Synthesis of (η^6-Arene)NiR$_2$ and CoR$_2$ (R = σ-Bound Halosilanes and Haloarenes) by (Allyl)$_2$Ni/HR Reactions and Combined Metal Trifluoroacetate/Grignard Reagent Methods

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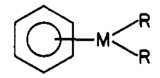
Conventional solution methods, rather than metal atom/vapor methods, have been devised for synthesis of (η^6-arene)MR$_2$, where M = Co and Ni and R = SiF$_3$, SiCl$_3$, SiCl$_2$Me, C$_6$F$_5$, C$_6$F$_4$H, and C$_6$Cl$_5$. The halosilane derivatives as well as polymeric Ni(SC$_6$F$_5$)$_2$ and Ni(OC$_6$F$_5$)$_2$ were prepared by reaction of HSiF$_3$, HSiCl$_3$, HSiCl$_2$Me, HOC$_6$F$_5$, and HSC$_6$F$_5$ with (2-methylallyl)$_2$Ni in arene solvents. A different approach was necessary for the R = haloaryl derivatives. Such a sequence involved preparation of (CF$_3$CO$_2$)$_2$Ni from CF$_3$COOAg followed by reaction with C$_6$Cl$_5$Li to form (C$_6$Cl$_5$)$_2$Ni etherate which was converted to (C$_6$Cl$_5$)$_2$Ni(η^6-arene) by reaction with an arene/BF$_3$ mixture (although simply heating with the arene worked with some systems). This method allowed more convenient syntheses of known (η^6-arene)MR$_2$ complexes and, for the first time, synthesis of the C$_6$F$_4$H and C$_6$Cl$_5$ derivatives.

Introduction

The discovery of a novel series of (η^6-arene)MR$_2$ compounds was possible due to the use of metal atom/vapor synthetic techniques.[1] These materials are highly reactive due to the extreme lability of the η^6-arene, and they are only stable when R is an electron-attracting σ-bonded ligand capable of dπ–pπ back-bonding:



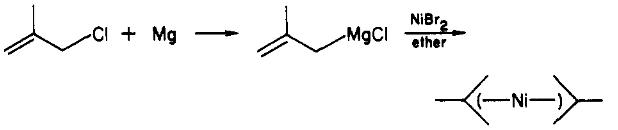
R=SiF$_3$, SiCl$_3$, SiF(CH$_3$)$_2$, C$_6$F$_5$, M=Ni, Co

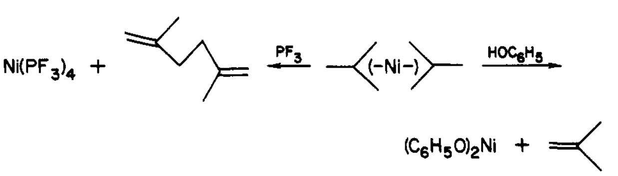
In order to make these interesting compounds more accessible, as well as allow wider scope in the choice of arene and the R group, we have been attempting to devise new but more conventional approaches to their syntheses. We report here further results on the reactions of (2-methylallyl)$_2$Ni with active hydrogen compounds[2] and on a new and versatile silver salt/Grignard reagent method for synthesis of the haloaryl derivatives.

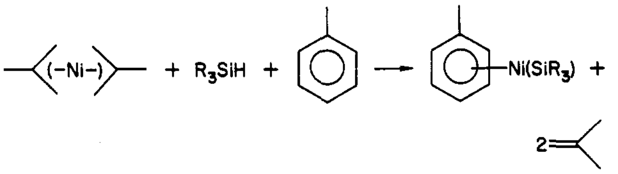
Results and Discussion

A. Bis(allyl)nickel and Bis(2-methylallyl)nickel Reactions with Active Hydrogen Compounds. Bis(allyl) derivatives of nickel are readily available through Grignard reagent methods.[3] Formally, the oxidation state in such complexes is Ni(II), although by a reductive coupling scheme Ni(0) derivatives also are available, as recently demonstrated by Parry and co-workers using PF$_3$.[4] However, by addition of appropriate protonic species, alkene can be eliminated[5] (eq 1 and 2).

As we reported earlier, carrying out active hydrogen compound reactions with pure bis(allyl)nickel or bis(2-methylallyl)nickel in arene solvents allowed the preparation of new (η^6-arene)NiR$_2$ derivatives.[2] We have been able to prepare bis(silyl) derivatives by this procedure (eq 3). The reaction proceeds smoothly when the silane is distilled onto the frozen pure allylnickel derivatives in toluene followed by slow warming.





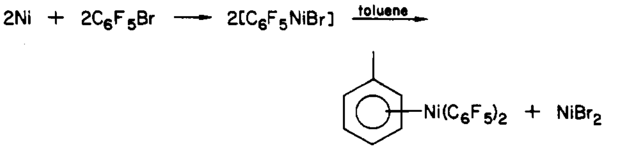


R$_3$Si=SiF$_3$, SiCl$_3$, SiCl$_2$CH$_3$

Other compounds will undergo this reaction. However, only those where R is an electron-attracting ligand capable of back-bonding yield stable (η^6-arene)NiR$_2$ derivatives. A further requirement is the absence of nonbonding electron pairs that can be used in bridging. For example, HOC$_6$F$_5$ and HSC$_6$F$_5$ reacted readily but yielded polymeric derivatives 1 and 2.

$$\underset{1}{[(\mathrm{C_6F_5O})_2\mathrm{Ni}]_n} \qquad \underset{2}{[(\mathrm{C_6F_5S})_2\mathrm{Ni}]_n}$$

Bis(2-methylallyl)nickel Reactions with SiCl$_4$, GeCl$_4$, and C$_6$Cl$_5$H. The carbon–bromine bond of bromopentafluorobenzene oxidatively adds to nickel atoms to form (pentafluorophenyl)nickel bromide, which undergoes disproportionation to give NiBr$_2$ and (η^6-toluene)Ni(C$_6$F$_5$)$_2$ in the presence of toluene[1] (eq 4). In the same manner, in the presence of toluene, the silicon–



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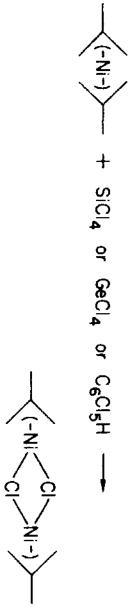
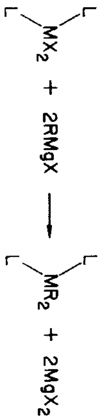
chlorine bond of tetrahclorosilane oxidatively adds to nickel atoms followed by disproportionation yielding some (η^6-toluene)Ni($SiCl_3$)$_2$. However, when bis(2-methylallyl)nickel was allowed to react with $SiCl_4$, 2-methylallylnickel chloride dimer was produced.[6] Germanium tetrachloride behaved similarly (eq 5).



(5)

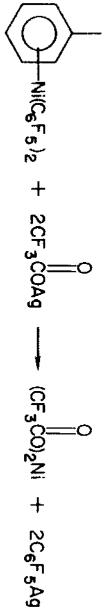
An additional unsuccessful series of experiments were carried out with C_6F_5H and C_6Cl_5H. Since C_6F_5Ni(arene) derivatives are stable, we also studied reactions of bis(2-methylallyl)nickel with C_6F_5H. However, no reaction between the allylnickel derivative and C_6F_5H took place even at 60 °C over a 12-h period. In the case of C_6Cl_5H, the (2-methylallyl)nickel chloride dimer was formed as a major product.[7] However, other methods proved successful for obtaining the C_6F_5 and C_6Cl_5 derivatives, which are discussed in the following section.

B. Silver Salt/Grignard Reagent Methods for Preparation of (η^6-Arene)bis(haloaryl)metal Derivatives. A use of the Grignard reagent in organometallic chemistry is the replacement of halides by alkyl or aryl groups (eq 6). THF and other ethers often are used as



$$L_2MX_2 + 2RMgX \longrightarrow L_2MR_2 + 2MgX_2 \qquad (6)$$

solvents in Grignard reactions. Since THF and most other ligands readily displace the arene in (η^6-arene)NiR_2, there was not much hope of using "classical" Grignard methods to prepare the desired (η^6-arene)MR_2 derivatives. As an alternative, Miller's reagent C_6F_5Ag,[8] which was known to react with ZnI_2, CuCl, or $HgBr_2$ in ether to yield $(C_6F_5)_2Zn$, $(C_6F_5)Cu$, or $(C_6F_5)_2Hg$, respectively, was examined. However, we were not able to extend this reaction to $NiBr_2$, $CoBr_2$, or CoI_2. In fact, we found that (η^6-$C_6H_5CH_3$) M(C_6F_5)$_2$ where M = Co or Ni would arylate silver trifluoroacetate (eq 7). However, this observation pointed



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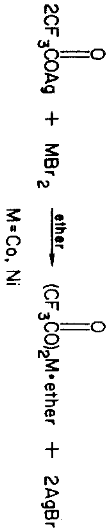
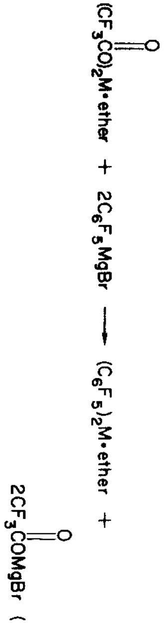
the way to another method, which is shown in the reaction sequence (8)–(10). This reaction scheme takes advantage



$$2CF_3\overset{O}{\overset{\|}{C}}OAg + MBr_2 \xrightarrow{ether} (CF_3\overset{O}{\overset{\|}{C}}O)_2M\cdot ether + 2AgBr \qquad (8)$$

M=Co, Ni



$$(CF_3\overset{O}{\overset{\|}{C}}O)_2M\cdot ether + 2C_6F_5MgBr \longrightarrow (C_6F_5)_2M\cdot ether + 2CF_3\overset{O}{\overset{\|}{C}}OMgBr \qquad (9)$$

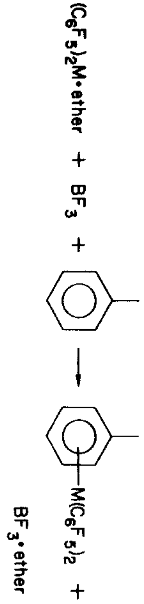


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Table I. Yields and Physical Properties of (η^6-arene)MR_2 Derivatives Prepared

M	arene	R	prep method	yield, %	color	mp, °C	anal. found (calcd)	NMR, δ	IR (KBr pellet), cm^{-1}
Ni	toluene	C_6F_5	Ag/Grignard[a]	45	red-brown	139–140[b]			
Ni	toluene	2,3,5,6-C_6F_4H	Ag/Grignard	17	red-brown	162–160	poor stability[e]	2.17 (s, 3 H), 7.10 (m, 5 H), 7.35 (s, 2 H)	3090 (w), 1595 (s, br), 1492 (m), 1455 (s), 1413 (m), 1383 (w), 1342 (w), 1215 (w), 1165 (s), 1095 (w), 1045 (w), 940 (w), 892 (s), 839 (w, sh), 825 (w, sh), 818 (m), 792 (m), 708 (s), 545 (w)
Co	toluene	C_6F_5	Ag/Grignard[a]	64	red-brown	135–139[c]			
Co	toluene	2,3,5,6-C_6F_4H	Ag/Grignard	56	red-brown	184–186	C, 50.07 (50.41) H, 2.44 (2.24) F, 33.96 (33.84)	paramagnetic	3075 (w), 1578 (m), 1523 (w), 1445 (vs), 1408 (m), 1378 (m), 1330 (m), 1218 (w), 1180 (s), 1156 (s), 1088 (m), 1028 (m), 948 (w), 880 (s), 830 (s), 820 (w), 808 (s), 788 (w), 722 (w), 702 (s), 650 (w), 538 (m)
Ni	toluene	C_6Cl_5	Ag/Li	26	dark red	278–279	C, 39.52 (39.02) H, 1.41 (1.70) Cl, 52.24 (51.97)	2.34 (s, 3 H), 7.12 (br, 5 H)	2920 (m), 2850 (w), 1650 (m, br), 1445 (w, sh), 1423 (vs, br), 1200 (m), 1175 (w), 1090 (w), 795 (w), 728 (s), 692 (w), 462 (w)
Co	toluene	C_6Cl_5	Ag/Li	35	dark brown	254–257	C, 39.17 (38.84) H, 1.11 (1.72) Cl, 48.88 (50.96)	paramagnetic	2960 (m), 2920 (m), 2850 (w), 1525 (w), 1495 (w), 1460 (m), 1390 (w, sh, 1332 (vs), 1260 (w, sh), 1168 (w), 1080 (w), 880 (w), 825 (m), 810 (w, sh), 758 (w), 730 (m), 693 (m), 655 (w), 563 (w), 405 (w)
Ni	toluene	SiF_3	d						
Ni	toluene	$SiCl_3$	d						
Ni	toluene	$SiCl_2CH_3$	(allyl)Ni/ $HSiCl_2CH_3$	75	orange	20	poor stability	0.87 (s, 3 H), 2.70 (s, 3 H), 6.72 (m, 5 H)	3050 (w), 2955 (m), 2920 (w), 2860 (w), 1600 (w), 1620 (s), 1470 (m), 1395 (m), 1375 (m), 1345 (w), 1255 (w, sh), 1245 (s), 1075 (w), 1015 (s), 990 (s), 900 (m), 785 (s, br), 730 (w), 705 (s)

[a] Earlier prepared by the metal atom/vapor method, (η^6-toluene)Ni(C_6F_5)$_2$[1] and (η^6-toluene)Co(C_6F_5)$_2$.[1] [b] Lit.[1] 137–140 °C. [c] Lit.[1] 133–138 °C. [d] Reference 2. [e] This compound exhibited poor shelf life. It was allowed to react with PEt_3 and the corresponding $L_2Ni(C_6F_4H)_2$ adduct characterized (see Experimental Section).

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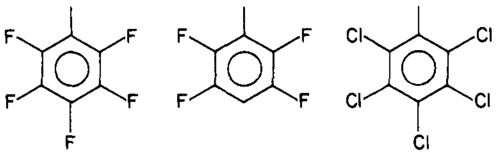
of the ready availability of silver trifluoroacetate, the great driving force to form AgBr, the stability of the M–C_6F_5 link, and the affinity of BF_3 for ether. Both 2,3,5,6-C_6F_4HMgBr and C_6Cl_5Li were successfully employed in such synthesis. Table I lists all the compounds prepared and the method used.

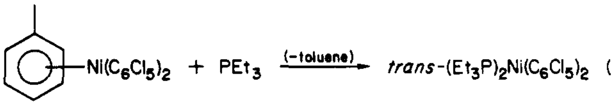
The applicability of these syntheses was limited to the introduction of phenyl substituents bearing at least four halogens:



Di- and trihalophenyl derivatives apparently are not stable, as has been observed during our studies of metal atom syntheses.

A comparison of Ni with Co in these reactions is of interest. The formation of $(CF_3C({=}O)O)_2Ni$·ether is much more facile than with the Co analogue (2 h vs. 12 h reaction time) from CF_3CO_2Ag. However, the time required for the formation of $(CF_3C({=}O)O)_2Ni$·ether and $(CF_3C({=}O)O)_2Co$·ether are the same (3 h) from CF_3CO_2Cu. Later, when the ether was being removed from $(C_6F_5)_2Ni$·ether, it was found that purging with BF_3 was necessary. However, the Co derivative gave up its ether much more readily and the use of BF_3 was not necessary; only distillation of the ether with an excess of toluene present was necessary. Apparently Et_2O binds to $(C_6F_5)_2Co$ less strongly than to $(C_6F_5)_2Ni$. However, earlier work has shown that THF binds strongly to both.[9]

Reaction of (η^6-Toluene)NiR_2 and Phosphine. The labile toluene in the complex (η^6-toluene)$M(C_6F_5)_2$ (M = Ni, Co) can be exchanged with phosphine.[1] In this work we carried out the same displacements with the C_6Cl_5 derivative, thereby preparing $L_2Ni(C_6Cl_5)_2$ (eq 11).[10] The η^6-arene was easily displaced and apparently caused no steric hindrance during the formation of a very "crowded" molecule. Similarly, (η^6-toluene)$M(C_6F_4H)_2$ reacted with PEt_3 to yield stable $(Et_3P)_2Ni(C_6F_4H)_2$.



(11)

Experimental Section

Reagents and Solvents. Manipulations of solids and solutions were carried out either in a drybox (Vacuum Atmosphere Dri Lab with a Model He-493 Dri Train) employing prepurified nitrogen or in airless glassware employing prepurified nitrogen (passed over Chem. Dyn. Cat. R3-11 deoxygenation catalyst at 110 °C just prior to use). Solvents were continuously refluxed over sodium benzophenone ketyl under nitrogen (diethyl ether, pentane, toluene) and fresh portions used. Pentafluorobromobenzene, 2,3,5,6-tetrafluorobromobenzene, 2,4,5-trifluorobromobenzene, 2,4,6-trifluorobromobenzene, and 2,6-difluorobromobenzene were purchased from Fairfield Chemical and used as received. 1-Bromo-3-chloro-4-(trifluoromethyl)benzene, 3,5-dichlorobromobenzene, benzyl chloride, trifluoroacetic acid, trifluoroacetic anhydride, anhydrous cobalt chloride, nickel bromide trihydrate, and *n*-butyllithium in hexane solution were purchased from Aldrich and used as received. Nickel bromide trihydrate was dehydrated at 140 °C. 1,3,5-Trifluorobenzene was purchased from PCR, hexachlorobenzene from Eastman Org. Chem., and triethylphosphine from Organometallics Inc. Silver trifluoroacetate was prepared from 50% aqueous trifluoroacetic acid and silver oxide.[11] Cuprous trifluoroacetate was prepared from cuprous oxide and trifluoroacetic acid with the presence of trifluoroacetic anhydride as dehydrating reagent.[12]

Physical Measurements. ^1H NMR spectra were obtained on a Varian T-60 spectrometer with Me_4Si as the internal standard. Infrared spectra were obtained on a Perkin-Elmer 1330. Mass spectra were obtained from a Finnigan 4000 quadrapole mass spectrometer. Elemental analyses were performed by Galbraith Laboratories (samples handled under inert atmosphere).

General Procedures. Grignard reagents were prepared from the halides (5 mmol) and magnesium (0.14 g, 5.8 mmol) in 25 mL of diethyl ether at room temperature, which resulted in dark brown solutions. Aryllithium reagents were prepared by addition of 3.3 mL of 1.55 M *n*-BuLi (5.1 mmol) in hexane solution to a 25 mL of diethyl ether solution containing the aryl halide (5 mmol) at −78 °C with stirring, followed by slow warming to room temperature (color changed from colorless to brown during this operation).

Nickel trifluoroacetate solutions (light green) were prepared by stirring $NiBr_2$ (0.57 g, 2.6 mmol) and CF_3CO_2Ag (1.13 g, 5.1 mmol) in 30 mL of diethyl ether for 3 h. Dark violet cobalt trifluoroacetate solutions were obtained by stirring $CoBr_2$ (0.57 g, 2.6 mmol) and CF_3CO_2Ag (1.13 g, 5.1 mmol) in 30 mL of diethyl ether for 12 hr. The alternative method of preparation was stirring $NiBr_2$ or $CoBr_2$ with $(CF_3CO_2)Cu$ in ether solution for 3 h.

Preparation of (η^6-Arene)NiR_2 and (η^6-Arene)CoR_2, Where R = C_6F_5, C_6F_4H, and C_6Cl_5. To prepare the (η^6-arene)nickel complexes, the nickel trifluoroacetate solution (described above) was filtered and slowly dripped into the appropriate Grignard reagent solution or organolithium solution (described above) at 0 °C. The mixture became dark brown. After the mixture was warmed to room temperature and stirred for 2 h, 20 mL of toluene was added, and all solvents then were removed under vacuum. The residue was extracted with 20 mL of toluene, yielding a dark red solution. If the greenish color persisted, the solution was purged with BF_3 gas by bubbling for 5 min. After the solution was filtered, the volatiles were removed from the filtrate under vacuum and the resulting red product washed with several portions of pentane. When C_6Cl_6 was the halide used, the unreacted C_6Cl_6 and the side products C_6Cl_5H and Cl_6Cl_5–C_6Cl_5 were removed by continuously extracting with pentane for 12 h.

The same procedures were used to prepare the (η^6-arene)cobalt complexes. The only difference was the initial color of the mixture (deep violet).

Table I summarized the yields and properties of new compounds.

Preparation of (η^6-Arene)NiR_2, Where R = SiF_3, $SiCl_3$, and $SiCl_2CH_3$. These complexes were prepared as described previously for SiF_3 and $SiCl_3$.[2] The new complex where R = $SiCl_2CH_3$ was prepared in the same way, and Table I summarizes physical properties.

Preparation of $[(C_6F_5O)_2Ni]_n$ and $[(C_6F_5S)_2Ni]_n$. Bis(2-methylallyl)nickel was prepared as previously described.[2] Pentafluorothiophenol (2 g, 10 mmol) in 10 mL of toluene was added to frozen, freshly prepared bis(2-methylallyl)nickel (5 mmol) in 20 mL of toluene. The mixture was allowed to warm to room temperature, and the solution color changed from yellow to deep maroon. After solvent removal under vacuum, 1.9 g (83.3%) of $[(C_6F_5S)_2Ni]_n$ as a dark maroon solid was obtained; mp 251 °C dec. (lit.[13] 250 °C dec). Heating in the mass spectrometer caused the formation of $(C_6F_5)_2S_2$ which showed a parent ion at 398 (41%) and $C_6F_5S^+$ at 199 (100%). IR (Nujol): 1643 (w), 1510 (s), 1490 (vs), 1395 (w), 1292 (w), 1260 (m), 1092 (s), 1080 (w, sh), 1020 (w), 983 (s), 918 (w), 900 (w), 855 (m), 800 (m), 725 (w) cm^{-1}. The same procedure was applied to the reaction with pentafluorophenol (1.68 g, 10 mmol) and resulted in 1.83 g (86.2%) of $[(C_6F_5O)_2Ni]_n$ as

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a brown solid; mp 325–328 °C dec. The IR spectrum was identical with that of an authentic sample.[14] Anal. Calcd for $C_{12}F_{10}O_2Ni$: C, 33.92; F, 44.73. Found: C, 34.48; H, 0.06; F, 44.06.

Reaction of Bis(2-methylallyl)nickel with $SiCl_4$, $GeCl_4$, and C_6Cl_5H. To bis(2-methylallyl)nickel, prepared as previously described (5 mmol) in 20 mL of toluene at −78 °C, was added $SiCl_4$ (2 g, 12 mmol). The mixture was allowed to warm to room temperature and was stirred for an additional 2 h. The color changed from yellow to dark red during this time. The solvent and volatile materials were removed under reduced pressure which left deep red crystals, 0.43 g (29%) of (η^3-2-methylallyl)nickel chloride: mp 117–118 °C dec (lit.[15] 118 °C dec); ^1H NMR ($CDCl_3$) δ 1.95 (s, 2 H), 2.38 (s, 3 H), 2.70 (s, 2 H); MS (70 eV), *m/e* (relative intensity) parent ion 298 (16), 241 (2), 168 (90), 113 (66), 55 (90), 41 (100). Isotopic distribution for the parent peak $C_8H_{14}Ni_2Cl_2$: calcd M, 69.5%; M + 2, 100%, M + 4 52.1%, M + 6, 12.1%; M + 8, 1.1%; obsd M, 68.5%; M + 2, 100%; M + 4, 54.2%; M + 6, 9.3%; M + 8, 1.0%.

The same procedure was carried out in the reaction of bis(2-methylallyl)nickel (5 mmol) and $GeCl_4$ (2.5 g, 12 mmol) and resulted in 0.38 g (26%) of (η^3-2-methylallyl)nickel chloride.

The reaction of bis(2-methylallyl)nickel (5 mmol) and C_6Cl_5H (2.8 g, 11 mmol), same procedure except the solution was heated at 50 °C for 6 h, gave after workup 0.13 g (9%) of (η^3-2-methylallyl)nickel chloride.

Reaction of C_6F_5Ag with $NiBr_2$, $CoBr_2$, and CoI_2. A mixture of C_6F_5Ag (2.75 g, 10 mmol)[8] and $NiBr_2$ (1.1 g, 5 mmol) in 40 mL of diethyl ether was refluxed under nitrogen for 48 h. Only unreacted C_6F_5Ag was recovered upon cooling, filtering, and solvent removal.

The same results were observed for $CoBr_2$ and CoI_2.

Reaction of (η^6-$C_6H_5CH_3$)M(C_6F_5)$_2$ (M = Ni, Co) with CF_3CO_2Ag. To 5 mL of a toluene solution containing the (η^6-arene)nickel complex (0.1 g, 0.2 mmol) was added solid CF_3CO_2Ag (0.09 g, 0.4 mmol). The mixture was stirred at room temperature for 5 min which yielded a light green solution. Solvent was removed under vacuum and the residue extracted with 5 mL of diethyl ether, leaving white C_6F_5Ag behind (0.08 g, 73%); mp 269–273 °C dec (lit.[8] 270–275 °C dec). The IR spectrum matched that of an authentic sample.

A similar result was obtained with the (η^6-arene)cobalt complex except that the color of the resulting solution was violet and the yield of C_6F_5Ag and was 64%.

***trans*-Bis(triethylphosphine)bis(pentachlorophenyl)nickel(II).** To a 10-mL toluene solution containing (η^6-toluene)Ni(C_6Cl_5)$_2$ (0.22 g, 0.34 mmol) at room temperature was added triethylphosphine (0.2 g, 1.68 mmol). The color of the solution changed from red to dark brown. The mixture was allowed to stand at room temperature for 2 h and then dried under vacuum. The residue was recrystallized from pentane. The crystals were washed with cold pentane and then dried under vacuum, yielding a dark brown solid: 0.23 g (94%); mp 243–246 °C; ^1H NMR ($CDCl_3$) δ 1.32 (q, 3 H, $J_{H-H} = J_{P-H} = 6$ Hz), 1.68 (q, 2 H, $J_{J-H} = 6$ Hz); IR (KBr) 2950 (m), 2870 (w, sh), 1450 (m), 1405 (w), 1325 (vs), 1200 (w), 1175 (m), 1135 (m), 1030 (m), 775 (w, sh), 765 (m), 715 (m), 450 (w) cm^{-1}. Anal. Calcd for $C_{24}H_{30}Cl_{10}NiP_2$: C, 36.32; H, 3.81; Cl, 44.67; P, 7.81. Found: C, 36.59; H, 3.51; Cl, 44.12; P, 7.50.

***trans*-Bis(triethylphosphine)bis(2,3,5,6-tetrafluorophenyl)nickel(II).** A procedure similar to the preceding description was employed with crude (η^6-toluene)Ni(C_6F_4H)$_2$ (0.35 g, 0.78 mmol) and triethylphosphine (0.32 g, 2.7 mmol) in 10 mL of toluene. The product was recrystallized from pentane yielding (Et_3P)$_2$Ni(C_6F_4H)$_2$ (0.30 g, 65% yeild): mp 184–185.5 °C; ^1H NMR ($CDCl_3$) δ 0.86–1.40 (m, 30 H), 6.5 (m, 2 H); IR (KBr) 2965 (m), 2940 (w), 2880 (w), 1575 (w), 1460 (w), 1440 (s), 1405 (w), 1380 (w), 1310 (w), 1255 (w), 1235 (w), 1178 (s), 1165 (s), 1080 (w), 1040 (s), 1005 (w), 888 (s), 818 (m), 805 (m), 766 (s), 720 (s), 702 (s), 630 (w), 545 (m), 470 (w), 415 (w) cm^{-1}. Anal. Calcd for $C_{24}H_{32}F_{10}NiP_2$: C, 48.59; H, 5.43; P, 10.44; F, 25.63. Found: C, 48.67; H, 5.71; P, 10.37; F, 26.63.

Metal Atom/Vapor Reactions. The reactions were carried out as previously described.[16] 2,4,5-Trifluorobromobenzene/toluene and Ni vapor yielded an unstable complex which reductively eliminated 2,2′,4,4′,5,5′-hexafluorobiphenyl (20% yield based on Ni consumed): mp 119–120 °C (lit.[17] 120.5 °C); MS (70 eV), M$^+$ 262 (100%). The Co analogue reaction behaved similarly although only a 3% yield of the substituted biphenyl was recovered.

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Registry No. (B)Ni(C_6F_5)$_2$ ($\beta = \eta^6$-toluene) (B)Ni(2,3,5,6-C_6F_4H)$_2$ (B = η^6-toluene), 66197-14-6; (B)Co(C_6F_5)$_2$ (B = η^6-toluene) (B)Co(2,3,5,6-C_6F_4H)$_2$ (B = η^6-toluene) (B)Ni(C_6Cl_5)$_2$ (B = η^6-toluene) (B)Co(C_6Cl_5)$_2$ (B = η^6-toluene) (B)Ni($SiCl_2CH_3$)$_2$ (B = η^6-toluene), 60528-58-7; [(C_6F_5S)$_2$ Ni]$_n$, 30824-28-3; [(C_6F_5O)$_2$Ni]$_n$ *trans*-(Et_3P)$_2$Ni(C_6Cl_5)$_2$ *trans*-(Et_3P)$_2$Ni(2,3,5,6-C_6F_4H)$_2$, 21459-33-6; (CF_3CO_2)$_2$Ni, 16083-14-0; (CF_3CO_2)$_2$Co, 6185-58-6; CF_3CO_2Ag, 2966-50-9; CF_3CO_2Cu, 25535-55-1; $CoBr_2$, 7789-43-7; $NiBr_2$, 13462-88-9; C_6F_5Br, 344-04-7; 2,3,5,6-C_6F_4HBr, 1559-88-2; C_6Cl_5Li, 6782-80-5; C_6F_5Ag, 30123-12-7; HSC_6F_5, 771-62-0; HOC_6F_5, 771-61-9; $SiCl_4$, 10026-04-7; $GeCl_4$, 10038-98-9; C_6Cl_5H, 608-93-5; Ni, 7440-02-0; Co, 7440-48-4; (η^3-2-methylallyl)nickel chloride, 12145-60-7; bis(2-methylallyl)nickel, 12261-14-2; 2,2′-hexafluorobiphenyl, 41860-45-1; 2,4,5-trifluorobromobenzene, 327-52-6; toluene, 108-88-3; Ni, 7440-02-0.

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