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Mechanism of Oxidative Addition. Reaction of Nickel(0) Complexes with Aromatic Halides

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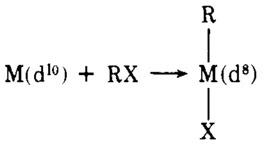
Abstract: The oxidative addition of aryl halides to triethylphosphinenickel(0) complexes affords *trans*-arylnickel(II) halides A, together with paramagnetic nickel(I) halides B as side products. The relative yields, A/B, are strongly dependent on the halide (I < Br < Cl), as well as the nuclear substituents and the solvent polarity. The second-order rate constants (log k_{obsd}) for various meta- and para-substituted iodobenzenes are linearly related to those of the corresponding bromo- and chloroarenes. However, the absence of a direct correlation between the reactivities of various aryl halides and the distribution between nickel(I,II) products demands that the rate-limiting activation process precedes, and is separate from, the product-forming step(s). Evidence for the paramagnetic ion pair [Ni(I)ArX$^{-}\cdot$] as the common intermediate which is partitioned between A and B is presented, and discussed in the light of electrochemical measurements of the one-electron oxidation of nickel(0) complexes and the reduction of aryl halides. According to the mechanistic Scheme III, the rate-limiting electron transfer from the nickel(0) donor to the aryl halide acceptor produces an ion pair which is subject to two competitive modes of decay, viz., (1) collapse to oxidative adduct and (2) fragmentation of the ArX$^{-}\cdot$ moiety, followed by diffusion of aryl radicals (observed by ESR spectroscopy) out of the solvent cage. The importance of electrostatic effects in the collapse of the ion pair to oxidative adduct is shown by the high sensitivity of A to the presence of charged nuclear substituents such as Me_3N^+– and ^-O_2C– groups. The aryl-halogen bond strength is the most important factor in the spontaneous fragmentation of the anion radical of the aromatic halide as determined from lifetimes obtained from electrochemical studies. Finally, the coordinatively unsaturated $Ni(PEt_3)_3$ is the kinetically active species and responsible for the inverse phosphine dependence on the rate of reaction. It is included in the preequilibrium formation of a π complex [$(Et_3P)_3NiArX$] as a possible precursor to electron transfer. Scheme III for oxidative addition is discussed in relation to other mechanisms involving either a concerted or a radical-chain process.

Introduction

Oxidative addition represents one of the most basic transformations in organometallic chemistry.[1-7] Its importance also lies in its key role in the conversion of organic substrates to reactive intermediates in many metal-catalyzed processes.[8] Oxidative addition is a generic term used to designate, without mechanistic implication, a ubiquitous class of reactions in which the formal oxidation of a metal complex by an electrophile is accompanied by a concomitant increase in its coordination number.[2-4] As applied to organohalogen compounds (RX), oxidative addition converts a metal complex such as a zerovalent d^{10} complex (M) to an organometal adduct, i.e.



$$M(d^{10}) + RX \longrightarrow \underset{\displaystyle X}{\overset{\displaystyle R}{M(d^8)}}$$

Two basic types of mechanisms have been proposed for this process, involving either (1) concerted 2-equiv transformations such as three-center additions[9] and S_N2 displacements[10] or (2) multistep successions of 1-equiv changes involving paramagnetic intermediates.[11] Our problem here is to reconcile these apparently diverse mechanisms, and to identify the basic interactions between metal complexes and organohalogen compounds which allow these 2- and 1-equiv pathways to evolve.

The system we chose for study is the reaction of nickel(0) complexes with aromatic halides. The latter was selected since meta and para substituents enable polar effects to be examined separately from steric effects (ortho) in the organic moiety. Furthermore, selectivities observed in the reactions of polyhaloarenes[12] suggest a mechanism analogous to the well-considered, nucleophilic aromatic substitution.[13,14] At the same time, paramagnetic nickel(I) complexes and products derived from radicals have been observed in the reactions of some aryl halides with nickel(0) complexes.[15] Importantly, the isolation and characterization of both the oxidative arylnickel(II) adducts as well as the paramagnetic nickel(I) complexes facilitate the direct observation and analysis of the primary products in this system.

Results

Oxidative additions with nickel(0) complexes were all carried out in this study with the triethylphosphine derivative. When crystalline, colorless tetrakis(triethylphosphine)nickel (for convenience, alternatively referred to as NiL_4) is dissolved in either a hydrocarbon or ethereal solvent, it readily dissociates to the purple-red, coordinatively unsaturated species, i.e.[16]

$$Ni(PEt_3)_4 \overset{K_1}{\rightleftharpoons} Ni(PEt_3)_3 + PEt_3 \qquad (1)$$

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Table I. Oxidative Nickel(II) Adducts and Paramagnetic Nickel(I) Complexes from $Ni(PEt_3)_4$ and Various Para-Substituted Aryl Halides[a]

solvent	*p*-SPhX S	*p*-SPhX X	$ArNi(X)L_2$, %[b]	$XNiL_3$, %[c]	Σ, %[d]
toluene	CH_3O	I	29	58	87
	H	I	18	71	89
	PhCO	I	*e*	7	
	CH_3CO	I	85	9	94
	CH_3OCO	I	17	69	86
tetrahydrofuran	CH_3O	I	17	83	100
	PhCO	I	101	4	105
	CH_3CO	I	55	17	72
	CH_3OCO	I	24	77	101
	^-OCO[f]	I	88	19	107
	$^-OCOCH_2$[f]	I	64	19	83
	CH_3O	Br	89	5	94
	H	Br	70	16	86
	CH_3OCO	Br	93	3	96
	$(CH_3)_3N^+$[g]	Br	38	62	100
	$(CH_3)_3N^+CH_2$[g]	Br	3	70	73
n-hexane	CH_3O	I	88	18	106

[a] At room temperature. [b] Based on eq 3, analysis by ^{31}P NMR, ±10%. [c] Based on eq 6, analysis by ESR, ±5–10%. [d] Material balance of nickel from columns 4 and 5. [e] In high yields, >90%. [f] As PPN salt. [g] As tetraphenylborate salt.

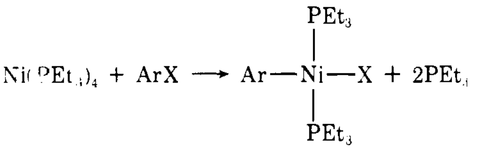
showing an intense absorption band at 500 nm (ϵ 3900 in THF and 4700 in *n*-hexane).[17] The dissociation constants K_1 are 1.0×10^{-2} and 0.53×10^{-2} M in THF and *n*-hexane, respectively.

I. **Products and Stoichiometry.** The facile reaction of the nickel(0) complex is visually apparent by the ready discharge of the color (λ_{max} 500 nm) upon the addition of aryl halide. The resulting yellow-brown solution contains two principal products derived from nickel(0)—the nickel(II) oxidative adduct $ArNi(X)L_2$ (A) and the paramagnetic nickel(I) species $XNiL_3$ (B).

$$Ni^0L_4 + ArX \rightarrow \underset{A}{ArNi^{II}XL_2} + \underset{B}{XNi^IL_3} \text{ etc.} \quad (2)$$

The relative amounts of A and B vary with the solvent and the aryl halide, both with regard to the element (I, Br, Cl) as well as the aromatic substituent, as shown in Table I and described in more detail in the following section.

Oxidative adduct A can be isolated from aryl chlorides and bromides in moderate to high yields[15] and characterized[18,19] as the trans isomer according to the stoichiometry of eq 3. The



$$Ni(PEt_3)_4 + ArX \longrightarrow Ar{-}\overset{PEt_3}{\underset{PEt_3}{Ni}}{-}X + 2PEt_3 \quad (3)$$

presence of the paramagnetic nickel(I) product was detected by ESR spectroscopy. The *g* values and line widths of the ESR spectra of these nickel(I) species were compared with those of authentic samples,[20] easily prepared by the ready synproportionation of nickel(II) and nickel(0), i.e.

$$Ni^0(PEt_3)_4 + X_2Ni^{II}(PEt_3)_2 \rightarrow 2XNi^I(PEt_3)_3 \quad (4)$$

The reverse process involving the disproportionation of nickel(I) is promoted by carbon monoxide

$$2XNi^I(PEt_3)_3 + 2CO \rightarrow Ni^0(CO)_2(PEt_3)_2 + X_2Ni^{II}(PEt_3)_2 + 2PEt_3 \quad (5)$$

to afford nickel(0) and -(II) species which are readily and quantitatively identified by their characteristic IR and electronic absorption spectra, respectively. With X = iodide, the resulting nickel(II) interacts with another CO to produce $I_2(CO)Ni(PEt_3)_2$ showing absorption bands at 475 nm and 2000 cm^{-1} in the visible and IR spectra, respectively. Conveniently, these reactions can be effectively utilized as an alternative method for the detection and quantification of nickel(I) species in eq 2.

In those cases where nickel(0) is mostly converted to nickel(I), the organic product derived from the aryl halide consists mainly of the corresponding arene (see Experimental Section). The arene is derived from the aryl radical which is the reaction intermediate formed by halogen atom transfer, with nickel(0), i.e.

$$Ni^0(PEt_3)_4 + ArX \xrightarrow{-PEt_3} XNi^I(PEt_3)_3 + Ar\cdot \quad (6)$$

$$Ar\cdot + SH \rightarrow ArH + S\cdot\text{, etc.}$$

Aryl radicals are known to react rapidly by hydrogen abstraction from solvent (SH).[21] Indeed, the ESR spectrum of the aryl radical from (2,4,6-tri-*tert*-butyl)bromobenzene can be detected directly in the reaction mixture. [The lifetimes of other aryl radicals in solution are too short to observe their ESR spectra, but steric encumbrance around the radical site (not stability) allows the persistent 2,4,6-tri-*tert*-butylphenyl radical shown in Figure 1 to be observed.[22]]

The formation of the nickel(II) oxidative adduct in eq 3 and the paramagnetic nickel(I) complex in eq 6 together account for most of the nickel(0) consumed, as shown in Table I.[23] It should be emphasized, however, that the nickel(I) product is subject to further reaction. Thus, if an excess of aryl halide is present, a *slower* reaction occurs in which nickel(I) species are eventually all converted to the dihalonickel(II) complex, e.g.[23b,c]

$$XNiL_3 + ArX \xrightarrow[-L]{} X_2NiL_2 + Ar\cdot\text{, etc.}$$

Since the studies in Tables I-III were carried out with equimolar amounts of NiL_4 and aryl halide, such a secondary reaction is not a serious complicating factor.

II. **Factors in the Competitive Formation of Nickel(II) and Nickel(I) Complexes.** The nickel material balance in Table I shows that competition in the formation of A and B is determined by (1) the halide, (2) the solvent, and (3) the polar substituent. In this section, we will also examine the effect on this competition of (4) the phosphine, (5) the paramagnetic nickel(I) product, and (6) potential inhibitors, as additives.

1. **Effect of the Halide.** Aromatic iodides afford the highest

Table II. Element and Solvent Effects on the Yields of Nickel(I) from *p*-Carbomethoxyphenyl Halides[a]

solvent	ArX = I	Br	Cl
	yield of halonickel(I), %		
hexane	46	2	0
toluene	76	6	0
tetrahydrofuran	91	7	0

[a] Based on eq 6, analysis by ESR, ±5-10%, reactions carried out at room temperature.

Table III. Substituent Effects in the Formation of Nickel(I) Complexes[a]

	yield of halonickel(I), %[b]		
substituent	ArI	ArBr	ArCl
p-MeO	83	5	0
p-Me	92	70	0
m-Me	87	54	0
H	90	16	0
p-Cl	79	7	0
m-Cl	84		0
p-CH_3CO	17		
p-PhCO	4		
p-MeO_2CO	91	7	0
p-Me_3N^+	100	75	32
p-$Me_3N^+CH_2$		72	0
p-^-O_2C	22		
p-$^-O_2CCH_2$	32		

[a] In THF at room temperature. [b] Based on stoichiometry in eq 6; 0 indicates <1%; blank space indicates not examined.

yields of nickel(I), but the oxidative adduct is the principal product derived from the chloride derivative under the same conditions (see Experimental Section). The yield of nickel(I) decreases in the order ArI ≫ ArBr > ArCl, shown in Table II.

2. Solvent Dependence. The reactions of aryl iodides are particularly sensitive to the solvent. As shown in Table II, the yields of nickel(I) increase as the solvent is changed from hexane to toluene and finally THF. Solvent polarity is independently measured by the parallel empirical parameters, Z and E_T*, described by Kosower and Reichardt, respectively.[24,25] Increasing solvent polarity for hexane, toluene, and THF is reflected in $E_T* = 31$, 34, and 37 kcal mol^{-1}, respectively.

3. Effects of Polar Substituents. The extent to which a nuclear substituent affects the yield of nickel(I) depends on the halide. Thus, the yield of nickel(I) from various aryl chlorides is consistently nil, with one outstanding exception, viz., that with the positively charged trimethylammonio (Me_3N-$^+$) substituent. On the other hand, for aryl iodides the yields of nickel(I) are always high, except for those with acyl (CH_3CO-and PhCO-) and negatively charged (^-O_2C-) substituents. Aryl bromides show dramatic variations in nickel(I) yields as a result of substituent changes listed in Table III. With all three halides, those derivatives with nitro substituents effected no oxidative addition nor afforded any nickel(I) product. The reaction of the nitro functionality with nickel(0) will be reported separately.[26]

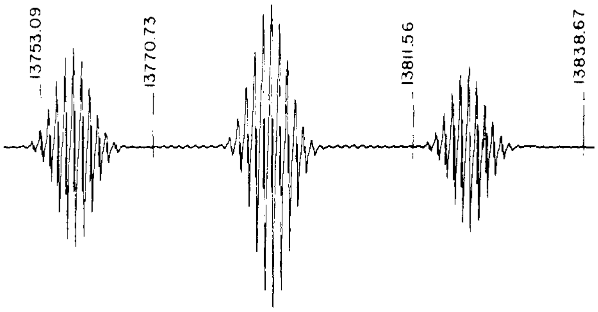
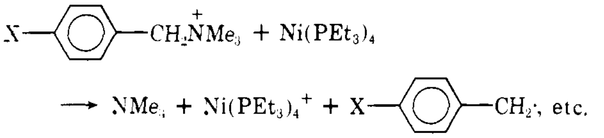


Figure 1. ESR spectrum of the 2,4,6-tri-*tert*-butylphenyl radical showing resolved *tert*-butyl protons. ^1H NMR field marker in kHz.

Special attention should be directed to those aryl halides with charged substituents—the positively charged $(CH_3)_3N$-$^+$ group *promoting* nickel(I) and the negatively charged ^-OOC-group *hindering* the same. The homologous halobenzylammonium cation afforded trimethylamine in its reaction with $Ni(PEt_3)_4$, presumably by reductive cleavage of the side chain, i.e.



(7)

4. Effect of Nickel(0) Ligation. Control by Phosphine. The extent of dissociation of tetrakis(triethylphosphine) in eq 1 is mediated by the phosphine. In the second dissociation

$$Ni(PEt_3)_3 \overset{K_2}{\rightleftharpoons} Ni(PEt_3)_2 + Et_3P \tag{8}$$

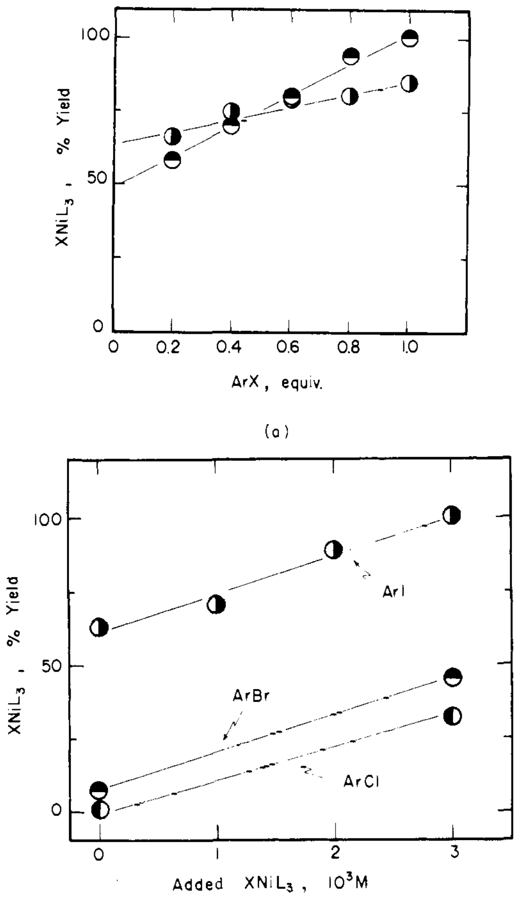
K_2 is less than 10^{-6} M, judging by this upper limit placed on the dissociation of the analogous, more hindered $Ni(PPh_3)_3$.[27,28] From K_1 and K_2, the relative amounts of $Ni(PEt_3)_4$, $Ni(PEt_3)_3$, and $Ni(PEt_3)_2$ can be reliably estimated at the various concentrations of nickel(0) and added phosphine listed in Table IV.

In order to determine whether the extent of phosphine ligation on nickel(0) influences the production of nickel(I), the reaction with aryl halide was carried out so that only small amounts of nickel(0) were converted, i.e., pseudo-first-order conditions in which [Ni(0)] ≫ [ArX]. The results in the last

Table IV. Effect of Nickel(0) Ligation. Variation in Nickel(I) Yields from Various $Ni(PEt_3)_n$

total nickel(0), 10^2 M[a]	NiL_4, 10^2 M[b]	NiL_3, 10^2 M[b]	NiL_4/NiL_3[c]	NiL_3/NiL_2 ($\times 10^3$)[d]	nickel(0) conversion, %[e]	INi^IL_3, %[f]
50	43	6.6	6.6	66	0.2	40
20	16	4.0	4.0	40	0.5	31
5.0	3.2	1.8	1.8	18	2	34
0.50	0.14	0.36	0.39	3.6	20	58
0.50[g]	0.28	0.22	1.3	10	20	65
0.50[h]	0.34	0.16	2.1	20	20	62

[a] Added as $Ni(PEt_3)_4$ in THF at room temperature. [b] Calculated from K_1. [c] From columns 2 and 3. [d] Assuming $K_2 = 10^{-6}$ M, and then $NiL_2 \sim 10^{-6}$ M, except in the presence of added L (see below). [e] Based on the complete reaction with 1×10^{-3} M *p*-$MeO_2CC_6H_4I$ as limiting reagent. [f] Based on ArI used in column 6. Added triethylphosphine, [g] 1×10^{-2} and [h] 2×10^{-2} M; NiL_n concentrations calculated accordingly.



(a)

(b)

Figure 2. Effect of the presence of nickel(I) species on the yield of XNi-$(PEt_3)_3$ in THF solution with 5.0 × 10^{-3} M $Ni(PEt_3)_4$: (a) as a function of aryl halide as the limiting reagent, (◓) *p*-$IC_6H_4NMe_3^+BPh_4^-$, (◑) *p*-$IC_6H_4CH_3$; (b) as a function of added $XNi(PEt_3)_3$ to (◑) *p*-$IC_6H_4CO_2Me$, (◓) *p*-$BrC_6H_4CO_2Me$, (◐) *p*-$ClC_6H_4CO_2Me$.

row of Table IV show that the nickel(I) production from aryl halide is rather insensitive to either the ratio of $[NiL_4]/[NiL_3]$ or of $[NiL_3]/[NiL_2]$. Therefore, we conclude that the major nickel products A and B are not separately derived from two different NiL_n species. The phosphine ligation may influence the reactivity of nickel(0) (vide infra), but not the product distribution.

5. Influence of the Paramagnetic Nickel(I) Product. The presence of nickel(I) induces the production of more nickel(I), as it can be inferred from the two sets of data obtained in Table IV at relatively low and high nickel(0) conversions. Unfortunately, the rapid rates precluded a direct product analysis at various stages of reaction, but the effect can be demonstrated in several alternative ways. For example, the *yield* of nickel(I) in Figure 2a actually increases with the extent of nickel(0) *conversion*, which is regulated by the use of various amounts of aryl halide as the limiting reagent. [A simple extrapolation of the curve suggests that 50–60% yields of nickel(I) are produced at zero conversion.] The equivalent effect is represented in Figure 2b, in which the reaction was carried out in the presence of various amounts of added $XNi(PEt_3)_3$. Aryl bromides and chlorides respond similarly. It is noteworthy that the presence of oxidative nickel(II) adducts, even up to equimolar amounts, exerts no effect on the production of nickel(I).[29]

6. Effect of Free-Radical Inhibitors. Additives such as quinones, nitrosoalkanes, dienes, and galvinoxyl have been effectively employed as inhibitors for radical chain processes involving various nickel complexes.[11] In every case it is important to establish that any reaction or complex formation of the inhibitor with nickel(0) does not affect its ability to scavenge free radicals. The yields of nickel(I) from the reactions of *p*-bromotoluene and methyl *p*-bromobenzoate were unaffected by the presence of 10% duroquinone, phenanthroquinone, galvinoxyl, or nitroso-*tert*-butane.[29,30] 1,4-Cyclohexadiene used partly as solvent (20% v/v) forms a π complex with nickel(0), but otherwise no dramatic changes were observed.

Table V. Phosphine Dependence of the Observed Pseudo-First-Order Rate Constant for $Ni(PEt_3)_4$ and Bromobenzene in THF Solution

$Ni(PEt_3)_4$, M	C_6H_5Br, M	added PEt_3, M	k_{obsd}, $M^{-1}\ s^{-1}$
0.416×10^{-3}	0.416×10^{-2}	0	2.86
0.416×10^{-3}	0.416×10^{-2}	2.25×10^{-3}	2.31
0.416×10^{-3}	0.416×10^{-2}	4.25×10^{-3}	1.75
0.416×10^{-3}	0.416×10^{-2}	6.75×10^{-3}	1.47
0.416×10^{-3}	0.416×10^{-2}	9.00×10^{-3}	1.27

Table VI. Substituent Effects on the Second-Order Rate Constants for the Reactions of Phenyl Halides (X) with Nickel(0) Complexes[a]

substituent	Hammett σ value[b]	log k_{obsd}, $M^{-1}\ s^{-1}$		
		X = I[c]	Br	Cl
p-CH_3O	−0.27	(0.88)	0.66	0.72
p-CH_3CH_2O	−0.24		0.66	
p-CH_3	−0.17	1.54 (0.64)	−0.25	−1.04
m-CH_3	−0.069	1.77 (0.82)	−0.066	−0.51
p-Ph	−0.01		−0.086	
H	0	1.98 (1.07)	0.49	0.27
p-Cl	0.23	2.38 (1.57)	1.50	1.53
m-Cl	0.37	2.81		1.64
p-MeOCO	0.46	2.38 (1.53)	1.28	1.38
p-$Me_3N^+CH_2$	0.57		1.02	
p-Me_3N^+	0.86		1.25	

[a] In THF solutions at 25 °C unless otherwise noted. [b] Values from ref 31. [c] Rate constants in parentheses refer to reactions in hexane.

III. Kinetics. The rates of reaction between various aryl halides and $Ni(PEt_3)_4$ were carried out under an argon atmosphere, and the absorbance change followed spectroscopically using the absorption band at 500 nm for the disappearance of $Ni(PEt_3)_3$. The reactions of the chloride and bromide derivatives were sufficiently slow to enable the kinetics to be determined under pseudo-first-order conditions with an excess of ArX. The reactions of aryl iodides were carried out with equimolar amounts of both reagents. By either method, the reaction was found to be first order in each reagent, i.e.

$$-\frac{d(NiL_3)}{dt} = k_{obsd}[NiL_3][ArX] \tag{9}$$

The rate of disappearance of nickel(0) is retarded by added triethylphosphine L, as shown in the last column of Table V. Quantitatively, the phosphine dependence of the observed second-order rate constant in eq 9 is given by the relationship

$$\frac{1}{k_{obsd}} = \frac{1}{k}\left\{1 + \frac{[PEt_3]}{K}\right\} \tag{10}$$

which is illustrated graphically in Figure 3. The phosphine-independent rate constant k = 2.86 $M^{-1}\ s^{-1}$ is obtained from the intercept, and K = 7 × 10^{-3} M from the slope. The phenomenonological phosphine dependence in eq 10 is readily interpretable as the direct involvement of the coordinatively

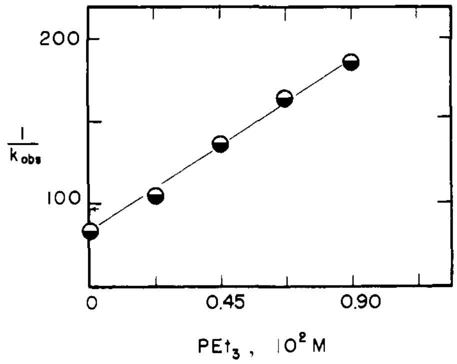


Figure 3. Phosphine dependence of the second-order rate constant for the reaction of 4.16 × 10^{-3} M bromobenzene and 4.16 × 10^{-4} M $Ni(PEt_3)_4$ in THF.

Table VII. Solvent Dependence of the Rate of Reaction of $Ni(PEt_3)_3$ with Aryl Halides

aryl halide	rate constant k_{obsd}, M^{-1} s^{-1} hexane	THF	toluene
C_6H_5Cl	0.93	1.87	2.25
C_6H_5Br	0.92	3.07	4.01
C_6H_5I	10.7	94	
p-$MeO_2CC_6H_4I$	34	240	

unsaturated species $Ni(PEt_3)_3$ in the oxidative addition as described further in the Discussion.

The effect of the halide and the nuclear substituent on the observed second-order rate constant is listed in Table VI. The rate constants for aryl iodides are more than an order of magnitude larger than those for either the corresponding aryl bromides or chlorides, which show comparable reactivity. Furthermore, the rates are highly dependent on the polarity of the solution. The second-order rate constant typically increases from hexane < THF < toluene as listed in Table VII for several aryl halides. The differences in rate constants are not due to variations in the concentration of $Ni(PEt_3)_3$ since (1) K_1 is only slightly solvent dependent and (2) the rates were measured with <5 × 10^{-4} M $Ni(PEt_3)_4$, where more than 95% of the species consists of $Ni(PEt_3)_3$.

Despite the differences in the absolute rates of reaction, however, the sensitivity to changes in substituent shows remarkable similarity in hexane and THF, as illustrated by the linear correlation in Figure 4.

The rate constants for the aryl iodides, bromides, and chlorides follow reasonable Hammett correlations if only the points of p- and m-methyl, phenyl, hydrogen, and m- and p-chloro are included. Using these data in Figure 5, the ρ values for aryl iodides, bromides, and chlorides are calculated to be 2.0, 4.4, and 5.4, respectively. Further examination reveals that the p-methoxy substituent suffers a positive deviation, whereas that of the p-carbomethoxy substituent is negative. More significantly, however, the data show internal consistency since all the points are included in a plot of k_{obsd} for one aryl halide against that of another halide as in Figure 6. Indeed, the striking linear correlations among the rates of all three series of halides represent strong evidence that the aryl iodides, bromides, and chlorides react with the nickel(0) species by the same rate-determining steps.

The absence of dominant steric effects on the reaction of nickel(0) with aryl halide has already been qualitatively indicated above by the reaction of the highly hindered 2,4,6-tri-*tert*-butylbromobenzene. A more systematic examination of steric effects is shown in Table VIII in which the effects of o-methyl groups[32] were examined.

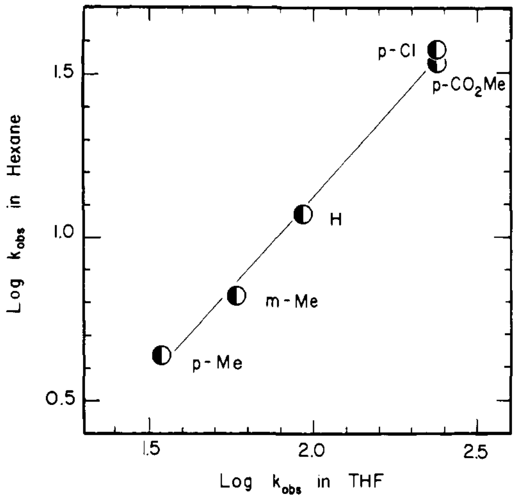


Figure 4. Solvent effect on the correlation of the second-order rate constants for substituted iodobenzenes obtained in THF and in hexane.

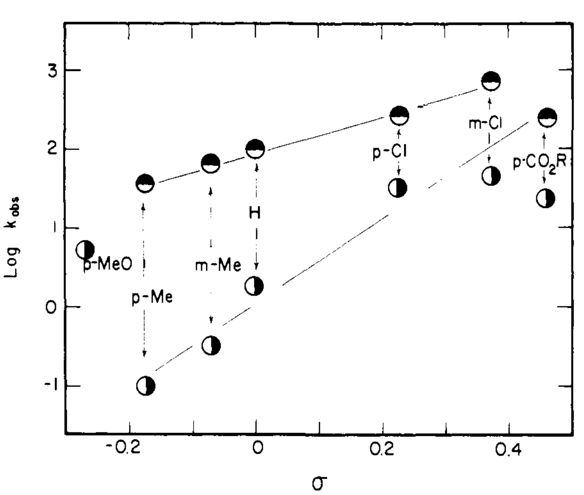


Figure 5. Attempted Hammett correlation of the second-order rate constants for the reactions of substituted (◑) chlorobenzenes and (◓) iodobenzenes in THF. Note deviation of p-MeO and p-CO_2Me substituents.

Table VIII. Steric Effects from o-Methyl Substitution on the Reaction of Nickel(0) with Bromobenzene in Toluene Solution

$Ni(PEt_3)_4$, M	aryl bromide	M	k_{obsd}, M^{-1} s^{-1}
0.416 × 10^{-3}	C_6H_5Br	0.832 × 10^{-2}	4.01
0.416 × 10^{-3}	4-$CH_3C_6H_4Br$	1.66 × 10^{-2}	0.82
0.416 × 10^{-3}	2-$CH_3C_6H_4Br$	1.66 × 10^{-2}	1.39
0.416 × 10^{-3}	$2,4$-$(CH_3)_2C_6H_3Br$	1.66 × 10^{-2}	1.04
0.416 × 10^{-3}	$2,4,6$-$(CH_3)_3C_6H_2Br$	1.66 × 10^{-2}	0.22

The second-order rate constant was unaffected by the products of reaction. For example, the addition of as much as equimolar amounts of either the oxidative arylnickel(II) adduct or the paramagnetic nickel(I) complex in Table IX caused no significant change in the rate constants.

IV. Electrochemical Measurements. The electrochemical oxidation of the nickel(0) complexes of triethylphosphine and triphenylphosphine were examined by cyclic voltammetry (CV) in THF and acetonitrile solutions. The CV of both series of complexes showed two anodic waves, one at around −0.4 to −0.7 V and another generally between +0.4 and +0.6 V vs. SCE as listed in Table X. The first wave corresponds to a Ni(0) → Ni(I) conversion, since the CV shown in Figure 7 of te-

Table IX. Effects of Products on the Rate of Reaction of Nickel(0) with Aryl Halides[a]

aryl halide	10^3 M	$Ni(PEt_3)_4$, 10^3 M	additive[b]	10^3 M	k_{obsd}, $M^{-1} s^{-1}$
p-$BrC_6H_4CO_2Me$	0.416	0.416	none		24.3
	0.416	0.416	$ArNiBrL_2$	0.416	22.8
	0.416	0.416	$BrNiL_3$	0.416	20.3
	4.16	0.416	none		19.0
	4.16	0.416	$BrNiL_3$	0.416	20.9
p-$IC_6H_4CO_2Me$	0.416	0.416	none		211
	0.416	0.416	$ArNiIL_2$	0.416	164
	0.416	0.416	$INiL_3$	0.416	180

[a] In THF solution at 25 °C. [b] $L = PEt_3$, $Ar = p$-$MeO_2CC_6H_4$.

Table X. Cyclic Voltammetry of Phosphinenickel(0) Complexes[a]

nickel(0) complex added[b]	additive	solvent	first anodic wave E,[c] V vs. SCE	first anodic wave ΔE_p,[d] mV	first anodic wave i_a/i_c[e]	second anodic wave[f] E, V vs. SCE
$Ni(PPh_3)_4$	PPh_3[g]	CH_3CN	−0.73	60	1.00	+0.62
	0	CH_3CN	−0.77	90	1.03	+0.62
$Ni(PEt_3)_4$	PEt_3[h]	CH_3CN	−1.06	70	1.07	+0.20
	0	CH_3CN	[f]			+0.20
$Ni(PPh_3)_4$	PPh_3[g]	THF	−0.41	80	0.90	
	0	THF	−0.45	110	[k]	+0.39
$Ni(PEt_3)_4$	PEt_3[i]	THF	−0.74	90	1.01	+0.36
	0[j]	THF	−0.81	85	1.00	+0.36

[a] At ambient temperatures with 0.1 M tetraethylammonium or 0.5 M tetrabutylammonium perchlorates as supporting electrolytes. [b] 1.0×10^{-3} M in CH_3CN or THF. [c] $2E = E_{pa} + E_{pc}$; error ±30 mV. [d] Peak potential separation of anodic and cathodic waves. [e] Ratio of anodic and cathodic peak currents. [f] No cathodic wave. [g] Saturated solution. [h] 100-fold excess. [i] 2.25×10^{-1} M; 96% of nickel(0) as $Ni(PEt_3)_4$. [j] 92% of nickel(0) as $Ni(PEt_3)_3$. [k] Poor cathodic wave.

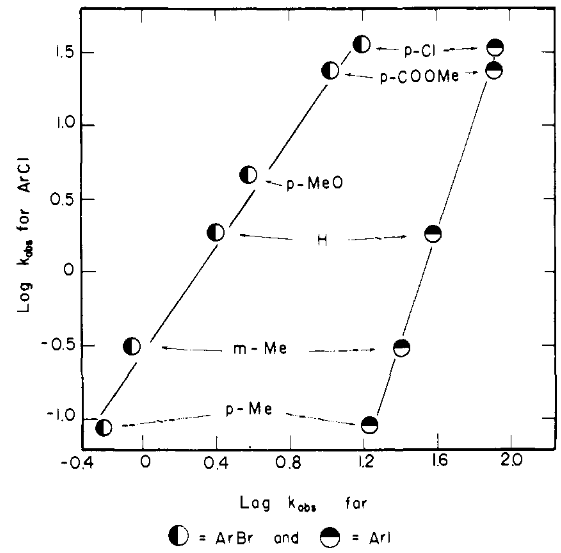


Figure 6. Correlation of substituents effects in the reactions of substituted chlorobenzenes with those in the corresponding (◐) bromobenzenes and (◓) iodobenzenes.

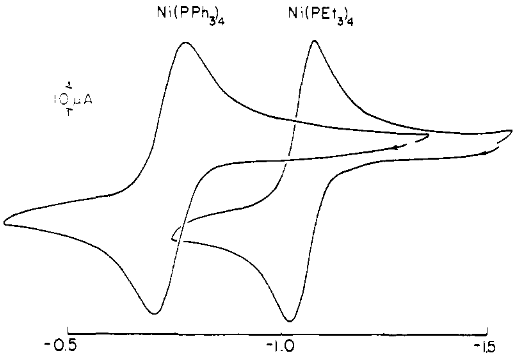


Figure 7. Initial scan cyclic voltammetry in acetonitrile solution of the first anodic wave of (left) 1.0×10^{-3} M $Ni(PPh_3)_4$ with saturated PPh_3 and (right) 4.5×10^{-4} M $Ni(PEt_3)_4$ with 4.5×10^{-2} M PEt_3.

trakis(triphenylphosphine)nickel dissolved in acetonitrile solution containing excess triphenylphosphine is reversible (see Experimental Section). The second wave is irreversible, showing no cathodic peaks even at high sweep rates, but it is tentatively assigned to a Ni(I) → Ni(II) oxidation. The first wave is shifted to −0.41 V in THF solution. Similarly, the first anodic wave of tetrakis(triethylphosphine)nickel in the presence of excess triethylphosphine occurs at −1.06 V in acetonitrile solutions, and is shifted to −0.74 V in THF solutions. The more negative potentials of about 0.3 V, observed in acetonitrile solutions, can be readily attributed to increased stabilization of the cation in this more polar solvent compared to THF. It is also clear from the data in Table X and Figure 7 that triethylphosphine complexes of nickel(0) undergo 1-equiv oxidation more readily than the triphenylphosphine analogues by about 300 mV.

The first electron transfer step in the reduction of simple aryl halides is known to be electrochemically irreversible owing to the transient nature of the anion radical (vide infra). The reversible electrode potentials are thus unavailable.

Discussion

Oxidative addition of aryl halides to zerovalent nickel complexes can be efficient provided that the principal side reaction to nickel(I) and arene is controlled. Any mechanistic formulation for oxidative addition must accommodate such a simultaneous transformation of nickel(0) to the diamagnetic nickel(II) adduct as well as to the paramagnetic nickel(I) product. Thus, oxidative addition in eq 3 formally represents

Scheme I

$$\mathrm{Ni^0 + ArX} \longrightarrow \mathrm{ArNi^{II}X} \tag{11}$$

$$\mathrm{Ni^0 + ArX} \longrightarrow \mathrm{XNi^I + Ar\cdot} \tag{12}$$

Scheme II

$$\mathrm{Ni^0 + ArX} \longrightarrow \mathrm{[Ni^I\ ArX^{-}\cdot]} \longrightarrow \mathrm{ArNi^{II}X} \tag{13}$$

$$\mathrm{[Ni^I\ ArX^{-}\cdot]} \longrightarrow \mathrm{XNi^I + Ar\cdot} \tag{14}$$

a *2*-equiv change for nickel(0), whereas the nickel(I) product derives from a *1*-equiv process involving halogen atom transfer in eq 6. It is possible that these apparently dissimilar transformations proceed via two entirely independent, but parallel, pathways represented schematically in Scheme I (presented without phosphine ligands for emphasis). Alternatively, these nickel(I) and nickel(II) products may be derived from a common intermediate, e.g., Scheme II. In this discussion we wish to show first how the competition between oxidative addition and halogen atom transfer provides an important key for unlocking the mechanism of the interaction of these nickel(0) complexes with aryl halides.

I. Criteria for a Common Intermediate. The evidence for a common intermediate rests firmly on three independent observations. First, substituent effects on the *rates* of reactions of nickel(0) with aryl iodides in Figure 6 are strongly correlated with those of aryl bromides as well as those of aryl chlorides. On the other hand, no such correlation exists in Table I for the distribution among nickel(II) and nickel(I) *products* with the changes in either the halide or the substituent. In other words, changes in the rate-limiting transition states are not directly reflected in a corresponding change of the product distribution. Such circumstances can only pertain if one or more intermediates intervene between reactants and products.

The same conclusion derives from the study of solvent effects. Thus, Figure 4 shows that the relative reactivities of aryl iodides are the same in hexane as in THF, despite a significant increase in rate. On the other hand, the product distributions, i.e., $[\mathrm{ArNi^{II}}]/[\mathrm{Ni^I}]$, included in Table I actually show *inversions* with changes in solvent. Therefore, the rate-limiting activation process cannot lead directly to the nickel(II,I) products.

Finally, the deliberate addition of the paramagnetic nickel(I) complex leads to increased yields of additional nickel(I), as shown in Figures 2a and 2b. However, there is no significant, corresponding change in the rates of reaction as measured by the disappearance of nickel(0) in Table IX. Therefore, the nickel(I) as well as the nickel(II) product must be formed subsequent to the rate-limiting step.

The nature of the common intermediate is readily deduced from the redox properties of the reactants. Thus, the zerovalent triethylphosphine complexes of nickel are strong reducing agents, and cyclic voltammetry in Figure 7 and Table X shows that they undergo facile 1-equiv oxidations to nickel(I). Similar transformations of nickel(0) occur chemically with a variety of one-electron acceptors, including quinones and cyano olefins.[33] Likewise, aryl halides are easily reduced electrochemically and they are known to participate effectively as acceptors in electron-transfer reactions with donors such as alkali metals, carbanions, and organometals.[19,34-36] Thus, electron transfer represents a reasonable pathway for the nickel(0) donor to interact with the electron-deficient aryl halide, i.e.

$$\mathrm{Ni^0 + ArX} \rightarrow \mathrm{[Ni^I\ XAr^{-}\cdot]} \tag{15}$$

Accordingly, we formulate the ion pair in eq 15 as the common intermediate which is partitioned between the nickel(II) and the nickel(I) products in the following way:

$$\mathrm{[Ni^I\ XAr^{-}\cdot]} \longrightarrow \mathrm{ArNi^{II}X} \tag{16}$$

$$\mathrm{[Ni^I\ XAr^{-}\cdot]} \longrightarrow \mathrm{Ni^IX + Ar\cdot} \tag{17}$$

Scheme III

$$\mathrm{NiL_4} \overset{K_1}{\rightleftharpoons} \mathrm{NiL_3 + L} \tag{18}$$

$$\mathrm{Ni^0L_3 + ArX} \xrightarrow{k_2} \mathrm{[Ni^IL_3\ ArX^{-}\cdot]} \tag{19}$$

$$\mathrm{[Ni^IL_3\ ArX^{-}\cdot]} \longrightarrow \mathrm{ArNi^{II}XL_2 + L} \tag{20}$$

$$\mathrm{[Ni^IL_3\ ArX^{-}\cdot]} \xrightarrow{\text{diffuse}} \mathrm{Ni^IL_3 + X^- + Ar\cdot}\text{, etc.} \tag{21}$$

Scheme IV

$$\mathrm{NiL_4} \overset{K_1}{\rightleftharpoons} \mathrm{NiL_3 + L} \tag{18}$$

$$\mathrm{NiL_3} \overset{K_2}{\rightleftharpoons} \mathrm{NiL_2 + L} \tag{22}$$

$$\mathrm{NiL_4 + ArX} \xrightarrow{k_1} \text{products} \tag{23}$$

$$\mathrm{NiL_3 + ArX} \xrightarrow{k_2} \text{products} \tag{24}$$

$$\mathrm{NiL_2 + ArX} \xrightarrow{k_3} \text{products} \tag{25}$$

This formulation provides a basis for a unified mechanism which accommodates the various, apparently divergent observations presented in the Results section above.

II. Mechanism of Oxidative Addition of Aryl Halides to $\mathrm{Ni(PEt_3)_4}$. To facilitate the discussion, we wish to first present the general mechanism for the reaction of nickel(0) and aryl halides in Scheme III, in which $\mathrm{L = PEt_3}$ and the formal oxidation states are included to allow emphasis of the redox changes. According to Scheme III, the equilibrium formation of the coordinatively unsaturated $\mathrm{Ni(PEt_3)_3}$ in eq 18 is followed by the slow rate-limiting electron transfer in eq 19 to afford an ion pair indicated in brackets. Cage collapse affords oxidative adduct in eq 20, which is competitive with diffusion in eq 21. The stability and lifetime of the caged ion pair then determine the product distribution. Each of the important facets of this mechanism will be treated separately below.

A. Coordinatively Unsaturated $\mathrm{Ni(PEt_3)_3}$ as the Reactive Species. The facile dissociation of phosphine from nickel(0) allows essentially three species to be considered for the direct reaction with aryl halides, as outlined in Scheme IV.

The inverse phosphine dependence of the observed second-order rate constant in eq 10 can be attributed to the mass law effect in eq 18 and 22, if either or both of the coordinatively unsaturated species $\mathrm{Ni(PEt_3)_3}$ and $\mathrm{Ni(PEt_3)_2}$ are directly involved. However, K_2 is at least 10^4 less than K_1, and the simplest formulation would include only eq 18 and 24, for which the kinetic expression is

$$-\frac{d[\mathrm{NiL_3}]}{dt} = \frac{K_1k_2}{K_1 + [\mathrm{L}]}[\mathrm{NiL_3}][\mathrm{ArX}] \tag{26}$$

Indeed, the phosphine dependence in Figure 3 shows that the observed second rate constant k_{obsd} can be quantitatively expressed as in eq 10, which is equivalent to the constant term in the rate expression above, with $K = K_1$ and $k = k_2$. Furthermore, it is noteworthy that the first dissociation constant $K_1 = 7 \times 10^{-3}$ M evaluated from eq 26 is in reasonable agreement with that (10×10^{-3} M) measured in eq 1 directly by the spectrophotometric method. The minor discrepancy between K and K_1 arises partly from the assumption that the phosphine remains constant, particularly at low concentrations. To obviate this difficulty, the slope in Figure 3 can be replotted by neglecting the first two points at low phosphine concentrations, and in this way an intercept (shown by the arrow) with $k = 2.45\ \mathrm{M^{-1}\ s^{-1}}$ is obtained. From the new slope, K is evaluated as 10×10^{-3} M, in excellent agreement with the independently measured value of K_1. In either case, the results are clearly consistent with three-coordinate $\mathrm{Ni(PEt_3)_3}$ as the principal, kinetically significant species in the reaction with aryl halides.

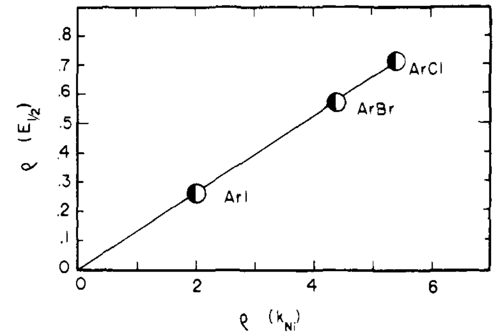


Figure 8. Relationship between the sensitivity of the polarographic half-wave potentials for the reduction of a series of substituted chlorobenzenes, bromobenzenes, and iodobenzenes (from ref 37) with the sensitivity to reaction with $Ni(PEt_3)_4$; plotted as the respective Hammett ρ values.

B. Electron Transfer as the Rate-Limiting Step. Electrochemical reduction represents a suitable model for the activation process in electron transfer to a series of aryl halides from $Ni(PEt_3)_3$ according to eq 27. Cyclic voltammetry is a useful technique for examining the reversible formation of the aromatic halide anion radical:

$$ArX \underset{(a)}{\xrightarrow{+\epsilon}} ArX^{-}\cdot \underset{(b)}{\xrightarrow{\tau}} Ar\cdot + X^{-} \tag{27}$$

which has been identified by its ESR spectrum particularly if it has polar substituents.[37] With most aryl halides, however, the anion radical is too unstable for study (vide infra).

The polarographic half-wave potentials of a series of substituted chlorobenzenes, bromobenzenes, and iodobenzenes follow a reasonable Hammett plot with a positive slope,[31] consistent with one-electron reduction in eq 27a. Significantly, the ρ values derived from $E_{1/2}$ are strongly dependent on the halide, increasing in the order ArI < ArBr < ArCl as $\rho(E_{1/2}) = +0.26, +0.57$, and $+0.71$, respectively. The same trend in ρ values is obtained from the rates of nickel(0) reaction with aryl halides, which also increase in the order ArI < ArBr < ArCl as $\rho(k_{Ni}) = +2.0, +4.4$, and $+5.4$, respectively. The relationship between the electrochemical reduction and the nickel(0) reductions is illustrated in Figure 8.

The linear correlation in Figure 8 with a slope of 7.7 implies that a strong similarity exists between the transition state for the nickel(0) reaction and the driving force for the electrochemical reduction of aryl halides. Indeed, the plot of the *individual* rate constants for the nickel(0) reaction in Figure 9 would represent a linear free energy relationship if the polarographic $E_{1/2}$ values represented the reversible reduction potentials of the various aryl halides. Under these circumstances the slope of 8.5 arbitrarily drawn with dashed lines through each of the three sets of points for aryl chlorides, bromides, and iodides is that predicted by Marcus theory for an outer-sphere electron-transfer process, i.e.[38,39]

$$\log k = 8.5E^0 + \text{constant} \tag{28}$$

The first polarographic wave for many simple aryl halides is irreversible, and there are kinetic terms to be included in $E_{1/2}$.[40] The extent to which the kinetic terms may be variable with changes in substituents could obscure the rigorous interpretation of this reaction as an outer-sphere process.[41,42] Nonetheless, the unmistakable trends in both Figures 8 and 9 establish the importance of electron transfer in the reaction of aryl halides with $Ni(PEt_3)_3$ as depicted in Scheme III. Such an electron-transfer process to afford an ion pair is to be distinguished from one in which electron transfer merely makes a partial contribution to the transition state of a concerted process. Indeed, the formation of this highly ionic product is supported not only by the correlations in Figures 8 and 9 but also the strong dependence on solvent polarity in Table VII. It is noteworthy that, despite the differences in the absolute rate constants for reactions carried out in hexane and in THF, they both show the same sensitivity to polar substituents in Figure 4; importantly, the slope of the correlation of 1.0 shows that charge development is the same in hexane and in THF, which (barring fortuitous coincidences) can only be readily accounted for by the formulation of ion pairs as actual intermediates.

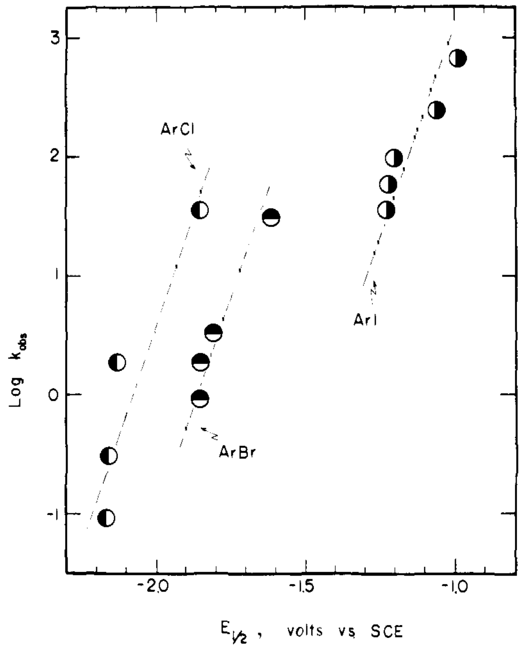


Figure 9. Correlation of the polarographic half-wave potentials for the reduction of substituted (◑) iodobenzenes, (◒) bromobenzenes, and (◐) chlorobenzenes (from ref 31) with the second-order rate constants for reactions with $Ni(PEt_3)_4$. The dashed lines are *arbitrarily* drawn with slope = 8.5 (see text).

Our attention is now drawn to the properties of the ion pair, which identify it as the common intermediate leading to oxidative addition or nickel(I) formation.

C. Ion Pairs as the Common Intermediates—Partitioning to Oxidative Adducts and Nickel(I) Products. According to Scheme III, the oxidative adduct is formed by the collapse of the tight ion pair in eq 20 which must compete with diffusion of aryl radicals out of the solvent cage. Since such a partitioning of the common intermediate occurs subsequent to the rate-limiting electron-transfer step, it can only be considered in the light of product formation. We focus thus on factors involved in (1) the collapse of the ion pair to oxidative adduct and (2) the formation of aryl radicals and nickel(I), using as variable probes the nature of the halide, the nuclear substituents (particularly those with charged poles), and the solvent as discussed individually below.

(1) **Cage collapse of the ion pair** derives part of its driving force from the formation of the nickel–halogen bond, since the highest yields of oxidative adducts are invariably obtained from aryl chlorides > aryl bromides > aryl iodides in accord with the expected metal–halogen bond strengths.[43] Moreover, the absence of any large, systematic effects of (uncharged) nuclear substituents on the yields of oxidative adducts suggests that the stabilization of the aryl moiety is not an important consideration.

The geometry of the ion pair is most likely to be that in which the nickel lies below the plane of the aromatic ring and displaced toward the halide (vide infra). The transition state for insertion stemming from the collapse of such an ion pair is depicted in Figure 10.

The importance of *electrostatic effects* in the collapse of the ion pair is shown by the significant influence of charged substituents (i.e., poles[44]) on the aromatic nucleus in affecting the yields of oxidative adducts. Thus, unusually high yields of oxidative adducts are formed from aryl halides with negative poles such as p-$IC_6H_4CO_2^-$ (88%) and p-$IC_6H_4CH_2CO_2^-$ (64%), compared to that obtained from their neutral counterpart, p-$IC_6H_4CO_2Me$ (24%). Conversely, the presence of positive poles in p-$BrC_6H_4NMe_3^+$ (38%) and p-$BrC_6H_4CH_2NMe_3^+$ (3%) inhibits the formation of oxidative adducts in comparison with that obtained from neutral, uncharged analogues such as p-$BrC_6H_4CO_2Me$ (93%) and p-$BrC_6H_4OCH_3$ (89%). Thus, *attractive* and *repulsive* electrostatic potentials, represented by aromatic substituents with negative and positive charges, respectively, accord with the ease of collapse of the ion pair to oxidative adduct.

(2) **Formation of aryl radicals and nickel(I)** derives from a competing homolysis of the $ArX^{-}\cdot$ moiety in the ion pair. Thus, an important feature of the ion pair $[Ni^{I}\ ArX^{-}\cdot]$ resides in the stability of the $ArX^{-}\cdot$ moiety which is itself highly prone to spontaneous dissociation.[45,46] For example, cyclic voltammetry has shown that the half-life τ for dissociation in eq 27b is strongly dependent on the nature of the halide, and it generally increases in the order $\tau_X = ArI^{-}\cdot < ArBr^{-}\cdot < ArCl^{-}\cdot$. In particular, for the series of $PhCOC_6H_4X$, the trend in first-order rate constants for the decomposition of the haloaromatic anion radical has been measured as p-Br > m-Br > p-Cl to be $10^{4.9}{:}10^{2.9}{:}10^{1}\ s^{-1}$ in dimethylformamide solutions.[37] Similarly, in the series of $O_2NC_6H_4X$, the rates of decomposition of the anion radical are p-I > p-Br as $10^{0}{:}10^{-2.4}\ s^{-1}$ and o-I > o-Br > o-Cl as $10^{3.9}{:}10^{2.0}{:}10^{-2.0}\ s^{-1}$ in the same solvent.[47] The anion radicals of the parent halobenzenes are too unstable to observe directly, but a recent indirect approach using homogeneous redox catalysis has provided a lifetime of about 10^{-7} s for chlorobenzene anion radical.[41] If the same dissociation of $ArX^{-}\cdot$ applies to that within the ion pair, i.e.

$$[Ni^{I}\ ArX^{-}\cdot] \rightarrow [Ni^{I}\ Ar\cdot\ X^{-}] \qquad (29)$$

or equivalently

$$[Ni^{I}\ ArX^{-}\cdot] \rightarrow [Ni^{I}X\ Ar\cdot]$$

it is expected that the formation of aryl radicals would be the greatest with aryl iodides and the least with aryl chlorides. Indeed, the yields of the nickel(I) side product in Table I uniformly increase in the order ArCl < ArBr < ArI as expected from the trend in stabilities of the anion radicals.

Thus, the partitioning of the ion pair between oxidative adduct and nickel(I) products can be readily represented by the competition between cage collapse and spontaneous fragmentation of the $ArX^{-}\cdot$ moiety, as elaborated in (1) and (2) above. However, the phosphine stoichiometry for the two processes differs; i.e., the oxidative adduct $ArNiXL_2$ is formed with loss of one phosphine ligand whereas all three phosphine ligands remain intact on the nickel(I) product, $XNiL_3$. The former may occur simultaneously with (or subsequent to) the collapse of the ion pair in eq 20. However, it is also possible that phosphine loss precedes the collapse of the ion pair,[48a] i.e.

$$[NiL_3^{+}\ ArX^{-}\cdot] \xrightarrow{-L} [NiL_2^{+}\ ArX^{-}\cdot] \rightarrow ArNiXL_2 \qquad (30)$$

If so, it may provide yet another factor in the partitioning of the ion pair between oxidative adduct and nickel(I) product.[48b]

D. π Complexes as Possible Precursors. A variety of nickel(0) compounds form π complexes with unsaturated ligands such as olefins, arenes, and carbonyl compounds.[49,50] These complexes show the earmarks of charge-transfer interactions (as a result of back-bonding from the nickel(0) moiety to the π* LUMO of the ligand), since ligand stabilization is effected by electron-withdrawing substituents or electronegative atoms. The crystal structure of the isolable π complex of anthracene and bis(tricyclohexylphosphine)nickel(0) showing 1,2-dihapto bonding is reproduced[51] below.

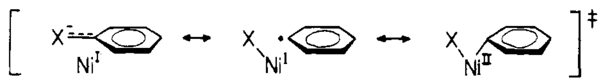
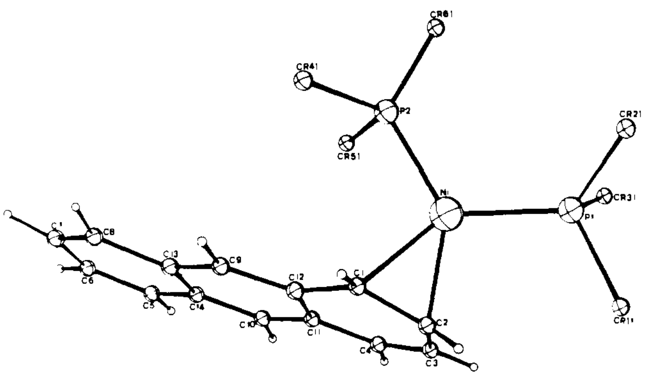
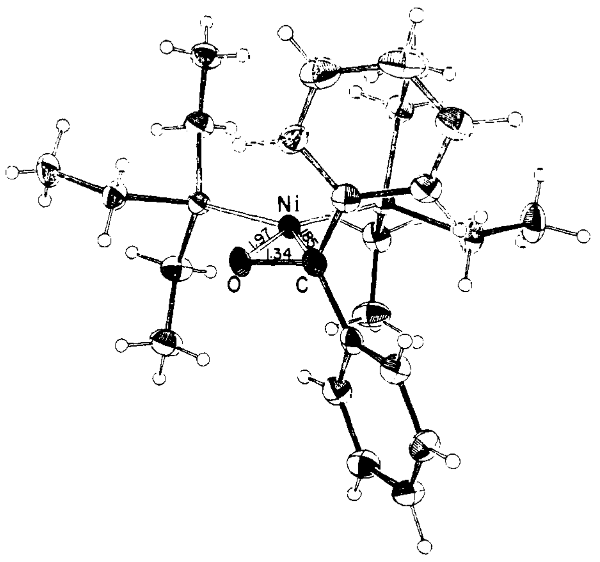


Figure 10. Contributions to the transition state for oxidative addition of aryl halides to $Ni(PEt_3)_3$ by collapse of the ion pair.



For the simple aryl halides, such π complexes are expected to be weak, and despite intensive efforts we have been unable to obtain direct evidence for such species. However, the formation of the π complex of p-iodobenzophenone can be followed spectrophotometrically and accords with those of other benzophenones which are π bonded locally to the carbonyl group [shown below for $(Ph_2CO)Ni(PEt_3)_2$].[52]



The formation of these π complexes has been examined kinetically, and accords with the rate expression

$$-\frac{d[NiL_3]}{dt} = \frac{K_1 k_2'}{K_1 + [L]}[NiL_3][Ar_2CO] \qquad (31)$$

which is essentially the same as that in eq 26 for oxidative addition of aryl halides.[52] A similar mechanism is suggested for both, i.e., Scheme V.

Scheme V

$$NiL_4 \overset{K_1}{\rightleftharpoons} NiL_3 + L \qquad (18)$$

$$NiL_3 + Ar_2CO \underset{-L}{\overset{k_2'}{\rightleftharpoons}} (Ar_2CO)NiL_2 \qquad (32)$$

However, the question as to whether the formation of the π complex actually precedes electron transfer in the oxidative addition of aryl halide, i.e.

$$\mathrm{ArX} + \mathrm{NiL_3} \overset{K'}{\rightleftharpoons} [\mathrm{NiL_3\,ArX}] \tag{33}$$

$$[\mathrm{NiL_3\,ArX}] \overset{k_2''}{\rightleftharpoons} [\mathrm{NiL_3}^+\,\mathrm{ArX}^-\cdot] \tag{34}$$

(where k_2 in eq 19 is equal to $K'k_2''$), or whether it is a spurious side reaction, e.g.

$$[\mathrm{NiL_3ArX}] \rightleftharpoons \mathrm{ArX} + \mathrm{NiL_3} \rightarrow [\mathrm{ArX}^-\cdot\mathrm{NiL_3}^+], \text{etc.} \tag{35}$$

is difficult to resolve rigorously.[53] We wish to present several lines of indirect evidence which suggest that it may be an intermediate.

The acyl derivatives, *p*-iodobenzophenone and -acetophenone, afforded exceptionally high yields of oxidative nickel(II) adducts, despite the fact that other aryl iodides in Table I were mostly diverted to nickel(I). A special interaction of these substrates with nickel(0) is also indicated by rates which are at least ten times faster than those expected on the basis of correlations with other aryl iodides in Figure 9. The polar effect in the rates of π-complex formation with substituted benzophenones follows a Hammett correlation with $\rho = +2.0$, which also compares with $\rho = +5.4$, $+4.4$, and $+2.0$ for the oxidative addition reactions of aryl chlorides, bromides, and iodides, respectively. Related transition states for π complexation and oxidative addition are indicated.

The second-order rate constants for π-complex formation of the series of *p*-halobenzophenones (Cl < Br < I as 6.3×10^2:7.9×10^2:10×10^2 $\mathrm{M^{-1}\ s^{-1}}$) are faster than the rate constants for oxidative addition (Cl < Br < I as 2.5×10^2:3.0×10^2:6.3×10^2 $\mathrm{M^{-1}\ s^{-1}}$), which can also be accommodated by Scheme III. It is important to consider, however, that π-complex formation as described is Scheme V is an inner-sphere process, in which phosphine loss from $\mathrm{Ni(PEt_3)_3}$ must be taken into account in eq 32, whereas the electron-transfer step in oxidative addition may proceed directly from the first-formed π complex, i.e., $[\mathrm{NiL_3\ ArX}]$, without an accompanying phosphine loss. To reconcile such differences between these apparently similar systems, we tentatively suggest that outer-sphere complexes are precursors, which provide parallel mechanisms, i.e.

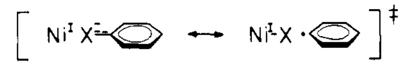
$$\mathrm{NiL_3} + \mathrm{ArX} \rightleftharpoons [\mathrm{NiL_3\,ArX}] \rightarrow [\mathrm{NiL_3}^+\,\mathrm{ArX}^-\cdot] \tag{36}$$

$$\mathrm{NiL_3} + \mathrm{Ar_2CO} \rightleftharpoons [\mathrm{NiL_3\,Ar_2CO}] \rightarrow \mathrm{NiL_2(Ar_2CO)} + \mathrm{L} \tag{37}$$

for the activation processes for electron transfer in eq 19 of oxidative addition and for π complexation in eq 32.

The difference between the formation of the ion pair in eq 19 and the neutral inner-sphere complex in eq 32 is reflected in their sensitivity to solvent effects. Thus, solvent polarity plays an important role in oxidative addition (see Table VII), as expected for a highly ionic product. On the other hand, the rate of π-complex formation is rather insensitive to the solvent polarity.[52]

The π character of outer-sphere complexes is akin to the transition state for oxidative addition in Figure 10. In both cases an important interaction derives from d-orbital overlap of the nickel(0) center with the π^* LUMO of the aryl halide.[31,54] Such a transition state also accords with the retention of stereochemistry observed in the oxidative addition of the vinylogous α,β-unsaturated halides such as *cis*- and *trans*-β-bromostyrene.[55] It is to be distinguished from an alternative formulation in which nickel lies adjacent to the halogen in the equatorial plane, as in the bridged activated complex:



which has been proposed for halogen transfer in a variety of organic and inorganic inner-sphere processes. Although such a linear transition state may pertain to saturated alkyl halides, it does not accord with the unusually high reactivity of aryl and vinyl halides to nickel(0), especially in view of the relatively high bond energies of halogens bonded to sp^2-hybridized carbon centers. The unimportance of steric effects imposed by *o*-methyl substituents[32] (see Table VIII) also argues against an intimate interaction of the nickel center with the halogen in the rate-limiting transition state for the reaction of nickel(0) with aryl halide.

Scheme VI

$$\mathrm{Ar}\cdot + \mathrm{NiL_3} \rightarrow \mathrm{ArNi^IL_3} \tag{38}$$

$$\mathrm{ArNi^IL_3} + \mathrm{ArX} \xrightarrow[-\mathrm{L}]{} \mathrm{ArNiXL_2} + \mathrm{Ar}\cdot, \text{etc.} \tag{39}$$

or

$$\mathrm{Ni^IL_3}^+ + \mathrm{ArX} \xrightarrow[-\mathrm{L}]{} \mathrm{ArNi^{III}XL_2}^+ \tag{40}$$

$$\mathrm{ArNi^{III}XL_2}^+ + \mathrm{NiL_3} \rightarrow \mathrm{ArNi^{II}XL_2} + \mathrm{NiL_3}^+, \text{etc.} \tag{41}$$

III. Alternative Radical and Concerted Processes for Oxidative Addition. The coproduction of the paramagnetic nickel(I) species during the oxidative addition of aryl halides to nickel(0) raises several questions: (A) Is there a radical chain pathway? (B) Is nickel(I) an innocuous bystander? (C) How is oxidative addition affected by the electron-donor ability of the nickel(0) complex?

A. Possibility of a Radical-Chain Process. A radical-chain process of the type previously presented for the oxidative addition of alkyl halides with d^{10} metal complexes[11f] or with π-allylnickel halide[56] could participate in our system since we have observed both aryl radicals and nickel(I) as paramagnetic species. The propagation sequence could be represented by several radical-chain processes such as Scheme VI.

However, our inability to observe inhibition or retardation by the use of various additives known to be effective in radical-chain processes disfavors these mechanisms. Moreover, it is not clear how such radical-chain processes can account for the lack of correlation between the rates of reaction and the distributions among nickel(I,II) products. Finally, the rates of both chain processes should be accelerated by added nickel(I) complexes, which they are not (see Table IX).

B. Effect of Nickel(I) Complexes on Product Formation. Although the presence of nickel(I) does not affect the rate of reaction, the results in Figure 2 clearly indicate that it diminishes oxidative addition by facilitating the formation of nickel(I).[20c] This apparent autocatalysis must therefore operate subsequent to the rate-limiting formation of the ion pair. Indeed, the variation of the line width ($\Delta H_{\mathrm{pp}} = 120$ G) of the ESR spectrum of iodotris(triethylphosphine)nickel at $g = 2.180$ provides an excellent probe for the interaction with various halogen compounds including $\mathrm{I_2Ni(PEt_3)_2}$, *trans*-$\mathrm{MeO_2CC_6H_4NiI(PEt_3)_2}$, *p*-$\mathrm{MeO_2CC_6H_4I}$, and *n*-$\mathrm{Bu_4NBr}$ with $\Delta\Delta H_{\mathrm{pp}} = 25$, 50, 60, and 25 g, respectively. It is noteworthy that nickel(0) exerts no noticeable effect. Several interesting mechanistic possibilities present themselves, but speculation is premature until further definitive studies have been made.

C. Oxidative Addition with Tris(triphenylphosphine)nickel. The triphenylphosphine complex of nickel(0) differs from the corresponding triethylphosphine complex in two important ways—first, it is more highly dissociated (e.g., $K_1 > 10^2$ M), and second, it is less readily oxidized (see Figure 7). Thus under comparable conditions, the reaction of aryl halides with $\mathrm{Ni(PPh_3)_3}$ is significantly slower than that with $\mathrm{Ni(PEt_3)_3}$.[57,58] Interestingly, the Hammett correlation with substituted chlorobenzenes shows a break at $\sigma = 0.2$.[59] The ρ value for electron-withdrawing substituents ($\sigma > 0.2$) is $+8.8$, whereas it is $\simeq 0$ with substituents with $\sigma < 0.2$. The dramatic change in gradient is diagnostic of a change in mechanism.[60] We would suggest that the correlation with $\rho = 8.8$ is related to the electron-transfer mechanism proposed in Scheme III, since it is in line with $\rho = +5.4$ obtained with $Ni(PEt_3)_3$ in this study. Two questions then arise—why is there a change in mechanism for electron-releasing substituents with $\sigma < 0.2$ and what is the new reaction pathway (if any)?[61] Part of the answer derives from the smaller reduction potential of $Ni(PPh_3)_3$ which, coupled with reduced electron-acceptor capabilities of aryl halides with donor substituents, would allow other mechanisms to participate. Whether there is a concerted three-center process proceeding without the intermediacy of ion pairs, as one possible pathway,[62] remains to be elaborated in further studies.

Summary and Conclusions

The mechanism in Scheme III presents a unified basis for simultaneous 2-equiv and 1-equiv transformations observed in the reactions of nickel(0) complexes with aryl halides. More generally applied, the driving force for the rate-limiting electron-transfer process derives from the metal complex acting as an electron donor and the organic halide as an electron acceptor. The concept is pervasive, since the same basic notion also applies to concerted processes, such as the S_N2 and three-center mechanisms, in which charge-transfer contributions in the transition states for oxidative addition provide a quantitative measure of the activation process, even in the absence of ion pairs as actual intermediates.[7] Furthermore, electron transfer is at the root of (1) the initiation process for radical-chain mechanisms for oxidative addition, as well as (2) the radical nonchain mechanisms.[5,11]

Experimental Section

Materials. The aryl halides—chlorobenzene, bromobenzene, iodobenzene, *p*-chlorotoluene, *p*-bromotoluene, *p*-iodotoluene, *m*-chlorotoluene, *m*-bromotoluene, *p*-chloroanisole, *p*-bromoanisole, *p*-bromophenetole, *p*-dichlorobenzene, *p*-chloroacetophenone, *p*-bromoacetophenone, *p*-bromobenzophenone, *m*-dichlorobenzene, and *p*-chloronitrobenzene—were obtained commercially and purified according to standard methods. The following aryl iodides were synthesized via the diazonium salts with iodide ions: *p*-iodoanisole, *p*-iodophenetole, *p*-chloroiodobenzene, *m*-chloroiodobenzene, *m*-iodotoluene, and *p*-iodobenzophenone. *p*-Iodoacetophenone was synthesized by iodide exchange with *p*-bromoacetophenone.[63] The esters—methyl *p*-chlorobenzoate, methyl *p*-bromobenzoate, and methyl *p*-iodobenzoate—were obtained by the esterification of the corresponding acids with boron trifluoride-methanol.[64] The salts—*p*-chlorophenyltrimethylammonium tetraphenylborate, *p*-bromophenyltrimethylammonium tetraphenylborate, and *p*-iodophenyltrimethylammonium tetraphenylborate—were obtained by exhaustive methylation of the corresponding *p*-halo-*N*,*N*-dimethylaniline or *p*-haloaniline with methyl iodide, followed by exchange with sodium tetraphenylborate. The other salts—*p*-chlorobenzyltrimethylammonium tetraphenylborate and *p*-bromobenzyltrimethylammonium tetraphenylborate—were obtained by alkylation of trimethylamine with the corresponding *p*-halobenzyl bromide followed by exchange with sodium tetraphenylborate.

Aryl halides with negatively charged substituents were synthesized as follows. *p*-Iodobenzyl bromide was converted to *p*-iodobenzyl cyanide with sodium cyanide, and then hydrolyzed to the corresponding acid. Exchange of PPN^+Cl^- with the sodium salt of the acid gave PPN^+ *p*-iodophenylacetate. Similarly, PPN^+ *p*-iodobenzoate was obtained from the exchange reaction of PPN^+Cl^- with the sodium salt of *p*-iodobenzoic acid. *p*-Iodobenzyl bromide was converted to the sodium salt of the *p*-iodobenzylsulfonic acid with sodium sulfite. Exchange with PPN^+Cl^- gave the PPN salt of *p*-iodobenzylsulfonic acid. 2,4,6-Tri-*tert*-butylbromobenzene was kindly provided by W. A. Nugent.

Tetrakis(triethylphosphine)nickel was prepared from bis(1,5-cyclooctadiene)nickel according to the procedure described by Schunn.[65] Unless otherwise specified, all manipulation of air-sensitive complexes was carried out under an argon atmosphere in a Schlenk-type flask using standard bench-top techniques.

All solvents were dried and redistilled twice under argon, first from sodium-benzophenone ketyl and then from $Ni(PEt_3)_4$. Melting points were determined in sealed capillary tubes in vacuo and are uncorrected. The instruments employed in this study follow: Perkin-Elmer Model 467 infrared spectrophotometer for IR data collection, Varian Associates T-60 NMR spectrometer for ^1H NMR spectra and XL-100 NMR spectrometer for ^{31}P NMR spectra, Beckman GC-5 for gas-liquid chromatographic analysis, Cary-14 spectrophotometer for UV and visible spectra and kinetic data collection, and Varian Associates E-4 or E-112 X-band spectrometers for ESR analysis.

Determination of Dissociation Constants. The equilibrium constant for the dissociation: $Ni(PEt_3)_4 \rightleftharpoons Ni(PEt_3)_3 + PEt_3$ was determined as follows. A 25-μL aliquot of 0.05 M solution of $Ni(PEt_3)_4$ was added to 3.0 mL of the solvent, and the absorbance was measured. Pure PEt_3 was then added in 2-μL aliquots, and the absorbance measured accordingly. Since the absorbance is directly proportional to the concentration of $Ni(PEt_3)_3$, a plot of $1/[Ni(PEt_3)_3]$ vs. $[PEt_3]$ afforded a straight line with a slope equal to $1/K[Ni]_{total}$. The equilibrium constant was then calculated from the slope using the relationship

$$[NiL_3] = \frac{K[Ni]_{total}}{K + [L]}$$

Isolation of the Oxidative Addition Product. The oxidative addition product A was isolated and identified using several aryl halides. A few typical procedures are described as follows. (The physical properties and the spectral data for new compounds are listed in Table XI.)

(a) *trans-p*-Acetylphenyliodobis(triethylphosphine)nickel(II). A solution of 0.28 g of *p*-iodoacetophenone in 10 mL of THF was slowly added to a stirred solution of 0.6 g of $Ni(PEt_3)_4$ in 10 mL of THF. The resulting red-brown solution was stirred at room temperature for 10 min. The solvent was removed in vacuo and the residue recrystallized from hexane to afford brown crystals. A yield of 0.4 g (65%) of *trans-p*-acetylphenyliodobis(triethylphosphine)nickel(II) was obtained, mp 174–177 °C.

(b) *trans-p*-Benzoylphenyliodobis(triethylphosphine)nickel(II). Similar to procedure (a), from 0.3 g of *p*-iodobenzophenone and 0.4 g of $Ni(PEt_3)_4$ in 20 mL of THF was obtained 0.4 g (88%) of brown *trans-p*-benzoylphenyliodobis(triethylphosphine)nickel(II), mp 106–109 °C.

(c) *trans-p*-Carbomethoxyphenylchlorobis(triethylphosphine)-nickel(II). A toluene solution of 0.1 g of methyl *p*-chlorobenzoate was added to a toluene solution of 0.25 g of $Ni(PEt_3)_4$ and stirred at room temperature for 25 min. Toluene was removed in vacuo and hexane added. A yellow powder was obtained which was washed with hexane and dried. The reaction afforded 0.15 g (83%) of *trans-p*-carbomethoxyphenylchlorobis(triethylphosphine)nickel(II), mp 176–178 °C.

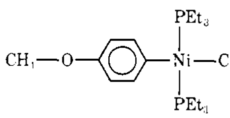
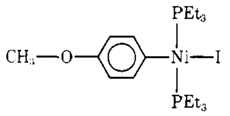
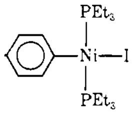
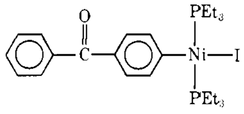
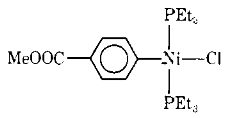
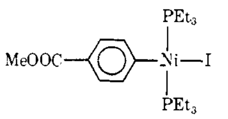
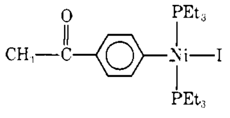
(d) *trans-p*-Carbomethoxyphenyliodobis(triethylphosphine)nickel-(II). A toluene solution of 0.3 g of methyl *p*-bromobenzoate was added to a toluene solution of 0.7 g of $Ni(PEt_3)_4$, and the mixture stirred at room temperature for 20 min. Toluene was removed in vacuo and a solution of 2.0 g of sodium iodide in acetone was added. The mixture was stirred until it became completely homogeneous. Acetone was then removed in vacuo, and the residue treated with 20 mL of benzene and 20 mL of water. The aqueous layer was separated and the benzene layer dried with anhydrous magnesium sulfate and filtered. The benzene solution was concentrated in vacuo and hexane added. Upon cooling, it yielded 0.4 g (55%) of brown, crystalline *trans-p*-carbomethoxyphenyliodobis(triethylphosphine)nickel(II), mp 173–176 °C.

(e) *trans-p*-Methoxyphenylchlorobis(triethylphosphine)nickel(II). A THF solution of 0.1 g of *p*-chloroanisole was added to a THF solution of 0.2 g of $Ni(PEt_3)_4$ and stirred at room temperature for 30 min. THF was removed in vacuo and hexane added. A yellow powder was obtained which was washed with hexane and dried to give 0.12 g (75%) of *trans-p*-methoxyphenylchlorobis(triethylphosphine)-nickel(II), mp 110–112 °C.

(f) *trans-p*-Methoxyphenyliodobis(triethylphosphine)nickel(II). A procedure similar to (d) was used. From 0.2 g of *p*-bromoanisole and 0.68 g of $Ni(PEt_3)_4$ was isolated 0.3 g of brown *trans-p*-methoxyphenyliodobis(triethylphosphine)nickel(II) (45% yield), mp 147–150 °C dec.

(g) *trans*-Phenyliodobis(triethylphosphine)nickel(II). *trans*-Bromophenylbis(triethylphosphine)nickel(II) (0.5 g) was mixed with 2.0

Table XI. Properties of New Arylhalobis(triethylphosphine)nickel(II) Complexes

complex	mp, °C	color	^{31}P NMR,[a] ppm	^{1}H NMR (in C_6D_6 relative to Me_4Si), δ	elemental anal. found, % C	H	calcd, % C	H
	110-112	yellow		PEt_3 (multiplet) 0.68-1.65 CH_3 3.4 aromatic (AB pattern) 6.71, 7.3 J_{HH} = 9 Hz				
	147-150 dec	brown	10.7	PEt_3 (multiplet) 0.7-1.8 CH_3 3.4 aromatic (AB pattern) 6.73, 7.31 J_{HH} = 9 Hz	43.63	6.85	43.13	7.05
	85-88	brown	10.4	PEt_3 (multiplet) 0.66-1.77 aromatic (multiplet) 6.68-7.48				
	106-109	brown	10.3	PEt_3 (multiplet) 0.62-1.75 aromatic (multiplet) 7.1-7.94	49.68	6.38	49.78	6.52
	176-178	yellow-brown		PEt_3 (multiplet) 0.60-1.50 CH_3 3.55 aromatic (AB pattern) 7.50, 7.88 J_{HH} = 8 Hz	51.61	8.20	51.59	8.01
	173-176	brown	10.1	PEt_3 (multiplet) 0.62-1.74 CH_3 3.57 aromatic (AB pattern) 7.45, 7.86 J_{HH} = 8 Hz	43.18	6.72	43.12	6.69
	174-177	brown	10.1	PEt_3 (multiplet) 0.63-1.77 CH_3 2.22 aromatic (AB pattern) 7.43, 7.63 J_{HH} = 8 Hz	45.21	7.24	44.39	6.89

[a] Lower field with respect to H_3PO_4.

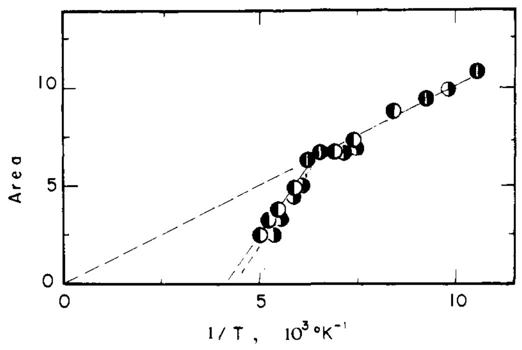


Figure 11. Temperature dependence of the ESR spectrum in hexane of (◑) 5.0 × 10^{-3} M $INi(PEt_3)_3$ and (◐) same with 5.0 × 10^{-2} M PEt_3 added.

g of sodium iodide in 20 mL of acetone. Several drops of water were added to allow complete dissolution. The solvent was then removed in vacuo, and 20 mL of benzene and 20 mL of water were added. The aqueous layer was separated and the resulting benzene layer dried with magnesium sulfate and filtered. The filtrate was concentrated in vacuo and hexane added. Upon cooling, it yielded 0.28 g (51%) of brown, crystalline *trans*-iodophenylbis(triethylphosphine)nickel(II), mp 85-88 °C.

(h) Attempted Synthesis of the Oxidative Addition Products Containing Charged Substituents. $Ni(PEt_3)_4$ (0.22 g) in 8 mL of THF was added to a solution of 0.18 g of PPN^+ *p*-iodobenzoate in 20 mL of THF. The reaction mixture was stirred for 10 min at room temperature whereupon some white solid precipitated. The yellow-brown solution was filtered. The precipitate was washed with additional THF and dried. The NMR spectrum of the white precipitate indicated it to be PPN^+I^-. The yellow-brown filtrate was concentrated in vacuo and hexane added. Upon cooling, no solid material could be isolated. The remaining oil decomposed upon exposure to air. In another attempt, the yellow-brown filtrate was concentrated in vacuo and toluene added. A solution of Bu_4NBr in toluene was added to provide a source of bromide. Upon cooling, only Bu_4NBr could be isolated.

Analysis of $NiX(PEt_3)_3$ and Arene. (a) The authentic nickel(I) complex was prepared by mixing 25 μL of 0.05 M $NiX_2(PEt_3)_2$ and 25 μL of 0.05 M $Ni(PEt_3)_4$ with 450 μL of the same solvent. The mixture was sealed in a 3-mm Pyrex ESR tube. No ESR signal was observed at room temperature. At low temperatures, an intense broad singlet was observed. As the temperature was changed, both the line width and the signal intensity varied, a higher intensity and narrower line width being observed at lower temperatures. When the solution was frozen, the integrated area under the ESR signal was inversely proportional to the absolute temperature, following the Curie law as shown in Figure 11. A sudden drop in intensity occurred at approximately −100 °C, which corresponds more or less to the melting point of the solvent. The same behavior was also observed when a tenfold excess of PEt_3 was added as shown in Figure 11.

Since the nickel(I) complex $NiX(PPh_3)_3$ is known to readily dissociate a phosphine ligand in solution, the same dissociation of phosphine probably also occurred with $NiX(PEt_3)_3$. Dimerization of the resulting coordinatively unsaturated $NiX(PEt_3)_2$ species is probably responsible for the disappearance of the ESR signal at higher temperatures.

$$NiX(PEt_3)_3 \rightleftharpoons NiX(PEt_3)_2 + PEt_3 \qquad (42)$$

$$2\mathrm{NiX(PEt_3)_2} \rightleftharpoons \mathrm{Ni_2X_2(PEt_3)_4} \qquad (43)$$

Although it is unreasonable to expect dimerization to be favored at higher temperatures, the first dissociation could force the dimer to dissociate at lower temperatures.

The concentration of $NiX(PEt_3)_3$ at low temperatures (−180 °C) was also determined by double integration, using DPPH as a calibrant, and shown to be quantitative.

(b) Analysis of the reaction mixture was carried out as follows. A stock solution of 0.05 M $Ni(PEt_3)_4$ was prepared in a Schlenk flask; 0.05 M solutions of each aryl halide were also prepared in a similar manner. $Ni(PEt_3)_4$ (50 μL) and 50 μL of the aryl halide solutions were mixed with 400 μL of the same solvent. The reaction mixture was degassed and sealed in a 3-mm Pyrex ESR tube. The yield of nickel(I) complex was analyzed at −160 °C, by measuring the area under the ESR signal, and carefully calibrated with an authentic nickel(I) complex prepared under the same conditions.

For reactions carried out with additives, the calculated amount of additive dissolved in the same solvent was added to the nickel(0) solution before the solution of aryl halide was added. The amount of solvent was then adjusted to enable the total, final nickel concentration to be reached at the specified level.

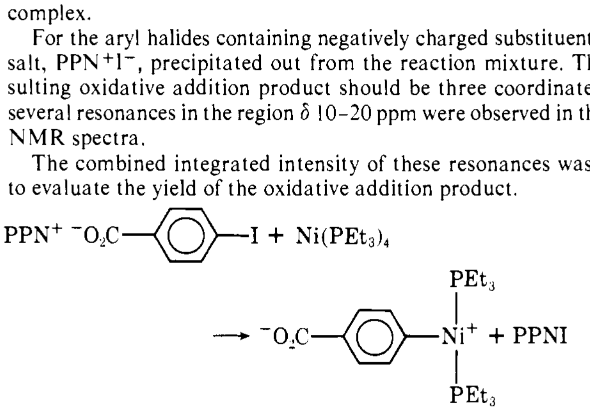
(c) Analysis of arene was determined by dissolving $Ni(PEt_3)_4$ (48 mg) in 10 mL of THF contained in a small Schlenk flask. An aliquot of 1.8 mL of 0.05 M *p*-iodotoluene in THF was added slowly. The reaction mixture was stirred for 15 min at room temperature. The volatile material was completely transferred to another flask in vacuo and analyzed by gas-liquid chromatography on a 10-ft 15% Apiezon L column. The yield of toluene was 0.06 mmol or 74%, based on the amount of $NiI(PEt_3)_3$ observed.

Detection of the Aryl Radical. Experimental conditions for the observation of the ESR spectrum of the 2,4,6-tri-*tert*-butylphenyl radical were predetermined by first carrying out the continuous photolytic generation of the radical with a mixture of the aryl bromide, trimethylsilane, and di-*tert*-butyl peroxide (see Figure 1). A 300-μL aliquot of 0.05 M $Ni(PEt_3)_4$ in hexane was transferred with a microsyringe to a serum-capped 4-mm Pyrex ESR tube which was previously purged with argon for 5 min. Another 300-μL aliquot of a 0.05 M hexane solution of 2,4,6-tri-*tert*-butylbromobenzene prepared under argon in a small Schlenk tube was then transferred with a syringe to the tube. The ESR tube was placed in the cavity and the spectrum recorded as rapidly as possible. An intense ESR signal was observed which disappeared rapidly and was completely gone in 10 min. The ESR signal consisted of a 1:2:1 triplet with $g = 2.0028$ and $a_H = 7.3$ G. The hyperfine structure due to *tert*-butyl group was not resolved in these conditions.

Nickel(I,II) Product Distributions. Stock solutions of 0.05 M $Ni(PEt_3)_4$ and tributylphosphine oxide (as internal reference) in the appropriate solvent were prepared in Schlenk flasks. Solutions of each aryl halide were also prepared in a similar manner. Three aliquots, 100 μL each, of $Ni(PEt_3)_4$, aryl halide, and phosphine oxide were mixed with 700 μL of the solvent, and the reaction mixture was sealed in an NMR tube. The ^{31}P NMR spectrum of the oxidative addition product A produced a sharp resonance at approximately δ 11 ppm, and its intensity was compared with the internal reference at 41 ppm downfield from phosphoric acid. The yield of arylnickel(II) complex was then calculated from calibration curves. The nickel(I) complex was analyzed using the same tube. The integrated area under the ESR signal was computed and compared with that from a carefully calibrated area-concentration curve prepared from the authentic nickel(I) complex.

For the aryl halides containing negatively charged substituents, the salt, PPN^+I^-, precipitated out from the reaction mixture. The resulting oxidative addition product should be three coordinate, and several resonances in the region δ 10–20 ppm were observed in the ^{31}P NMR spectra.

The combined integrated intensity of these resonances was used to evaluate the yield of the oxidative addition product.



(44)

Kinetic Study. For the less reactive aryl halides, the rate study was carried out under pseudo-first-order conditions using a large excess of aryl halide. A 0.05 M stock solution of $Ni(PEt_3)_4$ in THF was freshly prepared every day for kinetic runs. A 0.5 M solution of the corresponding aryl halide in THF was also prepared under argon in a small Schlenk tube. The kinetic study was carried out in a small Schlenk tube fused to a square cuvette. This Schlenk cell was also modified with a small side arm. A 25-μL aliquot of the $Ni(PEt_3)_4$ solution was transferred to the cell with the aid of a microsyringe and subsequently diluted with 3 mL of solvent. The appropriate amount of the aryl halide solution was transferred to the side arm. The two solutions were mixed by shaking the Schlenk cell vigorously for a few seconds and immediately placing it in the thermostated compartment of the spectrophotometer. The progress of the reaction was followed by monitoring the disappearance of the 500-nm band. For the more reactive aryl iodides, the reaction was too fast to follow under pseudo-first-order conditions. Equimolar amounts of $Ni(PEt_3)_4$ and aryl iodide were used and plots of $1/A - 1/A_0$ against time were linear to more than 75% completion.

Acknowledgment. We wish to thank R. J. Klingler for the electrochemical measurements, S. Fukuzumi for assistance with the ESR studies, Professor Larry L. Miller (Minnesota) for helpful discussions of the electrochemistry of the aryl halides, Professor Jean M. Savéant for a preprint of his paper, and the National Science Foundation for financial support.

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a tenfold excess of p-$IC_6H_4CO_2Me$ to produce I_2NiL_2, which is, however, not observed immediately after reaction. The same reaction in the presence of excess n-Bu_4NBr will produce Br_2NiL_2 within 20 min due to the enhanced reactivity of nickel(I) species with the aryl iodide, presumably by formation of the dibromonickelate(I) species, $Br_2NiL_2^-$. In the absence of excess aryl halide, no X_2NiL_2 was observed. The dihalonickel(II) complex $Cl_2Ni(PEt_3)_2$ has been isolated in the reactions of $Ni(PEt_3)_4$ with 3-chloro-2-norbornanone and hexachlorobenzene,[15] but in both cases excess chloro compound was used. (c) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, in press.

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Photochemical Oxidation and Rearrangement of Dibenzobarrelene and Dehydrojanusene

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Abstract: Dibenzobarrelene (**1**) and dehydrojanusene (**2**) are unreactive toward singlet oxygen under photosensitization with tetraphenylporphin (TPP), methylene blue (MB), or rose bengal (RB) in visible light. With a medium-pressure mercury vapor lamp, **2** gives a minor amount of epoxide and extensive di-π-methane rearrangement into **6**, whose structure was established by X-ray diffraction analysis. **6** was obtained in high yield by photosensitization with benzophenone or acetone; with acetone as solvent an addition product of ketone to hydrocarbon **6** (but not to **2**) was also formed, for which structure **10** is suggested. In mixtures, the rearrangement of **2** was 1.5–2.0 times as fast as the known rearrangement of **1** to **8**. Biacetyl and benzil photosensitize the epoxidation of both **1** and **2** to photounstable epoxides. Under the epoxidation conditions, the epoxide from **1** is converted into substantial amounts of anthraquinone. Under the conditions of photoepoxidation, anthracene (also observed in these reactions) is oxidized to anthraquinone along with some carboxylic and phenolic products.

Introduction

The known compounds dibenzobarrelene (**1**)[2a] and dehydrojanusene (**2**)[2b] belong to a general class of hydrocarbons that have proved important in the study of photooxidation. Along with 7,7′-binorbornylidene (**3**) and biadamantylidene (**4**), these hydrocarbons possess special hindrance to any re-

0002-7863/79/1501-6332$01.00/0