J. Am. Chem. Soc. **1980**, *102*, 4959–4966

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise–Bourdon tube gauge. Volatile starting materials and products were measured quantitatively by PVT techniques. Known products were confirmed on the basis of spectral data of authentic samples.

Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer with a 5-cm gas cell fitted with KBr windows. The ^{19}F NMR spectra were obtained by using a Varian HA-100 with CCl_3F as an internal reference. The ^{1}H NMR spectra were measured with a Varian EM-360 spectrometer with $(CH_3)_4Si$ as an internal standard. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 eV. All nuclear magnetic resonance shifts are assigned negative values for positions upfield from the reference.

***F*-Ethylamine.** *N,N*-Dichloro-*F*-ethylamine, $CF_3CF_2NCl_2$ (1 mmol) and $(CH_3)_3SiH$ (2 mmol) were condensed into a Pyrex glass reaction vessel at −196 °C. The mixture was allowed to warm slowly to −45 °C and was maintained at this temperature for 1.5 h. At −95 °C, the *F*-ethylamine, $CF_3CF_2NH_2$, was removed from the reaction vessel under dynamic vacuum and transferred into a tube at −196 °C. The yield was approximately 40%. Trimethylsilyl chloride, unreacted trimethylsilane, and *N,N*-dichloro-*F*-ethylamine remained in the trap at −95 °C. The new amine melted at ~−38 to −40 °C. Although $CF_3CF_2NH_2$ decomposes rapidly at room temperature, it is possible to obtain a gas-phase infrared spectrum with bands at 3465 (m) ($\nu_{as}(NH_2)$), 3385 m ($\nu_s(NH_2)$), 1605 (s) (δ (NH_2)), 1250 (sh), 1220 (vs, br), 1070 (s), 990 (w), 900 (vs), 845 (vs), 748 (s), 630 (w), 475 (s) cm^{-1}. A molecular ion is not observed in the mass spectrum but peaks at *m/e* 115 (CF_3CFNH^+, 18%), 114 ($C_2F_4N^+$, 18%), 95 ($C_2F_3N^+$, 58%), and 69 (CF_3^+, 100%) are present. The ^{19}F NMR spectrum showed a triplet at ϕ −87.0 ($^4J_{F-H}$ = 3 Hz) and a triplet at ϕ −86.1 ($^3J_{F-H}$ = 9 Hz). No CF_3–CF_2 coupling occurs. The formation of $CF_3CF{=}NH$ can be observed as $CF_3CF_2NH_2$ decomposes in the IR gas cell. The $\nu(NH_2)$ features rapidly decrease in intensity with the concomitant appearance of new $\nu(NH)$ bands. After 3 min, the decomposition to imine is complete.

Reaction of $CF_3CF_2NH_2$ with SF_4. Equimolar amounts (0.6 mmol) of *F*-ethylamine and SF_4 were condensed into a Pyrex glass reactor at −196 °C which contained an excess of CsF. The mixture was warmed slowly to −45 °C and then to 25 °C over 8 h. After trap-to-trap distillation, $CF_3CF_2N{=}SF_2$ (40%), which was collected in a trap at −78 °C, was identified by its infrared spectrum.[4]

***F*-Ethylimine.** If the mixture of $CF_3CF_2NCl_2$ and $(CH_3)_3SiH$ was maintained at −25 °C for 1 h, no $CF_3CF_2NH_2$ was obtained but rather $CF_3CF{=}NH$. The product mixture was held at −78 °C and the volatile materials were removed under dynamic vacuum. After trap-to-trap separation, $CF_3CF{=}NH$ (60% yield), $(CH_3)_3SiF$, and small amounts of HCl were recovered. The gas-phase IR spectrum has bands at 3325 (m) ($\nu(NH)$), 1680 (s) ($\nu(C{=}N)$), 1300 (s), 1225 (vs), 1190 (vs), 1140 (vs), 1065 (w br), 875 (s), 735 (s) cm^{-1}. A molecular ion is observed at *m/e* 115 (M^+, 20%) in the mass spectrum. In addition, other peaks at *m/e* 114 ($C_2F_4N^+$, 22%), 95 ($C_2F_3N^+$, 61%), and 69 (CF_3^+, 100%) are present. The ^{19}F NMR spectrum measured at ambient temperature showed a doublet at ϕ −71.8 and a quartet at ϕ −42.5 (J_{F-F} = 5.3 Hz). The ^{1}H spectrum consisted of a broad singlet at δ 5.49. After about 12 min in the infrared cell at ambient temperature, decomposition of the imine to nitrile, CF_3CN, is complete.

***N*-Chloro-*F*-ethylimine.** Equimolar amounts (0.7 mmol) of $CF_3CF{=}NH$ and ClF were condensed at −196 °C into a Pyrex tube which contained an excess of CsF. The mixture was allowed to warm slowly to −78 °C and finally to 25 °C overnight. It was separated by trap-to-trap distillation and $CF_3CF{=}NCl$ was isolated in a trap at −78 °C. It was identified from its infrared spectrum.[5]

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-7727395) for support of this research. We thank Charles Barinaga and Dennis Gage for mass and ^{19}F NMR spectral data.

---

(6) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.

π-Arene Complexes of Nickel(II). Synthesis (from Metal Atoms) of (π-Arene)bis(pentafluorophenyl)nickel(II). Properties, π-Arene Lability, and Chemistry

Robert G. Gastinger, Bruce B. Anderson, and Kenneth J. Klabunde*[1]

Contribution from the Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202. *Received August 29, 1979*

Abstract: A new series of transition-metal–π-arene complexes has been prepared by a metal atom synthetic method. The deposition of Ni vapor, C_6F_5Br, and arenes has produced high yields of $(C_6F_5)_2Ni$–π-arene complexes. A variety of π-arene ligands are η^6 bound by the $(C_6F_5)_2Ni$ moiety, resulting in soluble highly labile materials, where the π-arene ligand is exchangeable at room temperature. These complexes have not been isolable when σ-bonding ligands other than C_6F_5 have been employed. The formation of the π-toluene complex proceeds through a pseudostable C_6F_5NiBr species that can be trapped at −80 °C with R_3P but decomposes by reductive elimination of C_6F_5–C_6F_5 in the absence of R_3P or electron-rich arenes. It is likely that C_6F_5NiBr–π-arene is formed initially, which then disproportionates to $(C_6F_5)_2Ni$–π-arene and $NiBr_2$. Due to the high lability of the π-arene ligand, these complexes possess a rich chemistry. Displacement of the π-arene ligand can be carried out cleanly and in high yield by $P(Et)_3$, 1,5-cyclooctadiene, and THF to form $(C_6F_5)_2NiL_2$. Treatment of (π-toluene)bis(pentafluorophenyl)nickel (**1**) with norbornadiene at 0 °C causes the formation of a high polymer of norbornadiene as well as (π-norbornadiene)bis(pentafluorophenyl)nickel, which appears to be either the active polymerization catalyst or its precursor. Similarly, treatment of **1** with 1,3-butadiene at 25 °C and <1 atm causes the formation of a new organometallic compound and the production of cyclic tetramers of 1,3-butadiene. When **1** was treated with cyclopentadiene at 0 °C, a rapid production of C_6F_5H was observed with the subsequent formation of a dimeric nickel complex $(C_6F_5)_2(Cp)_2Ni_2(C_5H_6)$ where the Ni atoms appear to be bound together through a mutually π-bonded cyclopentadiene (C_5H_6) ligand. Reductive elimination reactions have also been induced under mild conditions by addition of CO or C_2H_4. With CO a nearly quantitative production of $C_6F_5C_6F_5$ and $Ni(CO)_4$ took place. Lastly, **1** served as a short-lived arene hydrogenation catalyst at room temperature.

Introduction

π-Arene complexes of the group 8 transition metals have been of considerable interest in recent years.[2] This interest is probably due to the high reactivity these complexes possess both chemically[2] and catalytically.[3] This high reactivity is manifested in the lability of the π-arene bond and the fact that arenes can bind to these metals in η^6-, η^4-, or η^2-coordination.

---

[1] Address correspondence to the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506.

[2] See R. G. Gastinger and K. J. Klabunde, *Transition Met. Chem.*, **4**, 1 (1979), a review of this area.

[3] J. W. Johnson and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 7395 (1977).

0002-7863/80/1502-4959\$01.00/0 © 1980 American Chemical Society

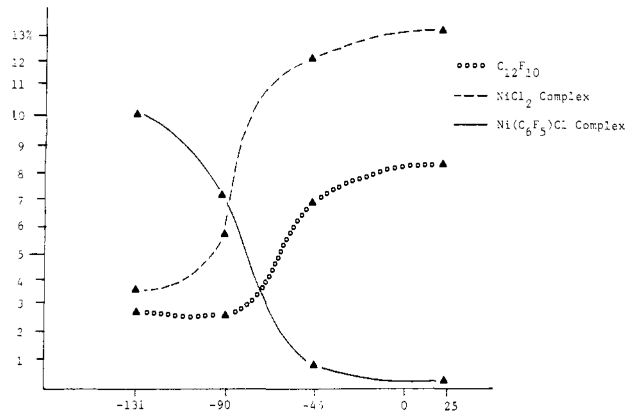


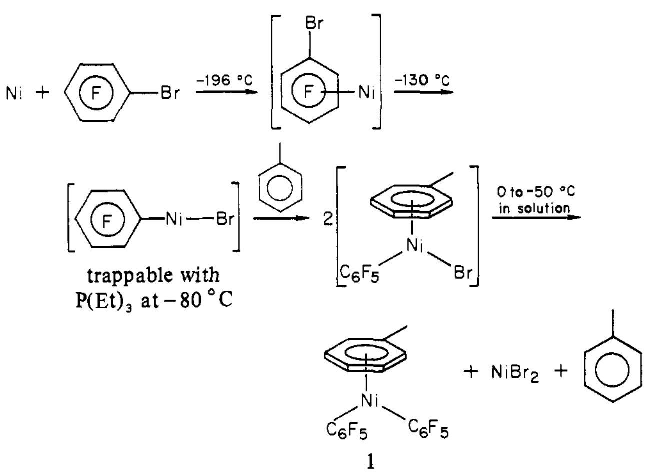
Figure 1. Plots of C_6F_5NiCl yield (trapped) and its decomposition products vs. trapping temperature.

A variety of synthetic techniques have been employed for the syntheses of π-arene complexes of the later transition metals, most of which involve some procedure for abstraction or displacement of ligands such that an arene can serve to fill the multiple open coordination sites generated. Halide abstraction,[4] trifluoroacetate abstraction,[5] dehydrogenation of complexed cyclic dienes,[6] trimerization of acetylenes,[7] and a variety of other methods have all been employed for production of these materials.[2]

The most widely studied group 8 π-arene compound is $[(C_6H_6)RuCl_2]_2$, and a variety of new π-arene–Ru complexes have been derived from it.[8] Again, the synthetic approach has been to attempt to generate available coordination sites by a variety of ligand abstractions or displacement processes.

In recent years metal vapor (atom) synthetic methods[9] have been shown to be useful for the generation of coordinatively unsaturated species that can bind arenes or other ligands in unusual fashion. Of course the simplest and most directly applicable coordinatively unsaturated species is the metal atom itself, and a variety of unstable but synthetically useful Fe–, Co–, and Ni(0)–π-arene complexes have been prepared.[2,10-12] However, in the present context, and of even more interest, is the use of metal atoms to generate coordinatively unsaturated RMX and R_2M species by oxidative addition reactions. These species in some instances have been found to coordinate arenes intramolecularly through π-benzyl bonding[13] or to coordinate π-arenes used as solvents in an η^6 fashion.[14,15] Thus, the metal atom method serves in one step to generate species that have open sites ready for arene (or other ligand) attachment.

Scheme I



The chemistry of these complexes is particularly interesting since displacement of the π-arene ligand is a potentially valuable procedure for the production of new organometallics. As the π-arene ligand leaves, essentially three coordination sites become available to other ligands. However, the π-arene ligand must be labile to be useful in this way, and this is indeed the case with the $(C_6F_5)_2M$–π-arene complexes discussed herein.

Results and Discussion

A. Formation of (Toluene)bis(pentafluorophenyl)nickel (1). The highest yields of **1** can be prepared by the simultaneous deposition of Ni vapor and a mixture of C_6F_5Br and arene (3.4:1.0 molar ratio, respectively). A high molar excess of C_6F_5Br vs. arene is necessary for an optimum yield of about 60% of the theoretical based on eq 1.

$$2C_6F_5Br + C_6H_5CH_3 + 2Ni \rightarrow \mathbf{1} + NiBr_2 \qquad (1)$$

The gross mechanism of the formation of **1** appears to involve the intermediacy of C_6F_5NiBr. Evidence for this species was obtained by carrying out Ni–C_6F_5X (X = Cl, Br) depositions followed by addition of Et_3P at various temperatures during warm-up. The trapped $C_6F_5NiX(P(Et)_3)_2$ yields were determined as well as the yields of the expected decomposition products $NiX_2(PEt_3)_2$ and $C_6F_5C_6F_5$. The chloride was studied in the most detail, and a graph of the product yields vs. temperature is shown in Figure 1. The overall product yields are based on Ni vaporized, and since the chloride is considerably less reactive than the bromide, the yields are about half of those found for the bromide under similar reaction conditions. With the chloride, a higher proportion of the Ni does not react by oxidative addition but instead repolymerizes to $(Ni)_n$ clusters. A similar reactivity trend has been established for Pd atom reactions; C–I > C–Br > C–Cl.[16]

It seems clear that C_6F_5NiX is unstable, and its decomposition products are C_6F_5–C_6F_5, NiX_2, and $(Ni)_n$. It is possible that $(C_6F_5)_2Ni$ is an intermediate en route to the observed decomposition products. This is difficult to prove, but it does seem likely that $(C_6F_5)_2Ni$ is formed at some stage since small amounts of **1** could be prepared by addition of toluene to the C_6F_5Br–Ni matrix at 25 °C after pump off of excess C_6F_5Br.

---

(4) (a) E. O. Fischer and R. Bottcher, *Chem. Ber.*, **89**, 2397 (1956); (b) L. Porri, G. Natta, and M. C. Gallazzi, *J. Polym. Sci., Part C*, **16**, 2525 (1967); (c) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3089 (1971); (d) M. Green and T. A. Kue, *J. Chem. Soc., Dalton Trans.*, 832 (1972); (e) D. J. Mabbott, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 294 (1977).

(5) P. M. Maitlis, *Acc. Chem. Res.*, **11**, 301 (1978).

(6) (a) E. O. Fischer and J. Muller, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **17**, 776 (1962); (b) E. O. Fischer and J. Muller, *Chem. Ber.*, **96**, 3217 (1963).

(7) (a) M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **83**, 825 (1961); (b) A. Lucherini and L. Porri, *J. Organomet. Chem.*, **155**, C45 (1978).

(8) (a) R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, **50**, 3063 (1972); (b) R. A. Zelonka and M. C. Baird, *J. Organomet. Chem.*, **44**, 383 (1972); (c) M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 233 (1974); (d) G. Winkhaus and H. Singer, *J. Organomet. Chem.*, **7**, 487 (1976); (e) H. Brunner and R. G. Gastinger, *ibid.*, **145**, 365 (1978); (f) H. Brunner and R. G. Gastinger, *J. Chem. Soc., Chem. Commun.*, 488 (1977); (g) A. S. Ivanov, A. Z. Rubezhov, and S. P. Gubin, *Isv. Akad. Nauk SSSR., Ser. Khim.*, 931 (1974); (h) D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, **116**, C29 (1976); (i) J. Mueller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.*, **108**, 273 (1975); (j) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, and P. A. Tucker, *J. Organomet. Chem.*, **121**, C18 (1976); (k) H. Werner and R. Werner, *Angew. Chem., Int. Edit. Engl.*, **17**, 683 (1978).

(9) (a) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975); (b) P. L. Timms and T. W. Turney, *Adv. Organomet. Chem.*, **15**, 53 (1977); (c) M. Moskovits and G. A. Ozin, "Cryochemistry", Wiley, New York, 1976. (d) K. J. Klabunde, P. L Timms, P. S. Skell, and S. Ittel, *Inorg. Synth.*, **19**, 59 (1979); (e) K. J. Klabunde, "Chemistry of Free Atoms and Particles", Academic Press, New York, 1980.

(10) P. S. Skell, Symposium on "Atomic Species Used in Synthesis", 170th National Meeting of the American Chemical Society, Chicago, IL, Aug 1975, INOR paper 57.

(11) K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. R. Roppel, *J. Am. Chem. Soc.*, **98**, 1021 (1976).

(12) K. J. Klabunde, D. Ralston, R. Zoellner, H. Hattori, and Y. Tanaka, *J. Catal.*, **55**, 213 (1978).

(13) J. S. Roberts and K. J. Klabunde, *J. Am. Chem. Soc.*, **99**, 2509 (1977).

(14) B. B. Anderson, C. Behrens, L. J. Radonovich, and K. J. Klabunde, *J. Am. Chem. Soc.*, **98**, 5390 (1976).

(15) K. J. Klabunde, B. B. Anderson, M. Bader, and L. J. Radonovich, *J. Am. Chem. Soc.*, **100**, 1313 (1978).

(16) K. J. Klabunde and J. Y. F. Low, *J. Am. Chem. Soc.*, **96**, 7674 (1974).

Table I. π-Arene Equilibration by Addition of Arenes to (π-Mesitylene)bis(pentafluorophenyl)nickel (3) in $CDCl_3$ (0.2 M)[a]

arene added	% mesitylene dissociated	arene added	% mesitylene dissociated
$C_6D_5CD_3$	38	$C_6H_5CF_3$	16
$C_6H_5OCH_3$	38	C_6H_5F	16
C_6D_6	27	C_6F_6	12

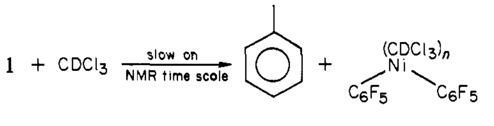
[a] The concentration of 3 in $CDCl_3$ was 0.2 M, and to 0.5 cm^3 of this solution (0.1 mmol of 3) was added 1.0 mmol of the displacing arene.

As mentioned earlier, it is known that homoleptic π-arene–Ni(0) complexes can be prepared at low temperature and are stable in cold solutions.[2,10–12] A toluene–nickel deposition was carried out followed by addition of C_6F_5Br on top of the frozen matrix to determine if formation of a π-arene–Ni(0) complex preceded oxidative addition in the formation of **1**. Formation of **1** did not take place. However, the higher melting point of C_6F_5Br did not allow for good mixing upon matrix melt down. Therefore another experiment was carried out where a Ni–toluene matrix was prepared prior to addition of a mixture of toluene and C_6F_5Br. After melt down, extraction, filtration, and addition of PEt_3, a small amount of $(C_6F_5)_2Ni(P(Et)_3)_2$ (**2**) was isolated. A repeat of this experiment, except that the mixture was stirred at −90 °C for 1 h, allowed the formation of slightly more phosphine adduct **2**. It would appear that good mixing and sufficient time at a temperature lower than the decomposition point of (π-toluene)nickel(0) are necessary in order for the $(\pi\text{-}C_6H_5CH_3)Ni(0)\text{–}C_6F_5Br$ reaction to occur. However, even with these conditions met, the yield of **1** (converted to **2** by PEt_3) was never very high and certainly did not approach the yield obtained by direct $Ni\text{–}C_6F_5Br(C_6H_5CH_3)$ tridepositions.

In view of these findings and the fact that large excesses of C_6F_5Br over toluene are required to maximize the yield, the reaction sequence in Scheme I seems reasonable.

Disproportionation reactions of this type are novel and have not been reported previously in metal atom syntheses. It is probable that the presence of the electron-rich trapping arene encourages this disproportionation process by temporarily solvating the C_6F_5NiBr intermediate. Apparently the π-toluene complex of C_6F_5NiBr must not be stable. We have also shown π-toluene complexes of $NiCl_2$ or $NiBr_2$ are not stable by carrying out direct codeposition reactions of NiX_2 vapors with toluene vapors. Only NiX_2 solid and unreacted toluene were recovered.

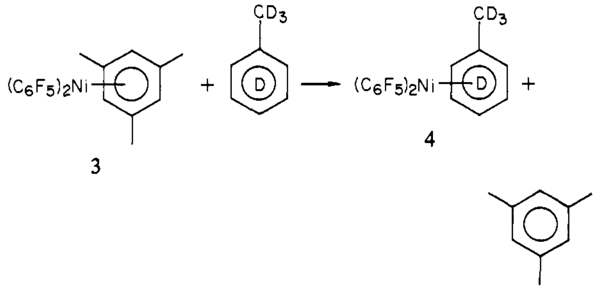
B. π-Arene Lability. Perhaps the most striking property of these $(C_6F_5)_2M$–π-arene complexes is the unprecedented extreme lability of the π-arene ligand. Dissolving pure crystals of **1** in $CDCl_3$ (0.2 M) causes a partial dissociation of approximately 10% at room temperature, as determined by NMR. An equilibrium where π-arene or $CDCl_3$ molecules can serve as ligands is established, and since both the undissociated and dissociated arene can be detected by NMR, the exchange process (eq 2) must be reasonably slow on the NMR time scale.



(2)

When **1** was dissolved in benzene and stirred at room temperature, complete arene exchange was complete is less than 30 min. In a similar way, toluene was completely displaced by mesitylene.

Analysis by NMR of mixtures of **1** with mesitylene in $CDCl_3$ indicated that it was possible to differentiate between complexed and uncomplexed mesitylene.[17] The aryl protons of mesitylene absorbed at δ 6.2 (complexed) and δ 6.8 (free) while the methyl protons absorbed at δ 2.1 (complexed) and δ 2.2 (free). The methyl absorption region was scanned repeatedly during a kinetic experiment, and complete resolution of free vs. complexed mesitylene was possible by this technique. In this way the exchange of mesitylene with toluene-d_8 was easily followed with time (see eq 3). (Note that in the presence of exchanging arene, small chemical shifts were observed compared with pure **3** in $CDCl_3$; cf. Experimental Section.) Kinetic analyses were carried out at 25, 35, 40, 45, and 55 °C and the required times for 50% exchange to take place varied from a few minutes (55 °C) to a few hours (25 °C).

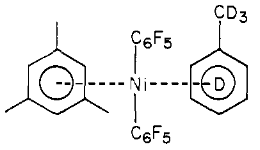


(3)

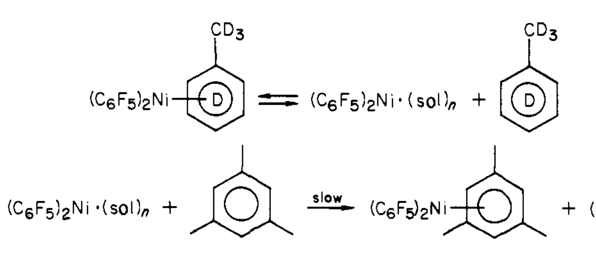
Perdeuteriotoluene–mesitylene exchange was studied from both directions, $\pi\text{-}C_6D_5CD_3 \rightarrow \pi\text{-}C_6H_3(CH_3)_3$ and $\pi\text{-}C_6H_3(CH_3)_3 \rightarrow \pi\text{-}C_6D_5CD_3$. Since mesitylene is the favored ligand, a higher concentration of perdeuteriotoluene was necessary to displace a significant amount of mesitylene than vice versa.

In addition to temperature variations, concentrations were also varied and initial rates of exchange determined. Treatment of the data by classical kinetic methods[18a] showed that the exchange process was first order in complex (**3** or **4** and exchanging arene $C_6D_5CD_3$ or $C_6H_3(CH_3)_3$). Furthermore, Arrhenius methods were employed to determine the E_a for exchange as 10–11 kcal/mol.

The 1:1 reaction kinetics could be rationalized in two ways: (1) Associative—the exchange process involves a backside "S_N2-like" displacement of one π-bonded arene by another; this is a mechanism that we initially supported.[15]



(2) Dissociative—a prior rapid equilibrium is set up such that the dissociated form $[(C_6F_5)_2Ni\cdot(solvent)_n]$ interacts in a first-order fashion with the arene reactant (second-order overall).



(4)

Since we have presented evidence that some dissociation of these complexes does take place when dissolved in $CDCl_3$, the dissociative mechanism might be considered most likely. However, the fact that on an NMR time scale the prior equilibrium must be slow makes the dissociative mechanism less attractive. Unfortunately further experimentation has not allowed us to differentiate between the associative or dissociative mechanistic possibilities.

C. Substituent Effects on π-Arene Exchange. It is clear that there is very high π-arene lability in these $(C_6F_5)_2Ni$–π-arene systems, probably higher than any other known, isolable transi-

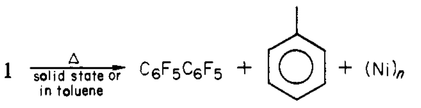
---

(17) Significant upfield chemical shifts were observed. For example the aromatic protons of free mesitylene moved δ 0.56 upfield upon complexation (in $CDCl_3$) and the methyl protons of mesitylene moved δ 0.15 upfield ($C_6D_5CD_3$) was also in the solution).

(18) (a) K. J. Laidler, "Chemical Kinetics", 2nd ed., McGraw-Hill, New York, 1965; (b) Electron-rich arenes are also preferred in other π-arene complexes. See ref 2 for examples.

tion-metal complex. Furthermore, there is a significant effect of substituents on the arene lability. A study of a series of arenes was carried out in order to determine the effects of certain substituents on the exchange equilibria. First, **3** was dissolved in $CDCl_3$, the ^1H NMR spectrum recorded, then 1 mmol each of the arenes shown in Table I added, and equilibrium allowed to be established. The percent of free mesitylene was determined by integration of methyl proton resonances for free and complexed mesitylene. It is clear that electron-rich arenes are preferred ligands for $(C_6F_5)_2Ni$, and of the arenes studied, mesitylene is the most preferred.[18b] However the lability of even the mesitylene ligand is quite remarkable. Further experiments are needed in order to determine steric effects that may be important, and whether polynuclear aromatics are preferentially complexed.

D. The Ni–C_6F_5 Bond. The X-ray structure of **1** indicates that the C_6F_5–Ni bond is quite short (1.891 (4) Å), indicating a very strong bond.[15,19] Accordingly, the thermal stability of this complex is reasonably good. However, heat treatment in the solid state (150 °C) or in refluxing toluene did cause reductive elimination of the C_6F_5 groups, release of toluene, and formation of Ni particles (eq 5). Some C_6F_5H was also found, although in small amounts (<1% from pyrolysis of solid and 7% from refluxing toluene). This result would seem to support a non-free-radical mechanism for the reductive elimination since it would be expected that if C_6F_5 radicals were involved, the refluxing toluene experiment would allow for production of much larger quantities of C_6F_5H.



(5)

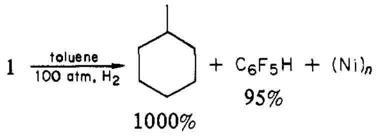
Hydrolysis. Water was added to fresh crystals of **1** at room temperature. No apparent reaction was observed after several minutes, so a small portion of 12 M HNO_3 was added to the slurry. Upon warming of the solution, complete reaction took place, yielding Ni salts, C_6F_5H, and toluene in a molar ratio of 1:2:1.

To summarize, the C_6F_5–M bond is strong and only mildly susceptible to hydrolytic cleavage. So far we have found no other halo, aryl, or alkyl substituent that can be successfully employed to give stable π-arene complexes other than C_6F_5.[15] The C_6F_5 ligand is indeed unique in this system and the analogous Co system.[14] This uniqueness[15,19] apparently stems from the excellent π-acid characteristics of C_6F_5 and the fact that it bonds tenaciously to the metal without the possibility for momentary dissociation (as can take place with CO as a ligand). A further advantage of the C_6F_5 ligand is that its presence allows very good solubilities for these complexes.

We have made a number of attempts to synthesize **1** by conventional methods of C_6F_5 incorporation. Reactions of C_6F_5Li and C_6F_5MgBr with $NiBr_2$ were not successful. One immediate problem was choice of solvent. Toluene or other arenes are not satisfactory solvents for the organolithium and -magnesium compounds. Ethers are good solvents, but **1** cannot be prepared in ether solvents because ethers displace the π-bonded toluene[19] (cf. later discussion).

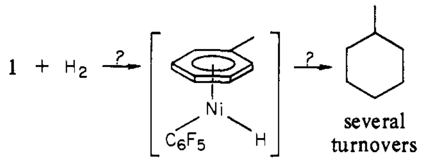
E. Hydrogenation Catalysis by 1. Treatment of **1** with H_2 at room temperature and atmospheric pressure in toluene solution did not initiate a reaction. Even after several days no change was noted and no C_6F_5H had been generated. A search for Ni–H species was carried out by NMR, but no evidence of such species was found.

By increasing the pressure of H_2 to about 100 atm a slow catalytic reaction could be initiated. At room temperature in toluene, the complex served as a catalyst for the hydrogenation of toluene to methylcyclohexane. After 5 days the pressure vessel contained >1000% methylcyclohexane and a 95% yield of C_6F_5H along with a black powdery residue that appeared to be nickel metal (eq 6). A similar experiment at 68 atm of H_2 yielded only a 90% yield of methylcyclohexane.



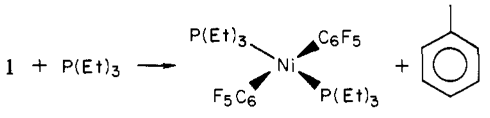
(6)

Our results indicate that **1** serves as a short-lived homogeneous (probably) hydrogenation catalyst for arenes. However, the C_6F_5–M σ bond is quite susceptible to hydrogenolysis which may be the cause of their short lifetimes. It is possible that hydrogenolysis of one C–M bond would be necessary for generation of an active catalyst,[2] perhaps then possessing an active Ni–H bond that could serve to add hydrogen to a complexed arene (see eq 7). There is some support for this idea found in our studies of addition of CpH to **1** where one C_6F_5 group is very rapidly reductively cleaved (cf. later discussion).



(7)

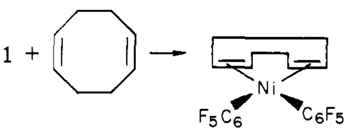
F. π-Arene Displacement for Synthetic Purposes. The treatment of (η^6-toluene)bis(pentafluorophenyl)nickel with $P(Et)_3$ at room temperature led to the rapid displacement of π-arene with the formation of $(C_6F_5)_2Ni(P(Et)_3)_2$ in very high yield (eq 8). This adduct (**2**) is a known compound[20] in the trans geometry.



2

(8)

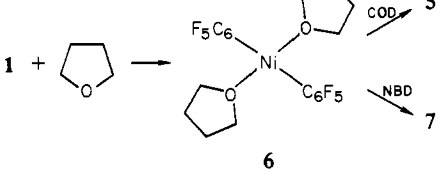
In a similar way, **1** was found to react with a variety of organic dienes under mild conditions (25 °C or less and <1-atm pressure). Of course in these cases the cis geometry is required. For example, 1,5-cyclooctadiene (COD) with **1** yielded the COD complex **5** shown in eq 9 simply on mixing **1** and COD together in toluene solution at room temperature. A 73% isolated yield of **5** was obtained. The ^1H NMR spectrum of **5** revealed a strong upfield shift in the position of the vinyl proton resonances for COD: δ 5.44 for free COD and δ 4.97 for **5**. Moreover, the methylene protons for free COD exhibited a multiplet at δ 2.20 whereas the complexed COD exhibited two multiplets centered at δ 2.19 and 1.53. These two multiplets must originate from the two sets of methylene protons, endo and exo, for the complexed COD.



5

(9)

The most striking example of π-arene displacement from **1** was demonstrated by use of a simple ether THF for complete displacement of π-toluene. As with the phosphine and diene reactions, the reaction of THF with **1** took place rapidly at room temperature in toluene (eq 10). The yellow complex $(C_6F_5)_2$-



6

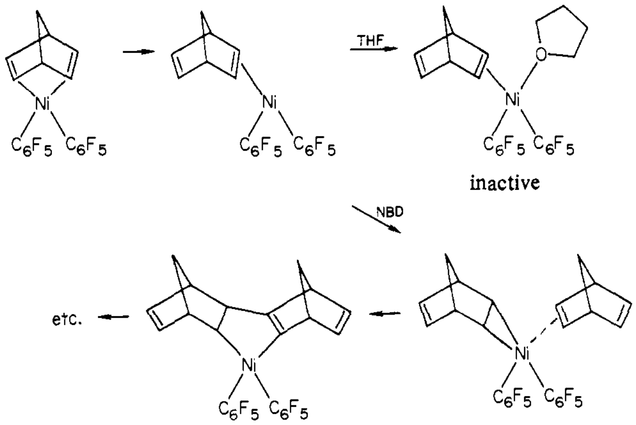
(10)

---

[19] For a complete structural analysis see: L. J. Radonovich, F. Koch, B. B. Anderson, and K. J. Klabunde, *Inorg. Chem.*, in press.

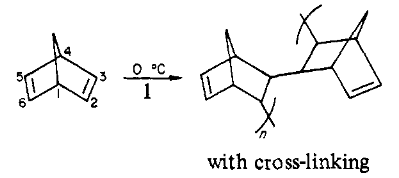
[20] J. R. Phillips, D. T. Rosevear, and F. G. A. Stone, *J. Organomet. Chem.*, **2**, 455 (1964).

Scheme II. Possible Scheme for Norbornadiene Polymerization



Ni(THF)$_2$ precipitated. The ^{1}H NMR spectrum of **6** revealed an upfield shift for the α-protons of THF. A trans geometry is assumed for **6**. The chemistry of **6** is interesting in that the coordinated THF molecules are quite labile, as indicated by facile THF displacement by COD yielding **5** at room temperature. In a similar way, THF can be displaced by norbornadiene (cf. later discussion of (norbornadiene)bis(pentafluorophenyl)nickel) and by cyclopentadiene (cf. later discussion).

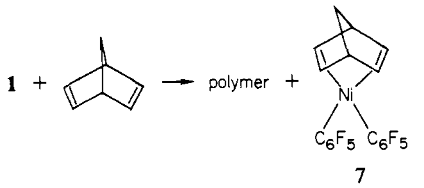
G. π-Arene Displacement with Diene Polymerization. Treatment of **1** in toluene at 0 °C with norbornadiene caused the displacement of the π-toluene and simultaneous polymerization of norbornadiene. The polymerization is smooth and controllable, and its rate is very temperature dependent. The polymer itself is quite high in molecular weight or highly cross-linked; it is not soluble in either cold or hot toluene. The color of the final polymer was dependent on the time and temperature and ranged from light yellow to nearly black, suggesting the presence of incorporated organometallic or nickel metal. The IR spectrum of the polymer was almost identical with that previously reported for polynorbornadiene.[21] The spectrum suggests that a 2,3 polymerization took place with probable cross-linking on the 5,6 carbons, rather than a 2,6 polymerization (eq 11). It is possible, of course, that a mixture of these polymers is formed, although this seems unlikely.



(11)

with cross-linking

Extraction of the polynorbornadiene with toluene yielded a yellow organometallic complex, which has been identified as (norbornadiene)bis(pentafluorophenyl)nickel (**7**) (see eq 12). The ^{1}H NMR spectrum showed a strong upfield shift for all the protons of the diene upon complexation: vinyl, δ 6.65 → 5.53; methylene, δ 3.38 → 3.06; bridgehead, δ 1.96 → 0.81. (We note in passing that the $(C_6F_5)_2$ Pt(NBD) analogue has been prepared, but, to our knowledge, the Pd analogue has not.[22])



(12)

7

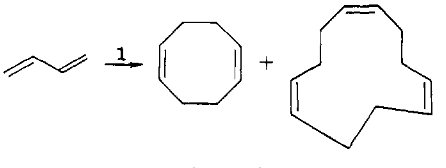
Table II. ^{1}H NMR Data for Complexes Possessing Bridging C_5H_6 Ligands[a]

complex	C_5H_5 ring	C_5H_6 vinyl	C_5H_6 vinyl	C_5H_6 CH_2	ref
C_5H_6 free		6.50	6.29	2.66	this work
$(C_5H_5)_2Pd_2(C_5H_6)$	5.85	5.08	3.98	2.13	24a
$(C_5H_5)_2Ni_2(C_5H_6)$	5.07	5.24	2.82	1.79	24a
$(C_5H_5)_2Ni_2(C_6F_5)_2(C_5H_6)$	4.57	5.44	3.92	1.99	this work

[a] Solvent for all was C_6D_6; values in δ.

Norbornadiene polymerization is also caused by **7** under the same conditions discussed above for **1** with norbornadiene. It seems likely that **1** is first converted to **7** by π-arene substitution and that **7** is either the active catalyst (but isolable) or the active catalyst precursor. In addition the polymerization of norbornadiene by **7** is totally inhibited by the presence of THF. Since THF in $(C_6F_5)_2$Ni(THF)$_2$ can be displaced by norbornadiene to yield **7**, the inhibition cannot be due to conversion of **7** → **6**, an inactive catalyst. Instead, THF must hinder the incorporation of the second diene molecule. It is possible that the complexed norbornadiene molecule can partially dissociate from Ni before a second diene molecule can enter the Ni coordination sphere and that in the presence of THF the open site generated is filled by THF, not the second diene molecule (Scheme II).

1,3-Butadiene is also affected in a catalytic way by **1**. Polymerization does not occur, but instead cyclic telomerization occurs (see eq 13). A mixture of COD and dodecatriene were produced, which is suspicously similar to the same cyclic telomerization caused by (COD)$_2$Ni.[23] It is possible that in the presence of 1,3-butadiene some reductive elimination of $C_6F_5C_6F_5$ could occur (cf. later discussion) and thus a source of Ni(0) generated. However, $C_6F_5C_6F_5$ and C_6F_5H were only generated in small amounts (cf. Table III). No clear-cut choice can be made, but it is possible that the catalytically active species is a $(C_6F_5)_2Ni^{II}$ derivative rather than a Ni(0) derivative. It does seem curious, however, that two such very different sources of Ni (Ni(0) vs. Ni(II)) should give rise to such similar products. We have no current rationale for this.



(13)

H. π-Arene Displacement by Cyclopentadiene with Partial Reductive Elimination of C_6F_5. Perhaps the most interesting reaction of **1** was found when **1** was treated with cyclopentadiene at 0 °C. The solution underwent a change from red-brown to dark green over a period of 1.5 h with the precipitation of a green powder which was filtered off. Analysis of the volatile components of the reaction mixture for several experiments repeatedly showed the presence of C_6F_5H in a ratio of 0.7–0.8 mol:1.0 mol of **1** employed.

^{1}H NMR investigation of the very air- and temperature-sensitive green powder indicated the presence of two cyclopentadienyl rings (C_5H_5, δ 4.57 (singlet, 10 H)) as well as one cyclopentadiene ring (C_5H_6, multiplets at δ 1.99, 3.92, and 5.44 (each 2 H)). Also, a molecular weight determination in benzene indicated a weight of 655. Thus, it appeared likely that a dimer was formed, perhaps with a bridging C_5H_6 ring. Other complexes with bridging C_5H_6 rings are known, and the NMR data for these materials are shown in Table II. Note the considerably large upfield shifts for complexed C_5H_6 moieties and the large magnetic nonequivalence of the two sets of vinyl protons. This apparently results from a

---

(21) (a) F. Hojabri, *J. Appl. Chem. Biotechnol.*, **23**, 601 (1973); (b) M. B. Roller, K. J. Gillham, and J. P. Kennedy, *J. Appl. Polym. Sci.*, **17**, 2223 (1973).

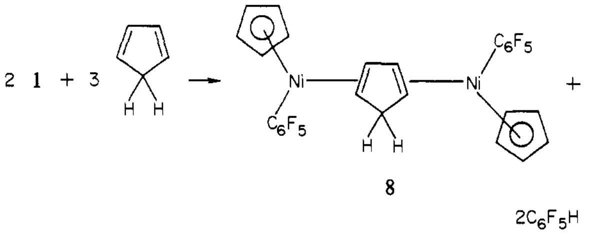
(22) M. D. Rausch and F. E. Tibbetts, *J. Organomet. Chem.*, **21**, 487 (1970).

(23) K. Jonas, P. Heimbach, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **7**, 949 (1968).

(24) (a) E. O. Fischer, P. Meyer, C. G. Kreiter, and J. Muller, *Chem. Ber.*, **105**, 3014 (1972); (b) E. O. Fischer and H. Schuster-Woldan, *Chem. Ber.*, **100**, 705 (1967); (c) K. K. Cheung, R. T. Cross, K. P. Forrest, R. Wandle, and M. Mercer, *Chem. Commun.*, 875 (1971).

slightly different proximity of the metal atoms to the bridging C=C groups.

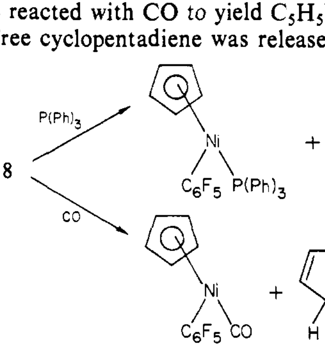
On the basis of the available data, including infrared and satisfactory elemental analysis, a formula for the green complex can be proposed as $(C_5H_5)_2Ni_2(C_6F_5)_2C_5H_6$ (**8**) as shown in eq 14. For every Cp ring formed, one C_6F_5H group is also formed and released. A Ni–Ni bond is probably not formed, although this statement is only based on the observation that the "18-Electron Rule" is obeyed for **8** without a Ni–Ni bond. Crystals for X-ray structural analysis have not yet been obtainable due to the sensitive nature of **8**. We assume a trans arrangement.[25,26]



8

(14)

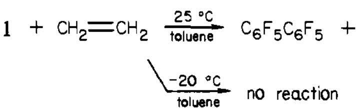
Some support of the structural formulation of **8** was derived from reactions with other ligands. Addition of $(C_6H_5)_3P$ to **8** in toluene at room temperature yielded $C_5H_5Ni(C_6F_5)P(C_6H_5)_3$. Likewise, **8** reacted with CO to yield $C_5H_5Ni(C_6F_5)(CO)$ (see eq 15). Free cyclopentadiene was released in each reaction.



(15)

I. π-Arene Displacement and Complete Reductive Elimination of C_6F_5 Groups. Treatment of **1** with CO at room temperature caused the complete reductive elimination of $C_6F_5C_6F_5$ and the formation of $Ni(CO)_4$. This behavior demonstrated that **1** can serve as a source of Ni(0) as well as Ni(II). Thus, we anticipated the production of some novel Ni(0) complex from **1** and so carried out the reaction of **1** with ethylene. At room temperature and atmospheric pressure, $C_6F_5C_6F_5$ was generated rapidly with the simultaneous precipitation of Ni particles (eq 16). Since the anticipated product $(C_2H_4)_3Ni$ is not thermally stable at 25 °C,[27] an attempt to prepare the ethylene complex at lower temperature (−20 °C) was carried out (eq 17). This attempt did not meet with success as the reductive elimination would not take place under such mild conditions. Thus, we were not able to show if $Ni(C_2H_4)_3$ could be prepared in this fashion or not.

$$\mathbf{1} + CO \xrightarrow[\text{toluene}]{25\ °C} C_6F_5C_6F_5 + Ni(CO)_4 \tag{16}$$



$$\mathbf{1} + CH_2{=}CH_2 \xrightarrow[\text{toluene}]{25\ °C} C_6F_5C_6F_5 + (Ni)_n \qquad \xrightarrow[\text{toluene}]{-20\ °C} \text{no reaction} \tag{17}$$

Conclusions

A series of $(C_6F_5)_2Ni–\eta^6$-arene complexes are available by metal vapor synthetic methods. The C_6F_5 group appears to be unique in the stabilization of these compounds. However, a wide variety of arenes can be employed, although electron-rich arenes such as mesitylene are preferred by the $(C_6F_5)_2Ni$ moiety.

The extreme lability of the π-arene ligand makes these complexes unique among other group 8 π-arene compounds. This lability along with high solubility in organic solvents allows these complexes to have a rich chemistry and presents a rare opportunity for investigating the organic chemistry of a highly reactive Ni(II) species. Thus $(C_6F_5)_2Ni(\eta^6-C_6H_5CH_3)$ (**1**) serves as a short-lived homogeneous (probably) hydrogenation catalyst. Also, a variety of new $(C_6F_5)_2NiL_2$ complexes are available by simple displacement of the π-arene ligand (where L = dienes, ethers, phosphines, etc.). Finally, derivatives of **1** are capable of diene polymerization catalysis, and in some instances the active catalysts are probably $(C_6F_5)_2Ni–(diene)_n$ species.

Reductive cleavage of C_6F_5 groups occurs when ligands possessing labile hydrogen atoms (or protons) are allowed to react with **1**. With cyclopentadiene and **1**, a novel Ni_2 organometallic is formed which possesses a bridging C_5H_6 unit. Complete reductive elimination of C_6F_5 as $C_6F_5C_6F_5$ takes place if small strongly interacting ligands such as CO or C_2H_4 are added to **1**. Thus, **1** can serve as a source of Ni(0) as well as Ni(II) in organic solutions.

Experimental Section

Reagents and Solvents. Manipulations of solids and solutions were carried out either in a drybox (Vacuum Atmospheres Dri Lab with a Model HE-493 Dri Train) employing prepurified nitrogen (99.998%) or in airless glassware employing purified nitrogen (passed over Chem. Dyn. Cat. R3-11 deoxygenation catalyst at 110 °C just prior to use). Ligands were degassed by freeze–thaw procedures on a vacuum line. Solvents were continuously refluxed over benzophenone ketyl under purified nitrogen (pentane, toluene, THF) and only aliquots of fresh solvent used. Deuterio solvents $CDCl_3$, CD_2Cl_2, and $C_6D_5CD_3$ were obtained from Merck and used (degassed) as received. Bromopentafluorobenzene was purchased from PCR, Inc., and used as received after degassing. Prepurified hydrogen was purchased from Chemetron and used as received. Carbon monoxide was purchased from Linde and used as received after passing through a liquid-nitrogen trap on the vacuum line. Ethylene was purchased from Linde and used as received. COD and NBD were purified by distillation. Triethylphosphine was purchased from Orgmet and used as received after it was degassed. Butadiene was purchased from Linde and purified by condensation over KOH at −78 °C followed by pumping to a trap cooled by liquid N_2 (trap to trap). Cyclopentadiene was prepared from dicyclopentadiene by cracking and distillation.

Physical Measurements. Melting points were determined on an aluminum block apparatus designed and built in this laboratory and are uncorrected.

Solution ^1H and ^{19}F NMR spectra were obtained with a Varian EM-390 spectrometer using tetramethylsilane or $CFCl_3$ as standards. Samples were prepared with deoxygenated solvents often in the inert-atmosphere box. For the kinetic trials the NMR tubes were sealed by means of rubber septum caps shaved on the top to avoid extra weight and poor balance (for spinning). Chemical shifts are reported in δ.

Infrared spectra were recorded on a Beckman IR-12 in Nujol, KBr pellets (not oxygen free), or solutions as noted.

Elemental analysis and molecular weights were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, or by Dornis and Kolbe, Mulheim, West Germany.

Gas chromatographic analyses were performed on a Varian Aerograph Model P-90 with the columns indicated.

Metal Atom (Vapor) Apparatus and Techniques. Our apparatus has been described before.[9a,28] The most detailed description can be found in ref 9d.

(π-Toluene)bis(pentafluorophenyl)nickel (1) was prepared as previously described.[29]

(η^6-Mesitylene)bis(pentafluorophenyl)nickel(II), $(C_6F_5)_2Ni(\eta^6-C_6H_3(CH_3)_3$ (3). This complex was prepared by the same procedure as the toluene complex **1** except that purified mesitylene was substituted for toluene as a coreactant and as solvent.

^1H NMR ($CDCl_3$): 2.22 (s, 9 H), 6.48 (s, 3 H), 6.78 (s, very small absorbance for free mesitylene). X-ray structural analysis has been completed.[30]

PEt_3 Trapping of C_6F_5NiCl. After a normal C_6F_5Cl–Ni codeposition reaction was carried out,[29] the matrix was brought from −196 °C to the desired temperature with appropriate slush baths (−131, −90, −45, 0, and

---

(25) W. Bathelt, M. Heberhold, and E. O. Fischer, *J. Organomet. Chem.*, **21**, 395 (1970).

(26) G. Hullner, V. Bejenke, and H. D. Muller, *Cryst. Struct. Commun.*, **5**, 437 (1976).

(27) K. Fischer, K. Jones, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **12**, 565 (1973).

(28) K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).

(29) K. J. Klabunde, B. B. Anderson, and M. Bader, *Inorg. Synth.*, **19**, 72 (1979).

(30) L. J. Radonovich and coworkers, to be submitted for publication.

25 °C). About 1 mL of PEt_3 was distilled into the mixture (refreezing necessary for the −45, 0, and 25 °C experiments), and it was warmed to room temperature, extracted with CH_2Cl_2, filtered, and evaporated to dryness; recrystallization of the residue from 1-butanol yielded the $NiCl_2(P(Et)_3)_2$ and $C_6F_5NiCl(P(Et)_3)_2$ products. $C_6F_5C_6F_5$ in the mother liquor was analyzed by gas chromatography using mesitylene as an internal standard.

Arene-Exchange Reactions of 1. As a typical example, benzene displacement of toluene from **1** will be described.

Crystals of **1** (0.0554 g, 0.114 mmol) were placed in a Schlenk tube under N_2. Ten milliliters of deoxygenated benzene was added along with a small amount of methylcyclohexane as an internal standard. The crystals dissolved and the solution was stirred for $^1/_2$ h. The volatile materials were removed under vacuum and analyzed by GC, which indicated that 0.124 mmol of toluene was present (109% released).

Triethylphosphine (2 mL) was added to the residue, the resulting yellow solution was dried under vacuum, the residue was dissolved in acetone, the solution was filtered, decolorized, and filtered, and the acetone was removed. Recrystallization from benzene–methanol yielded pure $(C_6F_5)_2Ni(P(Et)_3)_2$.

Similar experiments with mesitylene as solvent yielded 102% toluene displacement and with hexafluorobenzene, 109% toluene displacement. The slightly high values in each probably indicates the entrapment of some toluene solvent in the crystals of **1** (in addition to π-complexed toluene).

Arene-Exchange Kinetics. As an example of the procedure used for studying the kinetics of arene exchange, the displacement of mesitylene from **3** with toluene-d_8 at different temperatures will be described.

In the inert-atmosphere box 0.291 g of **3** was placed in a vial with a rubber septum cap, and deoxygenated $CDCl_3$ (5.167 g, 3.44 mL) was added. The resulting solution was used to prepare five NMR samples by syringing 0.25 mL of the solution into NMR tubes equipped with rubber septums. Each sample was heated to the desired temperature (25, 35, 40, 45, and 55 °C) and 0.5 mL of toluene-d_8 added,[31] with preheated toluene-d_8 and a preheated syringe. NMR spectra were recorded at regular intervals with the methyl absorption region expanded.

Arene-Exchange Equilibration Studies. A sample of **3** was dissolved in $CDCl_3$. Seven aliquots (0.25 mL) were removed via syringe and transferred to NMR tubes, and the NMR tubes were freeze–thaw degassed, filled with N_2, and sealed with rubber septum caps. NMR spectra were recorded, and then six of the samples were treated by syringe with 1 mmol of various arenes: C_6D_6, $C_6D_5CD_3$, $C_6H_5OCH_3$, $C_6H_5CF_3$, C_6H_5F, and C_6F_6. The samples were mixed and allowed to come to equilibrium (only minutes generally required at room temperature). NMR spectra were repeatedly taken to ensure that equilibria had been established. The methyl resonances for free and complexed mesitylene were used as a measure of percent exchange, and Table I illustrates our findings.

Hydrolysis of $(C_6F_5)_2Ni(\eta^6\text{-}C_6H_5CH_3)$ (1). Crystals of **1** (0.379 g, 0.782 mmol) were dried overnight under dynamic vacuum. Degassed water (20 mL) was added to the sample. No apparent reaction took place. About 1 mL of 12 M HNO_3 was added and the solution turned yellow. The sample was heated in a hot water bath for several minutes, and the solution turned green and a yellow organic layer formed. Methylcyclohexane was added as an internal standard. The organic phase was diluted with benzene and separated from the aqueous phase. The aqueous phase was placed in a volumetric flask and diluted to 25 mL. The concentration of nickel was determined by the UV–visible absorption at 393.4 nm (max) and the appropriate Ni(II) standards. The nickel found was 36 mmol/L or 0.90 mmol total (115%). The organic phase was analyzed by GC, at 80 °C. Toluene (0.81 mmol, 104%) and pentafluorobenzene (1.50 mmol, 96%) were found.

Hydrolysis of **3** by a similar procedure yielded similar results.

Pyrolysis of $(C_6F_5)_2Ni(\eta^6\text{-}C_6H_5CH_3)$ (1). (a) Dry Crystals. (Toluene)bis(pentafluorophenyl)nickel (0.162 g, 0.335 mmol) was heated in an evacuated tube at 150 °C for 1 h. The tube was cooled and opened, and the residue was extracted with methylene chloride and filtered. Gas chromatographic analysis of the filtrate indicated the presence of decafluorobiphenyl (0.254 mmol) and toluene (0.281 mmol) in yields of 76 and 84%, respectively. Trace amounts of pentafluorobenzene were also observed.

(b) 1 in Toluene Solution. (Toluene)bis(pentafluorophenyl)nickel (0.194 g, 0.400 mmol) in 5 mL of toluene was refluxed under nitrogen for 6 h. The mixture was cooled and filtered. Gas chromatographic analysis of the filtrate gave a 73% yield of decafluorobiphenyl (0.293 mmol) and a 7% yield of pentafluorobenzene (0.056 mmol) (based on available pentafluorophenyl groups).

Hydrogenation Experiments. As a typical example, the hydrogenation of toluene with **1** as catalyst will be described.

Crystals of **1** (1.026 g, 2.27 mmol) were placed in a 128-mL Hastaloy C Parr bomb under a flow of nitrogen. A magnetic stirring bar and 30 mL of dry deoxygenated toluene were added, and the bomb was sealed and pressurized with H_2 to 1500 psi. With rapid stirring at room temperature the pressure dropped to 1100 psi overnight. It was repressurized to 1500, and after 5 days the pressure was stabilized at 1250 psi. The bomb was vented and then opened, and benzene was added as an internal standard. The contents were transferred to a Schlenk tube and then volatiles removed under vacuum and analyzed by GC.

Pentafluorobenzene (4.32 mmol, 95%) and methylcyclohexane (24.2 mmol, 1070%) were found.

A similar experiment was carried out at 1000 psi, yielding only 90% methylcyclohexane.

A control experiment, employing a fresh nickel catalyst made by Ni vapor–toluene codeposition and melt down[12] (no catalyst support was employed) was carried out. This very active Ni hydrogenation catalyst did not affect hydrogenation of toluene under the conditions that **1** did.

Reaction of 1 with Phosphines. (a) Triphenylphosphine. To a deoxygenated solution of (toluene)bis(pentafluorophenyl)nickel (0.095 g, 0.20 mmol) in 5 mL of toluene was added triphenylphosphine (0.224 g, 0.85 mmol) and the mixture stirred overnight at room temperature. A light yellow solution was obtained which when reduced in volume and cooled to −78 °C yielded yellow crystals of bis(triphenylphosphine)bis(pentafluorophenyl)nickel (**2**) (0.094 g, 48% yield), mp 211–213 °C dec (lit.[20] 201–204 °C dec).

(b) Triethylphosphine. A similar reaction with $P(Et)_3$ (distilled, then followed by slow warming from −196 °C) resulted in a >80% yield of $(C_6F_5)_2Ni(P(Et)_3)_2$, mp 212–213 °C (lit.[20] 213–214 °C), recrystallized from toluene.

Reaction of 1 with THF. Synthesis of $(C_6F_5)_2Ni(THF)_2$. (π-Toluene)bis(pentafluorophenyl)nickel (0.461 g, 0.951 mmol) was dissolved in 5 mL of THF and the solution stirred at room temperature for 2 h. The solution was then filtered and the solvent removed in vacuo. Crystallization of the residue in THF at 0 °C yielded 0.208 g (41% yield) of $(THF)_2Ni(C_6F_5)_2$, slow decomposition above 100 °C, no melting point. IR (in THF): 2990 (w), 2910 (w), 1658 (w), 1520 (sh), 1504 (vs), 1460 (vs), 1360 (w), 1265 (m), 1080 (m), 1060 (s), 1040 (m), 958 (vs), 892 (w), 880 (m), 790 (m) cm^{-1}. NMR (C_6D_6): δ 0.90 (s, broad, 2 H), 1.35 (s, broad, 2 H), 3.0–3.8 (m, broad, 4 H). Anal. Calcd: C, 44.73; H, 3.00; F, 35.38. Found: C, 44.83; H, 2.93; F, 34.92.

Reaction of 1 with COD. Synthesis of 1,5-COD$(C_6F_5)_2$Ni. To a solution of **1** (0.210 g, 0.433 mmol) in 10 mL of toluene was added 1,5-cyclooctadiene (0.093 g, 0.86 mmol) and the solution stirred for 1.5 h at room temperature. The solvent was then removed and the residue dried in vacuo. Crystallization from toluene afforded 0.158 g (73% yield) of honey colored (1,5-cyclooctadiene)bis(pentafluorophenyl)nickel, mp 151–152 °C. NMR (C_6D_6): δ 1.53 (m, 4 H), 2.19 (m, 4 H), 4.97 (br s, 4 H). IR (KBr): 1500 (s), 1455 (s), 1425 (s), 1355 (m), 1050 (s), 968 (s), 785 (s), 757 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{12}F_{10}Ni$: C, 47.95; H, 2.41; F, 37.92. Found: C, 48.04; H, 2.19; F, 37.94.

Reaction of 1 with Norbornadiene. Synthesis of (Norbornadine)bis(pentafluorophenyl)nickel and Polynorbornadiene. To a solution of **1** (0.200 g, 0.412 mmol) in 10 mL of toluene held at 0 °C was added 0.5 mL (0.455 g, 4.93 mmol) of norbornadiene and the solution stirred until a bright red gel had formed (approximately 1 h). The solvent and excess diene were then removed in vacuo. A yellow-brown polymeric residue resulted which upon extraction with toluene, filtration, and solvent removal yielded a yellow solid (0.020 g, 10% yield) of (norbornadiene)bis(pentafluorophenyl)nickel. An analytical sample was obtained by recrystallization from toluene, mp 142–143 °C. NMR (C_6D_6): δ 0.81 (m, 2 H), 3.05 (m, 2 H), 5.53 (m, 4 H). IR (KBr): 1505 (s), 1475 (vs), 1357 (m), 1160 (s), 960 (s), 948 (s), 795 (m), 783 (s) cm^{-1}. Anal. Calcd for $C_{19}H_8F_{10}Ni$: C, 47.06; H, 1.66; F, 39.17. Found: C, 46.94; H, 1.72; F, 39.20.

The polynorbornadiene residue from the extraction (0.475 g) was found to be insoluble in a variety of organic solvents. An infrared spectrum (KBr) of this residue showed the following major absorptions: 3065 (m), 2965 (m), 2890 (m), 1730 (w), 1500 (w), 1332 (w), 730 (sh), 720 (s) cm^{-1}.

Reaction of 1 with 1,3-Butadiene. Synthesis of Cyclooctadiene and Cyclododecatriene. A degassed solution of (toluene)bis(pentafluorophenyl)nickel in toluene (0.02–0.08 M) was allowed to stir under 1 atm of butadiene on a vacuum line. After about 10 min the solution turned a bright red orange. After extended reaction periods small amounts of black precipitate were observed on the sides of the reaction flask. The solvent and volatile products were collected in vacuo and analyzed by gas chromatography (see Table III). A red oily residue remained which

---

(31) Relatively high concentrations of toluene-d_8 were needed to displace mesitylene, whereas low concentrations of mesitylene were needed to displace toluene-d_8 at convenient rates.

Table III. Reaction of (Toluene)bis(pentafluorophenyl)nickel and Butadiene

				C_8		C_{12}				
temp, °C	time, h	penta-fluoro-benzene	deca-fluoro-biphenyl	4-vinyl-1-cyclo-hexene	1,5-cyclo-octadiene	trans,trans, trans	trans,trans, cis	unknown	total	molarity
26	0.5	trace	2.2	trace	0.9					0.05
27	1.3	trace	1.6	32.1	9.3	10.5			11	0.05
24	19	trace	2.6	7.6	4.5	65.1	9.0	11.2	85	0.08
24	26.7	trace	2.2	trace	20	115	8.7	9.3	134	0.02

slowly turned black. Analysis of this substance was hindered by its rapid decomposition. Addition of triphenylphosphine to the reaction mixture prior to workup gave a dark red solution which upon solvent removal drying yielded a stable red solid which exhibited an NMR that indicated the presence of only complexed phosphines.

Reaction of 1 with Cyclopentadiene. Synthesis of $(C_6F_5)_2(Cp)_2Ni_2(C_5H_6)$ (8). To a solution of (toluene)bis(pentafluorophenyl)nickel (0.321 g, 0.662 mmol) in 10 mL of toluene maintained at 0 °C was added 0.110 mL (0.088 g, 1.3 mmol) of freshly distilled cyclopentadiene and the mixture stirred for 1.5 h. During the reaction the color of the solution changed slowly from red-brown to dark green. The reaction mixture was filtered, and the volatile components were removed and collected in vacuo. A green powder remained (0.18 g, 83%), mp ~90 °C, dec. NMR (C_6D_6): δ 1.99 (m, 2 H), 3.92 (m, 2 H), 4.57 (s, 10 H), 5.44 (m, 2 H). IR (toluene): 1496 (s), 1470 (sh), 1450 (s), 1435 (m), 1344 (w), 1050 (m), 949 (s), 787 (m), 765 (m) cm^{-1}. Anal. Calcd for $C_{27}H_{16}F_{10}Ni_2$: C, 50.06; H, 2.49; F, 29.33. Found: C, 50.88; H, 2.39; F, 28.92. Molecular weight (VPO in benzene): 655; calcd 647.8.

Analysis of the volatile components of the reaction mixture by GC (25% SE-30, 10 ft × $^1/_4$ in., 110 °C) demonstrated the presence of pentafluorobenzene. For several experiments, the yield of C_6F_5H was always 70–80% based on Ni.

Reaction of 8 with $P(C_6H_5)_3$. Synthesis of $CpNi(C_6F_5)(P(C_6H_5)_3)_2$. Compound **8** was prepared as described above from 0.230 g (0.474 mmol) of (toluene)bis(pentafluorophenyl)nickel (**1**) and 0.079 mL of cyclopentadiene. After being dried, the green residue was dissolved in 5 mL of toluene, and to the solution was added 0.127 g (01485 mmol) of triphenylphosphine. The solvent and volatile products were removed in vacuo, and the residue was crystallized from toluene–pentane to give 0.105 g (40% yield) of (cyclopentadienyl)(pentafluorophenyl)(triphenylphosphine)nickel, mp 208.5–209.5 °C (lit.[32] 214–215 °C). NMR (C_6D_6): δ 5.14 (s, 5 H), 6.82–7.57 (m, 15 H). Mass spectrum (70 eV): M$^+$ 552–554, calcd 552–554. Anal. Calcd for $C_{29}H_{20}F_5PNi$: C, 62.97; H, 3.64; F, 17.17. Found: C, 63.12; H, 3.55; F, 17.25.

Analysis of the volatile products by GC (25% SE-30, 5 ft × $^1/_4$ in., 110 °C) indicated the presence of cyclopentadiene (0.086 mmol, 36% based on Ni).

Reaction of 8 with CO. Synthesis of $CpNi(C_6F_5)(CO)$. Compound **8** was prepared from 0.270 g (0.557 mmol) of (toluene)bis(pentafluorophenyl)nickel (**1**) and 0.091 mL of cyclopentadiene as described above. After being dried, the residue was redissolved in 10 mL of toluene and CO bubbled through the solution for 10 min. The color of the solution changed from green to red. The solvent was removed and the residue sublimed (30 °C (10^{-2} torr)) to give 0.042 g (42% yield) of cyclopentadienyl(pentafluorophenyl)carbonylnickel. NMR(C_6D_6): δ 4.64 (s). IR (toluene): 2070 (s), 1508 (s), 1462 (s), 1360 (w), 1160 (m), 956 (s), 804 (m), 786 (m) cm^{-1}. Mass spectrum (70 eV): M$^+$ 318–320, calcd 318–320. Anal. Calcd for $C_{12}H_5F_5NiO$: C, 45.20; H, 1.58; F, 29.79. Found: C, 45.11; H, 1.68; F, 30.43.

Reaction of 1 with CO. Carbon monoxide was bubbled through a solution of (toluene)bis(pentafluorophenyl)nickel (**1**) (0.270 g, 0.557 mmol) in 5 mL of toluene for 10 min at room temperature. During the reaction the color of the solution changed from red-brown to yellow. An infrared spectrum of the reaction mixture showed the presence of $Ni(CO)_4$, $\nu_{C{\equiv}O}$ 2040 cm^{-1}.[33] Analysis of the solution by GLC (25% SE-30, 5 ft × $^1/_4$ in., 150 °C) gave decafluorobiphenyl (72–79% yield) and a trace of pentafluorobenzene.

Reaction of 1 with C_2H_4. A solution of 0.486 g (1.00 mmol) of (toluene)bis(pentafluorophenyl)nickel in 7 mL of toluene was degassed and allowed to stir under an ethylene atmosphere (640 torr) for 17.5 h at room temperature. The solution became black from the formation of small nickel particles. The solvent and volatile products were removed in vacuo and analyzed by gas chromatography. The yield of pentafluorobenzene was 0.79 mmol (40%). No other volatile products were observed.

A NMR study of the residue indicated the presence of low molecular weight polyethylene.

Acknowledgments. The support of the National Science Foundation (Grant CHE-7402713) is acknowledged with gratitude. Discussions with Professor Lewis Radonovich have been very helpful, and the experimental assistance of James Y. F. Low and Michael Bader is greatly appreciated. We also acknowledge helpful discussions with Professor Earl Muetterties.

---

(32) M. D. Rausch, Y. F. Chang, and H. B. Gordon, *Inorg. Chem.*, **8**, 1355 (1969).

(33) G. Bor, *Spectrochim. Acta*, **18**, 817 (1962).