vacuum transfer. The air-sensitive yellow solid separating on cooling the solution to −78°C was washed with three aliquots of acetone: yield 4.0 g (50%); mp 280–290 dec.

Oxidative additions were examined with IV. It reacted with methyl iodide to produce ethane together with small amounts of methane and what appeared to be diiodobis(diphenylphosphino)ethanenickel(II) due to the close similarity of its proton NMR spectrum with that of the known dichloride. The latter was also produced from iodobenzene, but no reaction occurred with bromobenzene. Compound IV reacted with ethyl iodide to produce mainly a mixture of ethane and ethylene together with small amounts of butane.

Reaction of Ib with Oxygen and Water. A solution of 1.2 g (3.0 mmol) of methyl-*o*-tolylbis(triethylphosphine)nickel(II) in 10 ml of decalin was made up in a glovebox. Nine 1-ml aliquots were added to erlenmeyer flasks and sealed with rubber serum stoppers. The calculated amount of oxygen gas was added to each flask with a hypodermic syringe. After 60 min, 0.1 ml of acetic acid was added, and the methane evolved determined by gas chromatography (ethane as internal standard). The acetic acid was neutralized with calcium chloride and the *o*-xylene determined by gas chromatography (ethylbenzene as internal standard).

A solution of Ib (0.2 g, 0.5 mmol) in 5 ml of tetrahydrofuran (distilled from sodium benzophenone ketyl) was divided into three aliquots of 0.75, 1.0, and 1.25 ml, which were transferred to erlenmeyer flasks and sealed with serum stoppers. Sampling of the gas after aqueous hydrochloric acid (1 ml) of 0.2 *N*) was added showed only methane (as ethane). The yields of methane were 0.072, 0.098, and 0.123 mmol, respectively (ethane as internal standard). The yield of toluene was about 5%.

Exchange of I with Methyllithium. A 1.8 *M* solution (4 ml) of methyllithium (7.2 mmol) in ether was added to a solution of 0.5 g (1.25 mmol) of CD_3-Ib in ether at −70°C, whereupon a colorless precipitate formed slowly. After 30 min at −70°C, 1 ml (7.8 mmol) of trimethylchlorosilane was added with rapid dissolution of the solid. The solvent was removed in vacuo and the yellow powder dissolved in hexane (glovebox) from which Ib (0.32 g) was reisolated. Thermolysis afforded *o*-xylene which was separated by GLC and subjected to mass spectral analysis: *m/e* 109 (rel intensity 100). 108 (29), 107 (9.5), 106 (2.9), 105 (3.9), 94 (72), 93 (26), 92 (33), 91 (67). A similar procedure for CD_3-Ia (not reisolated pure) afforded toluene: 96 (7), 95 (100), 94 (97), 93 (52), 92 (27), 91 (31).

Catalytic Studies. The general procedure consisted of adding 0.05 mmol of the nickel catalyst, usually dibromobis(triethylphosphine)nickel(II), and 100 mmol of aryl halide to 10 ml of diethyl ether under a nitrogen atmosphere. A solution of methyllithium or methylmagnesium bromide was then added with a hypodermic syringe and the solution refluxed for 3 hr. The reaction mixture was then cooled in an ice bath, hydrolyzed with 2 ml of 10% hydrochloric acid, and extracted with saturated potassium bicarbonate. The extract was washed, dried over calcium chloride, and analyzed by gas chromatography. The internal standard method of analysis employed mixtures carefully calibrated over a range of concentrations approximating those present in the reaction mixtures. The analyses were carried out on Beckman GC-5 or Varian Aerograph 200 gas chromatographs. The aromatic compounds were analyzed on a 20-ft column of 15% FFAP on Chromosorb at 157°C, relative to an ethylbenzene internal standard (relative retention times: benzene, 0.52, toluene, 0.74, ethylbenzene, 1.0, *o*-xylene, 1.26) or a tandem column consisting first of a 10-ft SF 96 (10%) and second 10 ft of FFAP (10%) both on Chromosorb at 135°C relative retention times: benzene, 0.50, toluene, 0.74, ethylbenzene, 1.0, *o*-xylene, 1.22, bromobenzene, 1.91, *o*-bromotoluene, 2.80. The arenes were preparatively separated on an Aerograph A90P chromatograph using a 5 ft × 0.25 in. column of 5% SE-30 on Chromosorb W at 80°C, relative retention times: benzene 0.60, toluene, 0.75, and *o*-xylene, 1.0. Alkanes were analyzed on a 5-ft Porapak Q column operating at 130°C, relative retention times: methane, 0.54, ethane, 0.81, ethylene, 0.90, and propane, 1.00.

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(29) (a) Cf. H. O. House and M. J. Umen, *J. Org. Chem.*, **38**, 3893 (1973). (b) Based strictly on oxidation potentials, the oxidation of the nickelate complex in eq 23 is likely to be faster than that of the neutral complex in eq 21.

(30) Equation 24 represents one extreme of a charge transfer interaction of I with an acceptor in which electron transfer is complete and reactions subsequently proceed from the ion–radicals. On the other hand, an acceptor can *perturb* a donor such as I and cause labilization of the organometal bond by lowering of the energies of the d orbitals.[31] The latter has been described well by Yamamoto et al.[32] for the reductive elimination of butane from diethyl(dipyridyl)nickel(II) enhanced by various olefins and included in Kumada's original formulation.[1,7] From our work, the scrambling of aryl groups observed during the reaction of I and ArBr supports the first formulation and not the second. However, pending more extensive studies, we do not feel that a *rigorous* distinction between the two processes can be made at this juncture.

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The Decomposition of Phenolic Peresters. II. *tert*-Butyl 3,5-Di-*tert*-butyl-2-hydroxyperbenzoate and *tert*-Butyl 5-Methyl-3-*tert*-butyl-2-hydroxyperbenzoate[1]

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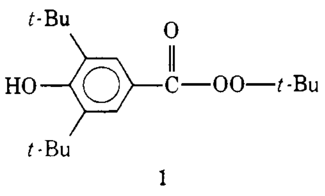
Abstract: The *o*-hydroxy-substituted *tert*-butyl perbenzoates **3a** and **3b** contrast remarkably with the *p*-hydroxy perester **1**[2] in two ways. First, the introduction of the hydroxyl group in the ortho position, unlike the introduction in the para position, causes a large increase in the first-order rate constant for the spontaneous decomposition of the perester. Second, the *o*-hydroxy-substituted peresters are quite insensitive to radicals and to bases, whereas such reagents induce a rapid decomposition of the para compound by abstracting H· or H^+ from its *p*-hydroxyl group. The rapid spontaneous decomposition of **3a** and **3b** is attributed to the intramolecular transfer of a hydrogen atom from OH to the carbonyl oxygen, an atom to which it is already hydrogen bonded. The same hydrogen bond protects the *o*-hydroxyl group from attack by external reagents.

The first paper of this series[2] was concerned with compound 1, a *p*-hydroxy-substituted *tert*-butyl perbenzoate. The reason for our interest in 1 was its use as a model for induced decomposition and carboxy inversion reactions of peroxides.

Compound 1 is sensitive both to radicals, which remove hydrogen atoms from the phenolic OH, and to bases, which remove protons. In both cases the intermediate produced is believed to be the triplet diradical 2.[3]



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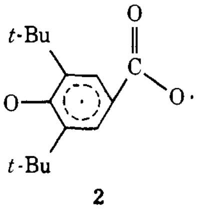
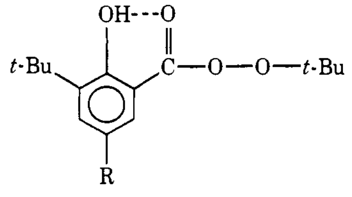


2

In contrast to the radical or base induced decomposition, the rate of the spontaneous decomposition of 1 is unexceptional and consistent with the substituent effects observed for ordinary *tert*-butyl perbenzoates.

In the present paper, we describe the almost precisely opposite behavior of *o*-hydroxy substituents.

Reaction Products. The products from the decomposition of the *o*-hydroxy-substituted peresters **3a** and **3b** are consistent with a simple homolysis. Thus the decomposition of 0.1 *M* **3a** in degassed tetrahydrofuran at 70° proceeds essentially according to eq 1. The yield of the acid **4a** is 92%, and



3a, R = methyl
3b, R = *tert*-butyl