hydrocarbon and lithium were used to make the radical anion solution, and the halide was added dropwise until the color of the radical anion just disappeared, leaving an intense red color. Lower ratios of halide to radical anion were run under conditions A with the calcuated amount of halide added as usual.

Inverse Addition. A 100-mL flask, equipped with a glass-covered stirring bar, was dried under a high vacuum for 1–2 h, and 30 mL of THF was transferred in from THF which had been dried over sodium benzophenone dianion. The flask was pressurized with nitrogen, and one of the stoppers was replaced with a septum stopper. The THF was cooled to the appropriate temperature and the internal standard was added, followed by the halide. A solution of LiDBB made under conditions A was then added dropwise at such a rate that 30–45 min was required for completion. The solution slowly took on a red color until the last drop, which caused the solution to turn green to blue-green. The quench with H_2O did not result in the usual formation of an organic phase, presumably due to the lessened amount of organic solute present. Thus the ratio of product to internal standard may be in considerable error (see internal standard section above).

Reaction of Lithium Naphthalene Dianion and Di-*tert*-butylnaphthalene Dianion with Alkyl Halides in Ether. The title dianions were prepared by treatment of 4.8 mmol of the corresponding hydrocarbon with 4.5 mmol of Li in 30 mL of diethyl ether as described for the radical anions. The temperature of the ether solution was maintained below −20 °C to prevent decomposition. Li seems to react more readily with DBN than with naphthalene. After all the lithium had dissolved, the deep purple solution was cooled to the appropriate temperature, and the internal standard and halide were added. Aliquots were then taken as previously described except that no pentane was added.

Reaction of Lithium Naphthalene-d_8 with 1-Chlorooctane. A lithium naphthalene solution was made from 0.340 g of naphthalene-d_8, 17 mg of Li, and 15 mL of THF (approximately half normal scale). To this solution, cooled to −78 °C, was added 50.0 μL of nonane, followed by 50.0 μL (43.3 mg) of 1-chlorooctane. The reaction was then treated as described above under general conditions. After the CO_2 quench aliquot had been taken, H_2O was added and the reaction worked up in the usual way. VPC collection of the octane using column F at 75 °C was followed by low-voltage mass spectral analysis, 90.8 ± 0.5% d_1, 0.2 ± 0.3% d_2. VPC analysis of the aliquots revealed that the yield of octane was 91% with an indicated RLi yield of 69%.

Repetition of the above sequence with undeuterated naphthalene, but not including the collection and analysis of the octane, indicated an 89% yield of octane with an indicated RLi yield of 53%. The deuterium isotope effect can be calculated as being 2.0 by assuming a competition between reaction of RLi with CO_2 or with the dihydronaphthalenedicarboxylate (see Discussion).

Reaction of Lithium Naphthalene with 1-Chlorooctane Followed by Deuterolysis. A solution of LiN was made under the same conditions as immediately above. Reaction with 50 μL (43.3 mg) of 1-chlorooctane was followed 15 min later by the addition of 0.75 mL of D_2O. Workup as usual was followed by VPC collection from column F at 75 °C. Low-voltage mass spectral analysis revealed the octane to be 96.0 ± 0.9% d_1 and 0.3 ± 0.3% d_2.

Registry No. 1-Chlorooctane, 111-85-3; 1-bromooctane, 111-83-1; 2-chlorooctane, 628-61-5; 2-bromooctane, 557-35-7; 3-chloro-3-methylheptane, 5272-02-6; 7-chloronorcarane, 1588-50-7; 1-lithiooctane, 3314-49-6; 2-lithiooctane, 61182-93-2; 3-lithio-3-methylheptane, 61182-94-3; 7-lithionorcarane, 61182-95-4; LiN, 7308-67-0; Li(2,6-DBN), 73049-04-4; Li(2,7-DBN), 73049-06-6; LiDBB, 61217-61-6; 4-*tert*-butyl-1-chlorocyclohexane, 62056-46-6; 3-chlorotricyclo[3.2.1.0^{2,4}]octane, 73088-62-7; 4-*tert*-butyl-1-lithiocyclohexane, 17530-01-7; 3-lithiotricyclo[3.2.1.0^{2,4}]octane, 73049-05-5; 4-*tert*-butyl-1-chlorocyclohexene, 6832-09-3.

Nickel Catalysis in Halogen Exchange with Aryl and Vinylic Halides

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Halogen exchange between haloarenes and inorganic halide salts is readily induced by catalytic amounts of certain nickel complexes. Exchange of *cis*- and *trans*-β-bromostyrenes with chloride is stereospecific. Although various nickel complexes with different formal oxidation states such as $\mathrm{Ni^0(PEt_3)_4}$, $\mathrm{Ni^{I}I(PEt_3)_3}$, and $\mathrm{ArNi^{II}Br(PEt_3)_2}$ may be employed as catalysts (or catalyst precursors), others such as $\mathrm{Ni^{II}Br_2}$ or $\mathrm{Ni^{II}Br_2(PEt_3)_2}$ are completely ineffective. The distinction between the two classes of nickel complexes lies in whether they are converted under reaction conditions to nickel(I) species, assigned as the active catalyst. The latter is supported by the study of direct halide exchange between haloarenes and arylnickel(II) halides, in which a radical-chain process showing an induction period and inhibition by quinones and nitro aromatics is attributed to a labile nickel(I) species. A mechanism for nickel(I) catalysis of halide exchange is proposed.

Introduction

Nucleophilic substitutions on aromatic systems are generally quite slow in the absence of catalysts.[1-4] Metal complexes, particularly those of copper(I), have been used extensively to effect halide exchange.[5-10]

Nickel complexes have recently been found to catalyze the substitution of aryl halides with nucleophiles such as amines, phosphines, and cyanide.[11-13] Such substitution processes are of synthetic value, particularly when viewed from the broader perspective of carbon-centered nucleophiles leading to the formation of aryl–carbon bonds.[14] Indeed in the course of our recent studies of the nickel-induced coupling of aryl halides to biaryls,[15] we discovered

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Table I. Aromatic Halide Exchange Induced by Nickel(II) Complexes[a]

catalyst	exchange, %	material balance, %
none	0	96
$NiBr_2$	0	96
$NiBr_2(PEt_3)_2$	0	96
$ArNiBr(PEt_3)_2$[b]	74	89
$NiBr_2(PPh_3)_2$	0	96
$ArNiBr(PPh_3)_2$[b]	54	98

[a] Reactions carried out in 2 mL of benzene at 80 °C for 20 h in a sealed tube containing 0.54 mmol of Bu_4NBr and 0.54 mmol of iodobenzene with 3 mol % catalyst added. [b] Ar = o-$CH_3C_6H_4$.

Table II. Effect of Solvent on the Aromatic Halide Exchange Reaction Catalyzed by o-$CH_3C_6H_4NiBr(PEt_3)_2$[a]

solvent	exchange, %	material balance, %
benzene	74	89
tetrahydrofuran	72	85
dimethylformamide	63	72
ethanol	48	91
dimethyl sulfoxide	20	91
acetone	2	94

[a] Reactions carried out in 2 mL of the specified solvent containing 0.54 mmol of Bu_4NBr and 0.54 mmol of iodobenzene at 80 °C for 20 h in a sealed tube with 3 mol % catalyst added.

a facile halide exchange reaction which is described in this study.[16]

Results and Discussion

No reaction occurs between iodobenzene and bromide ion present in benzene solution as the quaternary ammonium salt. However, the addition of small amounts of nickel complex catalyzes the halide exchange according to eq 1, where [Ni] = o-$CH_3C_6H_4Ni(PEt_3)_2Br$. Nickel catalysis of halide exchange can attain equilibrium, since the same mixture of phenyl halides is obtained from equimolar mixtures of either iodobenzene and tetra-n-butylammonium bromide or bromobenzene and tetra-n-butylammonium iodide, i.e.

$$C_6H_5I + Bu_4N^+Br^- \xrightleftharpoons{[Ni]} C_6H_5Br + Bu_4N^+I^- \quad (1)$$

$$\underset{(0.54)}{C_6H_5I} + \underset{(0.54)}{Bu_4NBr} \xrightarrow{[Ni]} \underset{(0.40)}{C_6H_5Br} + \underset{(0.08)}{C_6H_5I} \quad (2)$$

$$\underset{(0.50)}{C_6H_5Br} + \underset{(0.50)}{Bu_4NI} \xrightarrow{[Ni]} \underset{(0.36)}{C_6H_5Br} + \underset{(0.07)}{C_6H_5I} \quad (3)$$

where the numbers on the left represent millimoles of reactants employed and those on the right are the yields of the phenyl halides. From these results, an equilibrium constant of approximately 3 can be deduced for the exchange described in eq 1 for benzene solutions at 80 °C.

Other nickel(II) complexes listed in Table I were also examined for catalytic activity. Of these, only the complex with an organic ligand σ bonded to the metal, namely, *trans*-*o*-tolylbromobis(triethylphosphine)nickel(II), was effective. Thus this catalyst, hereafter referred to without phosphine ligands as tolylnickel(II) bromide, was employed in further studies of halide exchange.

Table III. Effect of Nuclear Substituents on the Halide Exchange Catalyzed by o-$CH_3C_6H_4NiBr(PEt_3)_2$[a]

ArI	exchange, %	material balance, %
C_6H_5I	74	89
o-$CH_3C_6H_4I$	74	88
p-$CH_3C_6H_4I$	73	88
m-$CH_3C_6H_4I$	76	94
p-$CH_3OC_6H_4I$	72	94
p-ClC_6H_4I	64	80[b]
α-naphthyl iodide	74	92

[a] Reactions carried out in 3 mL of benzene containing 0.50 mmol of Bu_4NBr and 0.51 mmol of bromobenzene at 80 °C for 20 h in a sealed tube with 3 mol % catalyst added. [b] p-Dichlorobenzene (0.003 mmol) also observed. p-Dibromobenzene probably also formed, but not assayed due to overlap with p-chloroiodobenzene in gas-chromatographic analysis.

Table IV. Vinylic Halide Exchange Catalyzed by o-$CH_3C_6H_4NiBr(PEt_3)_2$[a]

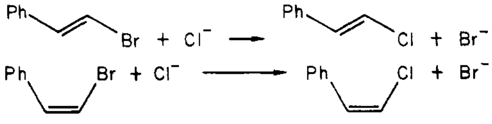
β-bromostyrene, mmol		β-chlorostyrene,[c] mmol		β-bromostyrene,[c] mmol	
cis	trans	cis	trans	cis	trans
0.50	0	0.48	0	0	0
0	0.50	0	0.44	0	0.01
1.00	0	0.44	0	0.45	0
0	1.00	0	0.50	0.006	0.45
0.50[b]	0	0	0	0.49	0

[a] Reactions carried out in 3 mL of benzene containing 0.5 mmol of Bu_4NCl and indicated amounts of β-bromostyrene at 80 °C for 20 h in a sealed tube with 3 mol % catalyst added. [b] No catalyst added. [c] Analysis of products.

The solvent effect was examined under a standard set of conditions shown in Table II. Benzene and tetrahydrofuran are the most desirable solvents. In the more polar solvents such as alcohols and dimethyl sulfoxide, the extent of halide exchange is reduced, probably owing to changes in the organonickel catalyst arising from degradation.[15] Changes in halide activity due to differences in solvation may also be a factor.[16,17]

Various aromatic substituents, including those with either electron-releasing or electron-withdrawing properties, can be accommodated in the catalytic exchange process. Importantly, even the sterically hindered ortho-substituted aryl halides participate in the halide exchange, as shown in Table III.

The halide-exchange process can be extended to vinylic halides.[18] Thus the exchange between chloride and β-bromostyrene afforded β-chlorostyrene (eq 4 and 5) in high



(4)[19]
(5)

yields and excellent stereospecificity as shown in Table IV. Furthermore, no cis–trans isomerization occurred during the exchange process, and the excess β-bromostyrene was recovered intact when 2 equiv of β-bromostyrene was em-

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(18) See ref 16b.

(19) For brevity, the halide ion will be presented hereafter without the tetraalkylammonium countercation.

Table V. Induction Periods Observed Prior to Halide Exchange between Arylnickel(II) Halide and Aryl Halides

arylnickel(II) halide[a]					
Ar	X	aryl halide[b]	additives	temp, °C	t_i,[c] min
o-$CH_3C_6H_4$	Cl	20 C_6H_5Br	0	80	80
o-$CH_3C_6H_4$	Br	20 C_6H_5Br	0	80	20
o-$CH_3C_6H_4$	I	20 C_6H_5Br	0	80	2
o-$CH_3C_6H_4$	Br	20 C_6H_5I	0	80	4
o-$CH_3C_6H_4$	Br	20 C_6H_5Br	$NiBr_2$	80	2
o-$CH_3OC_6H_4$	Br	20 o-$CH_3C_6H_4Br$	0	80	130
o-$CH_3OC_6H_4$	Br	20 C_6H_5Br	0	80	21
o-$CH_3OC_6H_4$	Br	40 C_6H_5Br	0	80	6
o-$CH_3OC_6H_4$	Br	20 C_6H_5I	0	70	5
o-$CH_3OC_6H_4$	Br	20 C_6H_5I	0	60	20
o-$CH_3OC_6H_4$	Br	20 C_6H_5I	0	55	40
o-$CH_3OC_6H_4$	Br	20 C_6H_5I	PEt_3 (0.2%)[d]	55	63
o-$CH_3OC_6H_4$	Br	20 C_6H_5I	$NiBr_2$	55	2
o-$CH_3OC_6H_4$	Br	20 C_6H_5I	MeOTf	55	9

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

ployed. Styryl halides appear to undergo catalytic exchange more rapidly than the phenyl analogues. For example, iodobenzene, which is more reactive than bromobenzene, is 10% exchanged under conditions in which 90% exchange was observed with β-bromostyrene.[20]

Other nucleophiles were also examined for the possibility of catalytic exchange with aryl halide. However, we found no substantial exchange with potassium thiocyanate, fluoride, or acetate which were solubilized in benzene solution with 18-crown-6. Roughly 2% benzonitrile was observed when the exchange was carried out with potassium cyanide.

Structural Effects on the Reactivity of Aryl Halides. For reactivity studies, the three-component catalytic system was simplified by replacing the quaternary ammonium halide with an equivalent amount of arylnickel(II) halide, since it could be readily shown that ligand substitution of halide is rapid, i.e.[21]

$$ArNiBrL_2 + I^- \xrightarrow{\text{fast}} ArNiIL_2 + Br^- \qquad (6)$$

Thus for the mechanism of catalysis, the kinetic problem is essentially reduced to ascertaining those factors involved with halide exchange in the two-component system, viz.

$$ArNiIL_2 + ArBr \rightarrow ArNiBrL_2 + ArI \qquad (7)$$

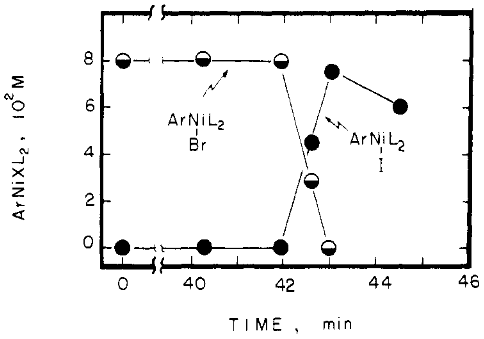

Figure 1. Halide exchange in the reaction of 0.08 M o-anisylnickel(II) bromide and 1.6 M iodobenzene in benzene solution at 55 °C, showing the induction period associated with the disappearance of o-$CH_3OC_6H_4Ni\mathbf{Br}(PEt_3)_2$ (◒) and the concomitant appearance of o-$CH_3OC_6H_4Ni\mathbf{I}(PEt_3)_2$ (●).

The stoichiometric interaction between arylnickel(II) iodide and aryl bromide in eq 7 provided valuable insight into the mechanism of halide exchange. For example, when a clear, homogeneous solution of iodobenzene and o-anisylnickel(II) bromide in benzene was heated at 55 °C, there was no apparent change for approximately 40 min. During this period of quiescence, there was also no change in the ^1H NMR spectrum of the solution. As the heating was continued, the solution gradually became opalescent, and changes in the NMR and absorption spectra clearly showed the conversion of o-anisylnickel(II) bromide [^1H NMR δ 3.30; ^{31}P NMR δ 11.0; λ_{max} 412 nm] to o-anisylnickel(II) iodide [^1H NMR δ 3.40; ^{31}P NMR δ 11.7; λ_{max} 425 nm]. The induction period associated with this halide exchange is illustrated in Figure 1. Gas-chromatographic analysis of the volatile fraction (see Experimental Section) indicated the formation of bromobenzene in amounts which are in accord with the stoichiometry in eq 8. Al-

$$o\text{-}CH_3OC_6H_4NiBrL_2 + PhI \rightarrow o\text{-}CH_3OC_6H_4NiIL_2 + PhBr \qquad (8)$$

though the reverse exchange between o-anisylnickel(II) iodide and bromobenzene was equally effective, the induction period was significantly lengthened (to beyond 1 h). Indeed, the element effect on the induction period t_i is manifested in both the aryl halide and the nickel halide in the order I < Br < Cl shown by entries 1–4 in Table V.

The induction period could also be deliberately manipulated by various additives. Thus, the duration of the induction period for the exchange in eq 8 was almost doubled when 0.2% triethylphosphine was added. Complete inhibition occurred in the presence of as little as 5% triethylphosphine, no exchange being observed after heating for more than 20 h. Control experiments showed that triethylphosphine did not separately react with either arylnickel(II) halide or aryl halide under these reaction conditions. Conversely, the induction period was shortened considerably by adding small amounts of either nickel bromide (heterogeneous) or methyl trifluoromethanesulfonate. It is striking that, as chemically dissimilar as nickel bromide and methyl trifluoromethanesulfonate are, they both effectively serve a common function in this system. Indeed, nickel bromide is so insoluble in benzene that the amount actually in solution could not be measured. Nonetheless, even under these conditions, it can coordinate with triethylphosphine:

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

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[20] The induction period (vide infra) somewhat obscures the significance of this comparison. Unfortunately, an intramolecular competition study was not carried out in order to assess the quantitative difference in reactivity.

[21] Due to the strong trans effect of aryl ligands. See: Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**, 2207. Adams, D. M.; Chatt, J.; Gervatt, J.; Westland, A. D. *Ibid.* **1964**, 734. See also ref 15.

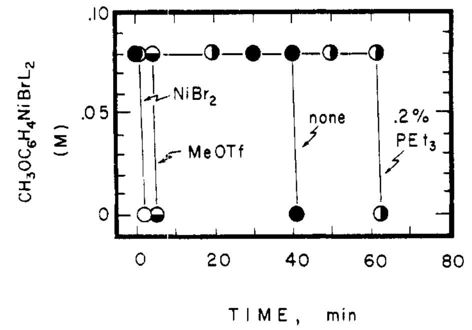

Figure 2. The effect of additives on the induction period to halide exchange between 0.08 M *o*-anisylnickel(II) bromide and 1.6 M iodobenzene in benzene solution at 55 °C: (○) NiBr$_2$ (heterogeneous); (◒) ~5% CH_3OTf; (●) no additive; (◑) 0.2% PEt$_3$. The rates of halide exchange shown by the almost vertical lines were too fast to measure.

In a similar vein, methyl trifluoromethanesulfonate readily alkylates triethylphosphine:

$$CH_3OSO_2CF_3 + PEt_3 \rightarrow CH_3PEt_3^+CF_3SO_3^- \quad (10)$$

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

The participation of radical-chain processes was examined with quinones and nitro aromatics which are known to be effective suppressors of radical-anion intermediates.[22] Their inhibitory effects were studied under a standard set of conditions employing *o*-tolylnickel(II) bromide and iodobenzene in the presence of 5% additive. Chloranil, which is a powerful electron acceptor, reacted with the arylnickel(II) complex upon mixing. However, subsequent to its immediate consumption, the usual halide exchange proceeded unabated. 1,4-Benzoquinone, which is a weaker electron acceptor, also reacted with arylnickel(II) bromide, but at considerably slower rates. The weakest acceptor, duroquinone, strongly retarded the rate of loss of arylnickel(II) complex. However, the exchange proceeded after prolonged heating. Nitrobenzene and *p*-dinitrobenzene both completely inhibited the exchange reaction. Strong retardation by 5% duroquinone and complete inhibition by 5% *p*-dinitrobenzene were also observed even in the presence of nickel bromide which was deliberately added to reduce the induction period. Furthermore, the addition of 5% dinitrobenzene just prior to the termination of the induction period inhibited halide exchange.

Once the induction period was over (i.e., by NMR examination or visual inspection), the halide exchange in eq 8 was found to be complete within 2 min as shown in Figure 2. The rates of halide exchange were generally too fast to follow conveniently, but it was qualitatively noted that the reactivity of aryl halides followed the order I > Br > Cl.

Accurate determination of the kinetics of halide exchange was also hampered by an accompanying, but slower, decomposition of the arylnickel(II) halide to biaryls and aryltriethylphosphonium salts according to the general stoichiometry in eq 11 established earlier.[15] Note: the

$$ArNiX(PEt_3)_2 + 3ArX \rightarrow Ar_2 + (ArPEt_3)_2NiX_4 \quad (11)$$

processes in eq 11 are also subject to the same inhibition observed with halide exchange, since no biaryls or arylphosphonium salts are formed during the induction period.

Table VI. Halide Exchange Catalyzed by Low-Valent Nickel Complexes[a]

catalyst	exchange, %	material balance, %
$Ni(PEt_3)_4$	76	96
$Ni(PPh_3)_4$	20	100
$NiBr(PEt_3)_3$	70	88
$NiBr(PPh_3)_3$	32	92
$NiBr(PEt_3)_3$[b]	0	100

[a] Reactions carried out in 2 mL of benzene containing 0.5 mmol of Bu_4NBr and 0.60 mmol of iodobenzene at 80 °C in a sealed tube with 3 mol % catalyst added. [b] Reaction carried out at room temperature without heating.

Studies of the Catalytically Active Nickel Species. The earlier detailed study of biaryl and arylphosphonium formation in eq 11 revealed a radical-chain process in which nickel(I) and arylnickel(III) species are reactive intermediates.[15] It is likely that these (or similar) nickel species are also involved in the catalytic halide exchange, because it is subject to the same rather unusual inhibition and induction period. To probe this point we examined each nickel species as a catalyst or catalyst precursor.

1. **Nickel(I).** The availability of authentic samples of nickel(I) complex, prepared by the spontaneous synproportionation of nickel(II) and nickel(0),[23] i.e.

$$Ni^{II}X_2(PEt_3)_2 + Ni^0(PEt_3)_4 \rightarrow 2Ni^IX(PEt_3)_3 \quad (12)$$

allows it to be tested directly. Indeed the addition of 3% of the nickel(I) complex $NiBr(PEt_3)_3$ to a solution of iodobenzene and tetrabutylammonium bromide caused the exchange reaction to be essentially complete within 20 min. The triphenylphosphine analogue $NiBr(PPh_3)_3$ was less effective, as shown in Table VI. It is noteworthy that under the same reaction conditions the halide exchange using an equivalent amount of *o*-tolylnickel(II) bromide required several hours for completion.

2. **Nickel(0).** The addition of catalytic amounts of the nickel(0) complex $Ni(PEt_3)_4$ also induces the halide exchange (see Table VI). However, its efficacy may also be related to nickel(I), which is known to be formed in the course of the rapid oxidative addition of iodobenzene to nickel(0), i.e.[24,25]

$$Ni(PEt_3)_4 + PhI \rightarrow PhNiI(PEt_3)_2,\ NiI(PEt_3)_3,\ \text{etc.} \quad (13)$$

Independent of whether nickel(I) or nickel(0) is employed, the nickel is recovered from the reaction mixture as nickel(II) halide.[26]

3. **Nickel(II).** Arylnickel(II) complexes, like nickel(0), are also capable of producing nickel(I) species in the presence of aryl halides, according to the sequential transformation:[15]

$$ArNiX(PEt_3)_2 + ArX \xrightarrow[-PEt_3]{} ArNiX(PEt_3)^+ + ArX^{-\cdot},\ \text{etc.} \quad (14)$$

$$ArNiX(PEt_3)^+ \xrightarrow{\text{fast}} ArPEt_3^+ + NiX,\ \text{etc.} \quad (15)$$

Two factors are important in the production of nickel(I)

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[23] (a) Heimbach, P. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 648. (b) Nilges, M. J.; Barefield, E. K.; Belford, R. L.; Davis, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 755 and references cited therein.

[24] Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

[25] (a) See also: Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501; 1976, *98*, 4499. (b) Furthermore, the oxidative adduct $PhNiI(PEt_3)_2$ also reacts with iodobenzene to produce more nickel(I).[15]

[26] In the presence of nickel, phosphine is arylated by haloarenes to arylphosphonium salt.[15]

Table VII. Competitive Rate Study of the Comparative Catalytic Activity of Nickel(0), Nickel(I), and Arylnickel(II) Complexes[a]

RC$_6$H$_4$I, R	σ	nickel catalyst	$\mathrm{RC_6H_4Br}/\mathrm{C_6H_5Br}$
p-MeO	−0.27	Ni(0)	0.76
		Ni(I)	0.76
		Ni(II)	0.76
p-Me	−0.17	Ni(0)	0.86
		Ni(I)	0.85
		Ni(II)	0.86
p-Cl	0.23	Ni(0)	1.39
		Ni(I)	1.50
		Ni(II)	1.25
m-MeOOC	0.32	Ni(0)	1.36
		Ni(I)	1.54
		Ni(II)	1.20
p-MeOOC	0.46	Ni(0)	1.94
		Ni(I)	2.46
		Ni(II)	1.82
		Ni(0)[b]	2.40
		Ni(I)[b]	2.40

[a] Reactions carried out in 3 mL of benzene at 80 °C for 20 h: Bu$_4$NBr, 0.03 M; RC$_6$H$_4$I, 0.6 M; C$_6$H$_5$I, 0.6 M; Ni catalyst, 0.002 M. [b] PEt$_3$ added (5 μL).

by this process. First, the presence of phosphine adversely affects the rate of nickel(I) formation owing to PEt$_3$ dissociation which controls eq 14. The importance of phosphine levels on the induction period and inhibition of halide exchange are associated with this effect. Second, the oxidation in eq 14 requires an aryl ligand to be coordinated to nickel(II),[15,27] which accounts for the trend in the catalytic activity shown by the various nickel complexes in Table I.

Clearly three different types of nickel complexes, each in different oxidation states, Ni^0(PEt$_3$)$_4$, Ni^{I}X(PEt$_3$)$_3$, and ArNi^{II}X(PEt$_3$)$_2$, can be used as the catalyst or catalyst precursor for halide exchange. In order to ascertain whether each of these nickel complexes is converted to a common, active catalytic species, we employed the comparative reactivities of various aryl halides as a mechanistic probe. However, a meaningful kinetic comparison was difficult to achieve, owing to the faster rates induced by the low-valent nickel(0) and nickel(I) complexes compared to that by arylnickel(II). The latter is also complicated by the induction period and the slow generation of the active catalyst. These problems are minimized in the competition method by using a large excess of an equimolar mixture of two aryl iodides (RC$_6$H$_4$I and C$_6$H$_5$I). The analysis of the aryl bromides in Table VII indicated that the extent of halide exchange was essentially the same for all three nickel complexes. The substituent effects are illustrated in Figure 3, indicating $\rho \sim 0.6$. Since the formation of nickel(I) is common to all of these nickel complexes, we conclude that it is the catalytically active species in halide exchange.

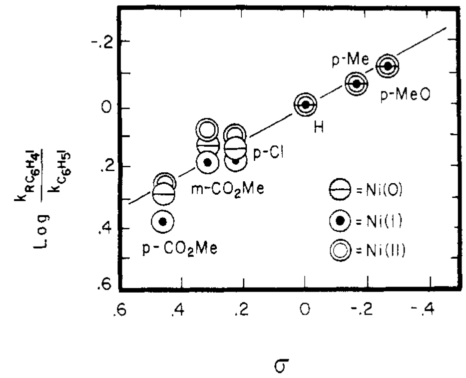


Figure 3. Hammett correlation of the relative rates of halide exchange between various aryl iodides and tetrabutylammonium bromide in benzene solution at 80 °C using catalytic amounts of nickel(0), nickel(I), and arylnickel(II), as described in the text.

Table VIII. Alteration of the ESR Line Width of NiI(PEt$_3$)$_3$ in the Presence of Halogen-Containing Compounds[a]

additive	line width, G
none	120
Ni(PEt$_3$)$_4$	120
NiI$_2$(PEt$_3$)$_2$	145
p-MeOOCC$_6$H$_4$I	170
ArNiI(PEt$_3$)$_2$[b]	180
Bu$_4$NBr	145[c]

[a] ESR spectra measured at −180 °C in frozen THF originally containing 5 × 10^{-3} M NiI(PEt$_3$)$_3$ and the additives indicated. [b] Ar = *p*-MeOOCC$_6$H$_4$. [c] NiBr(PEt$_3$)$_3$ is formed. (Note that pure NiBr(PEt$_3$)$_3$ under the same conditions has a line width of 80 G.)

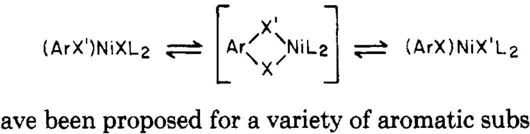
Comments on the Mechanism of Halide Exchange by Nickel(I) Species. Although the number of known paramagnetic nickel complexes in the formal oxidation state +1 is steadily increasing, they are still rather uncommon and their properties not well studied.[23] We employed electron spin resonance (ESR) spectroscopic techniques to probe the properties of these species, particularly with regard to ligand coordination. The ESR signal of NiI(PEt$_3$)$_3$ consists of a broad unresolved singlet with $\langle g \rangle = 2.180$ in a tetrahydrofuran solution frozen at −180 °C. The line width of 120 G in Table VIII is unaffected by the presence of the nickel(0) complex Ni(PEt$_3$)$_4$. However, upon the addition of a variety of halogen-containing compounds, including aryl halide, the line width broadened with little change in amplitude. The nickel(I) complex is also substitution labile. Upon the addition of tetrabutylammonium bromide, the light yellow color of NiI(PEt$_3$)$_3$ disappeared [note that NiBr(PEt$_3$)$_3$ is colorless], and the ESR signal was also converted to a broadened spectrum of NiBr(PEt$_3$)$_3$ [$g = 2.188$, $\Delta H_{\mathrm{mls}} = 145$ G]. We tentatively ascribe these spectral changes to coordination of halide to form the nickelate(I) complex:[28]

$$\mathrm{NiX(PEt_3)_3 + X^- \rightleftharpoons NiX_2(PEt_3)_2^- + PEt_3} \quad (16)$$

The other halogen-containing compounds, including aryl halides, probably also coordinate to nickel(I) to form analogous adducts:

$$\mathrm{NiX(PEt_3)_3 + ArX \rightleftharpoons (ArX)NiX(PEt_3)_2 + PEt_3} \quad (17)$$

There are basically two mechanisms for halide exchange involving these nickel(I) species. The most direct formulation involves the direct displacement on the coordinated aryl halide. Such a nickel(I)-assisted process could involve a four-center transition state or intermediate as shown in eq 18, where L is a phosphine ligand. Similar mechanisms



$$\mathrm{(ArX')NiXL_2} \rightleftharpoons \left[\mathrm{Ar}\overset{X'}{\underset{X}{\diamond}}\mathrm{NiL_2}\right] \rightleftharpoons \mathrm{(ArX)NiX'L_2} \quad (18)$$

have been proposed for a variety of aromatic substitutions promoted by copper(I) complexes.[5,6,29] An alternative mechanism in eq 19 involves a reversible sequence of ox-

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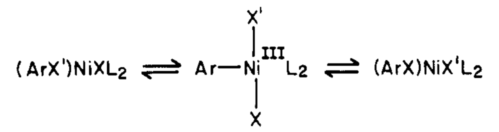
(27) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1634.

(28) The four-coordination of these adducts is assumed.

(29) Burdon, J.; Coe, P. L.; Marsh, C. R.; Tatlow, J. C. *J. Chem. Soc., Perkin Trans. 1* **1972**, 763.



$$(\mathrm{ArX'})\mathrm{NiXL_2} \rightleftharpoons \mathrm{Ar}-\overset{\overset{\mathrm{X'}}{|}}{\underset{\underset{\mathrm{X}}{|}}{\mathrm{Ni}^{\mathrm{III}}}}\mathrm{L_2} \rightleftharpoons (\mathrm{ArX})\mathrm{NiX'L_2} \qquad (19)$$

idative addition–reductive elimination steps in which arylnickel(III) species are intermediates. Analogous mechanisms involving oxidative addition to yield arylcopper(III) intermediates, followed by reductive elimination, have also been proposed for copper(I) catalysis.[7,8]

The distinction between the mechanisms in eq 18 and 19 is difficult to resolve rigorously since both are expected to be stereospecific.[30] However, we consider the latter to be less likely for several reasons. First, there is independent evidence that the metastable arylnickel(III) species undergo reductive elimination of phosphine ligand to afford arylphosphonium ($\mathrm{ArL^+}$) salt and not aryl halide (ArX).[27] Second, the apparent ρ value of ~ 0.6 is small compared to the values of 2.0 and 4.4 observed for oxidative addition of aryl iodides and bromides, respectively, to zerovalent nickel complexes.[24] Since the nickel(I) complexes are not as electron rich, we would expect a more pronounced substituent effect and a larger ρ value for nickel(I) than that observed for nickel(0). Third, the absence of crossover products with biaryl formation (compare eq 11) in which arylnickel(III) has been proposed[15] indicates this reactive intermediate is not shared with halide exchange.[31]

Summary and Conclusions

Nickel complexes are effective in promoting halogen exchange between haloarenes and inorganic halides. The stereospecific substitution in styryl halides suggests a concerted process in which a nickel(I)-promoted nucleophilic substitution in eq 18 is the most favored mechanism for halide exchange. Indeed nickel catalysis of halide exchange is so facile that the inorganic halide salt can be replaced by another aryl halide. The net effect is a redistribution of halogens between two different aryl groups, e.g.

$$\underset{(0.27)}{p\text{-}\mathrm{CH_3OC_6H_4Br}} + \underset{(0.24)}{\mathrm{C_6H_5I}} \xrightarrow{[\mathrm{NiX}]} \underset{(0.24)}{p\text{-}\mathrm{CH_3OC_6H_4I}} + \underset{(0.21)}{\mathrm{C_6H_5Br}} \qquad (20)$$

where the numbers in parentheses are the amounts (mmol) of each aryl halide formed upon equilibration of equimolar amounts (0.50 mmol each) of the reactants on the right of eq 20.

Experimental Section

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

Materials. Solvents and reagents used in this study were commercial reagent grade materials and repurified by standard methods.[32] Tetrahydrofuran, diethyl ether, and hydrocarbon solvents were purified by distillation from sodium benzophenone ketyl under argon prior to use. *N,N*-Dimethylformamide was dried with powdered barium oxide, followed by decantation and distillation under reduced pressure.

The aryl halides bromobenzene, iodobenzene, *p*-bromotoluene, *p*-iodotoluene, *m*-bromotoluene, *o*-bromotoluene, and *p*-bromoanisole were obtained commercially and purified according to standard methods. The following aryl iodides were synthesized from the corresponding diazonium salts and potassium iodide:[33] *p*-iodoanisole, *m*-iodotoluene, *p*-chloroiodobenzene, and α-naphthyl iodide. The esters methyl *p*-bromobenzoate, methyl *p*-iodobenzoate, methyl *m*-bromobenzoate, and methyl *m*-iodobenzoate were obtained by the esterification of the corresponding acids using boron trifluoride in methanol.

trans-β-Bromostyrene was obtained commercially and purified by distillation. *cis*-β-Bromostyrene was synthesized by using the procedure described by Cristol.[34] *cis*- and *trans*-β-chlorostyrenes were prepared according to the procedure of Dolby.[35]

Triethylphosphine was purchased from Pressure Chemical Co. and used without further purification. *trans*-Dibromobis(triethylphosphine)nickel(II) was prepared by the procedure described by Jensen and Nygaard.[36] Tetrakis(triethylphosphine)nickel(0) was prepared from bis(1,5-cyclooctadiene)nickel(0) according to Schunn.[37] Tetrakis(triphenylphosphine)nickel(0) was prepared according to Hidai.[38] Bromotris(triethylphosphine)nickel(I) and iodotris(triethylphosphine)nickel(I) were prepared by mixing equimolar amounts of the corresponding dihalobis(triethylphosphine)nickel(II) and tetrakis(triethylphosphine)nickel(0) in benzene and were used in situ.[23]

Preparation of Arylnickel Complexes. *trans-o*-Tolylbromobis(triethylphosphine)nickel(II) was synthesized from *trans*-dibromobis(triethylphosphine)nickel(II) as described earlier.[39]

***trans-o*-Anisylbromobis(triethylphosphine)nickel(II)** was prepared by a similar, but slightly modified, procedure. To a stirred ethereal solution of 6.0 g (13.2 mmol) of *trans*-dibromobis(triethylphosphine)nickel(II) at −10 °C was added a solution of *o*-anisylmagnesium bromide prepared from 3.5 g (18.7 mmol) of *o*-anisyl bromide, 1.0 g (41 mmol) of magnesium, and 2.0 g (10.6 mmol) of 1,2-dibromoethane in 30 mL of ether. After 10 min the reaction mixture was cooled further and a solution of 5% aqueous HBr added. Extraction followed by washing, drying, and evaporation of the solvent afforded a dark brown solid residue which included some starting material. The product was recrystallized from hot hexane several times, yielding 1.0 g of brown crystals, mp 108–110 °C. The proton NMR spectrum in benzene-d_6 consisted of a singlet (δ 3.30, 3 H) for the methoxy group and unresolved multiplets (δ 6.22, 6.81, 4 H) for the aromatic protons, in addition to multiplets (between δ 0.65 and 1.65, 30 H) for the ethyl groups. Anal. Calcd for $\mathrm{C_{19}H_{37}OP_2BrNi}$: C, 47.34; H, 7.74; P, 12.85. Found: C, 47.57; H, 7.84; P, 12.67.

***trans-o*-Anisyliodobis(triethylphosphine)nickel(II).** A mixture of *trans*-*o*-anisylbromobis(triethylphosphine)nickel(II) (0.5 g, 1.0 mmol) and 4.0 g of sodium iodide (3.3 mmol) was dissolved in 30 mL of acetone. After the mixture was stirred for 5 min, the acetone was removed in vacuo. Water (40 mL) was added and the mixture stirred for 10 min. Filtration of the mixture

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[30] Oxidative addition of vinylic halides to nickel(0) is stereospecific (Cassar, L.; Giarrusso, A. *Gazz. Chim. Ital.* **1973**, *103*, 793). Reductive elimination is also expected to be stereospecific (compare Smith, R. S.; Kochi, J. K. *J. Org. Chem.* **1976**, *41*, 502).

[31] However, uncertainty about the importance of phosphine ligation on the properties of these nickel intermediates obscures this point.

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[39] Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.

afforded an insoluble residue which was dissolved in a mixture of benzene and hexane and then dried with $MgSO_4$. The solvent was removed and the residue recrystallized from hexane to afford 0.23 g (43% yield) of brown crystals, mp 136–138 °C. The proton NMR spectrum of this material in benzene consisted of a singlet (δ 3.40, 3 H) for the methoxy group and multiplets (between δ 0.65 and 1.65, 30 H) for the ethyl groups. The resonance due to aromatic protons was not observed due to a large solvent (benzene) absorption.

***trans-o*-Tolyliodobis(triethylphosphine)nickel(II).** A mixture of *trans-o*-tolylbromobis(triethylphosphine)nickel(II) (0.5 g, 1.0 mmol) and 4.0 g of sodium iodide (3.3 mmol) was dissolved in 30 mL of acetone. After the mixture was stirred for 5 min, the solvent was removed in vacuo. Water (40 mL) was added, and the mixture stirred for 10 min. Filtration of the mixture afforded an insoluble residue which was dissolved in a mixture of benzene and hexane and then dried with $MgSO_4$. The solvent was removed and the residue recrystallized from hexane to afford 0.42 g (77% yield) of brown crystals, mp 121–123 °C.

***trans-o*-Tolylbromobis(triphenylphosphine)nickel(II)** was prepared via oxidative addition of *o*-bromotoluene to tetrakis(triphenylphosphine)nickel(0) complex as described by Hidai.[38]

Exchange Reaction of Aryl Halides Catalyzed by Nickel(II) Complex. Typical procedures were carried out as follows:

(a) Nickel(II) Complexes as the Catalyst. Tetrabutylammonium bromide (1.22 g, 3.78 mmol) and iodobenzene (0.77 g, 3.78 mmol) were dissolved in 12.6 mL of prepurified benzene. A 2-mL aliquot of this solution was transferred with the aid of a hypodermic syringe to a Pyrex glass tube. The appropriate nickel(II) catalyst (~8 mg) was then added. The glass tube was degassed and sealed in vacuo. After being heated in a constant temperature oil bath regulated at 80 ± 1 °C for 20 h, the tube was opened and the benzene solution washed with water to remove the ammonium salt. Analysis by gas chromatography employed a 10-ft column of 15% Apiezon L at 180 °C.

(b) Effect of Solvent. Tetrabutylammonium bromide (0.18 g, 0.56 mmol) and iodobenzene (0.11 g, 0.54 mmol) were dissolved in 2 mL of the specified solvent. *trans-o*-Tolylbromobis(triethylphosphine)nickel(II) (8 mg, 0.017 mmol) was added, and the entire solution degassed and sealed in a Pyrex glass tube. After being heated at 80 °C for 20 h, the contents of the solution were analyzed as in (a).

(c) Effect of Nuclear Substituents. Tetrabutylammonium bromide (0.85 g, 2.6 mmol) and *trans-o*-tolylbromobis(triethylphosphine)nickel(II) (0.04 g, 0.086 mmol) were dissolved in 10.5 mL of benzene. A 2-mL aliquot of this solution was transferred into a Pyrex tube. The appropriate aryl iodide (0.5 mmol) was added, and the glass tube degassed and sealed. After being heated at 80 °C for 20 h, the contents of the solution were analyzed as in (a).

(d) Vinyl Halide Exchange. Tetrabutylammonium chloride (0.78 g, 2.8 mmol) and *trans-o*-tolylbromobis(triethylphosphine)nickel(II) (0.04 g, 0.086 mmol) were dissolved in 16.5 mL of benzene. A 3-mL aliquot of this solution was transferred into a Pyrex tube and the specified amounts of β-bromostyrene were added. The glass tube was degassed, sealed, and heated in an 80 °C oil bath for 20 h. The contents of the solution were analyzed as in (a).

(e) Substitution for Other Nucleophiles. 18-Crown-6 (0.13 g, 0.5 mmol), iodobenzene (0.51 g, 2.5 mmol), and *trans-o*-tolylbromobis(triethylphosphine)nickel(II) (0.04 g, 0.086 mmol) were dissolved in 15 mL of benzene. A 3-mL aliquot of this solution was transferred into a Pyrex tube and potassium cyanide (0.032 g, 0.5 mmol) was added. The glass tube was degassed, sealed, and then heated in an 80 °C oil bath for 20 h. The contents of the solution were analyzed as in (a).

Stoichiometric Reaction of *trans*-Arylhalobis(triethylphosphine)nickel(II) Complex with Aryl Halide. (a) Halide Exchange. *trans-o*-Anisylbromobis(triethylphosphine)nickel(II) complex (0.35 g, 0.7 mmol; mp 108–110 °C; ^{1}H NMR δ 3.30 methoxy group; ^{31}P NMR 11.0 ppm downfield from H_3PO_4; λ_{max} 412 nm) and iodobenzene (2.9 g, 14.2 mmol) were dissolved in 8.4 mL of benzene in a small Schlenk tube. The solution was degassed and heated in a 55 °C oil bath. After 40 min, a hint of cloudiness developed, and the tube was heated for 2 additional min. The tube was cooled to room temperature and the volatile fraction removed by vacuum distillation into a cold trap, the contents of which were analyzed by gas chromatography. Quantitative analysis indicated the presence of bromobenzene (0.09 g, 82% yield). The brown residue was recrystallized from hot hexane to afford *trans-o*-anisyliodobis(triethylphosphine)nickel(II) (0.34 g, 89% yield; mp 136–138 °C; ^{1}H NMR δ 3.40 methoxy group; ^{31}P NMR 11.7 ppm downfield from H_3PO_4; λ_{max} 425 nm].

(b) Reactivity Studies. The progress of the reaction was followed by monitoring the changes in the ^{1}H NMR spectrum of the arylhalonickel(II) complex. A typical procedure is as follows. *trans-o*-Anisylbromobis(triethylphosphine)nickel(II) (50 mg, 0.105 mmol), iodobenzene (0.42 g, 2.1 mmol), and diphenylmethane (17.5 mg, 0.105 mmol, as an internal reference) were dissolved in 1.1 mL of dry benzene. The solution was transferred to an NMR tube with the aid of a hypodermic syringe and degassed via three freeze–pump–thaw cycles. The tube was then sealed in vacuo and placed into a 55 °C oil bath upside down. At prescribed time intervals, the tube was removed from the oil bath, cooled, and centrifuged until all the insoluble oily material was concentrated at the top of the tube. The NMR spectrum of the reinverted tube was recorded. When the tube was heated in the constant temperature bath, the contents (yellow solution) remained clear throughout the induction period without any apparent change in the ^{1}H NMR spectrum. However, a distinct cloudiness developed at the end of the induction period. The time required for the observation of the first hint of cloudiness was arbitrarily taken as denoting the induction period. Within 2 min after the induction period was complete, the methoxy resonance at δ 3.30 of the *trans-o*-anisylbromonickel(II) complex shifted to δ 3.40, corresponding to that of the *trans-o*-anisyliodonickel(II) complex, without any detectable loss in intensity.

A procedure similar to that described above was followed to study the effect of various additives. Thus, *trans-o*-anisylbromobis(triethylphosphine)nickel(II) (0.35 g, 0.72 mmol) and iodobenzene (2.9 g, 14.2 mmol) were dissolved in 8.4 mL of benzene contained in a small Schlenk tube under argon. Aliquots of this solution were transferred into several NMR tubes under argon with the aid of a hypodermic syringe. The calculated amount of various additives were added, and the solution degassed via three freeze–pump–thaw cycles. After sealing the tubes in vacuo, they were heated in a constant-temperature oil bath at 55 °C. The progress of the reaction was monitored by following the changes in the proton NMR spectrum. In the presence of 5 mol % nitrobenzene or *p*-dinitrobenzene, the NMR spectrum of *trans-o*-anisylbromobis(triethylphosphine)nickel(II) remained unchanged throughout the entire 24-h period of heating. The control experiment without any additives showed an induction period of approximately 40 min. The halide-exchange process was essentially complete within 2 min after the induction period. In the presence of 0.2 mol % added triethylphosphine, the induction period increased to 63 min; however, the subsequent halide exchange was also rapidly finished within 2 min. The addition of $NiBr_2$ (heterogeneous) and 10 mol % MeOTf shortened the induction period to 2 and 9 min, respectively.

Halide Exchange Catalyzed by Low-Valent Nickel Complexes. A typical procedure was carried out as follows. Tetrabutylammonium bromide (0.56 g, 1.7 mmol) and iodobenzene (0.36 g, 1.7 mmol) were dissolved in 7 mL of benzene in a small Schlenk tube under argon. A 2-mL aliquot of this solution was transferred with the aid of a hypodermic syringe to a Pyrex glass tube. A 50-μL aliquot of a $NiBr(PEt_3)_3$ solution previously prepared from 0.13 g (0.24 mmol) of $Ni(PEt_3)_4$ and 0.11 g (0.24 mmol) of $NiBr_2(PEt_3)_2$ in 2 mL of benzene was added via a microsyringe. The tube was degassed, sealed, and heated in a constant-temperature oil bath at 80 °C for 2 h. The tube was then opened, and the benzene solution was washed with water and analyzed by gas chromatography.

Comparison of the Catalytic Activities of Nickel(0), Nickel(I), and Arylnickel(II) Complexes. Competitive Rate Studies. A typical procedure was carried out as follows. Tetrabutylammonium bromide (0.11 g, 0.34 mmol), iodobenzene (1.4 g, 6.8 mmol), and *p*-iodotoluene (1.49 g, 6.8 mmol) were dissolved in 8.5 mL of benzene. Three separate 3.0-mL aliquots of this solution were transferred with the aid of a hypodermic syringe to Pyrex tubes. The appropriate nickel complex was added, and each tube was degassed, sealed, and heated at constant temperature. After 20 h at 80 °C, the tubes were opened and the benzene solutions washed with water and analyzed by gas chromatography.

Interaction of the Nickel(I) Complex with Halogen-Containing Compounds. An authentic sample of iodotris(triethylphosphine)nickel(I) complex was prepared by mixing 25 μL of a 0.05 M THF solution of $NiI_2(PEt_3)_2$ and 25 μL of a 0.05 M THF solution of $Ni(PEt_3)_4$ with 450 μL of THF. Methyl *p*-iodobenzoate (50 μL of a 0.1 M THF solution) was added, and the mixture was degassed and sealed in a 3-mm Pyrex ESR tube. No ESR signal was observed at room temperature, but at low temperatures an intense broad singlet with a *g* value of 2.180 was observed. As the temperature was varied the line width as well as the signal intensity changed, a higher amplitude and narrower line width being observed at low temperatures. These experiments were repeated at the same temperature (−150 °C) in the presence of various halogen-containing compounds as additives.

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Registry No. *trans-o*-tolylbromobis(triethylphosphine)nickel(II), 26521-33-5; *trans-o*-anisylbromobis(triethylphosphine)nickel(II), 66526-78-1; *trans*-dibromobis(triethylphosphine)nickel(II), 69460-30-6; *o*-anisyl bromide, 578-57-4; *trans-o*-anisyliodobis(triethylphosphine)nickel(II), 72111-04-7; *trans-o*-tolyliodobis(triethylphosphine)nickel(II), 59830-18-1; *trans-o*-tolylbromobis(triphenylphosphine)nickel(II), 41043-74-7; *cis-β*-bromostyrene, 588-73-8; *trans-β*-bromostyrene, 588-72-7; *cis-β*-chlorostyrene, 4604-28-8; *trans-β*-chlorostyrene, 4110-77-4; *trans-o*-tolylchlorobis(triethylphosphine)nickel(II), 28156-87-8; *α*-naphthyl iodide, 90-14-2; *α*-naphthyl bromide, 90-11-9; C_6H_5I, 591-50-4; *o*-$CH_3C_6H_4I$, 615-37-2; *p*-$CH_3C_6H_4I$, 624-31-7; *m*-$CH_3C_6H_4I$, 625-95-6; *p*-$CH_3OC_6H_4I$, 696-62-8; *p*-ClC_6H_4I, 637-87-6; C_6H_5Br, 108-86-1; *o*-$CH_3C_6H_4Br$, 95-46-5; *p*-$CH_3C_6H_4Br$, 106-38-7; *m*-$CH_3C_6H_4Br$, 591-17-3; *p*-$CH_3OC_6H_4Br$, 104-92-7; *p*-ClC_6H_4Br, 106-39-8; $Ni(PEt_3)_4$, 51320-65-1; $Ni(PPh_3)_4$, 15133-82-1; $NiBr(PEt_3)_3$, 62944-90-5; $NiBr(PPh_3)_3$, 15245-43-9; *m*-$MeOOCC_6H_4I$, 618-91-7; *p*-$MeOOCC_6H_4I$, 619-44-3; *m*-$MeOOCC_6H_4Br$, 618-89-3; *p*-$MeOOCC_6H_4Br$, 619-42-1.

Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 12.[1] New Convenient, Highly Active, and Selective Nickel Hydrogenation Catalysts

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Complex reducing agents (CRA) such as NaH–RONa–$Ni(OAc)_2$ are described as sources of new, atmospheric-pressure, heterogeneous hydrogenation catalysts. These catalysts (referred to as Nic) are cheap, easily and reproducibly prepared, not pyrophoric, and stable on long storage. They reproducibly allow highly selective semihydrogenation of alkynes to cis alkenes. Moreover, they promote the hydrogenation of alkenes. Their selectivity was exemplified by selective hydrogenations of dienes or alkene mixtures. Finally, Nic also exhibit good activity for carbonyl group hydrogenation at atmospheric pressure.

Although heterogeneous catalytic hydrogenation is a very old reaction,[2] intensive interest is still devoted to this important tool in organic synthesis.[3] Generally, the chemist calls for catalysts which are simultaneously very active and very selective, active for a large variety of functions but with a high selectivity for each group in polyfunctional substrates, very easily and reproducibly prepared, and, finally, stable on storage. If such a reagent existed, it should be an "alchemist's dream" rather than a catalyst.

With this definition in mind, it is always a challenge for the chemist to obtain a good catalyst, and numerous works have appeared on this subject.[3] Most metals have been studied, and various preparation methods have been described. Among them, reactions between transition-metal salts and reducing agents such as alkali metal/HMPA,[4] alkali metal/liquid NH_3,[5] zinc dust,[6] trialkylaluminums,[7] $LiAlH_4$,[8] or $NaBH_4$[9] have been widely used.

As part of our own research in the field of reductions, we have described the preparation of new versatile reducing systems, namely, complex reducing agents (CRA) of the type NaH–RONa–MX_n.[10] The chemical reductions performed with these reagents[11] led us to postulate metal hydrides as the reactive part of CRA. Taking into account that M–H bond formation is one of the postulated key

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(1) For part 11, see L. Mordenti, J. J. Brunet and P. Caubere, *J. Org. Chem.*, **44**, 2203 (1979). Part 12, together with ref 13, represents part of the research work of P. G. for his "these de Docteur-Ingénieur".

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