

clusters and enhanced metal-to-ligand charge transfer in the bare clusters. Calculations were also carried out on a  $\text{Co}_4$  clusters having the geometry of IV. The HOMO for  $\text{Co}_4$  is found to be -2.5 eV while that for  $\text{Co}_4\text{C}_2\text{H}_2$  is -2.8 eV demonstrating that in the cluster systems the "work function" does correlate with calculated charge transfer. Thus, the cluster model systems would suggest *carbanion* character for bound acetylenes on metal surfaces. We must conclude that either the cluster systems used here do not model a surface in a very fundamental fashion or the work function changes have been incorrectly interpreted.

Recently, Shustorovich<sup>40</sup> has pointed out that the simple surface dipole model for explaining work function changes is incomplete and cannot explain paradoxical work function changes (work function change negative and metal-to-ligand charge transfer). He has suggested that not only does the nature of the admolecule-surface metal dipole have to be considered but an internal surface dipole must

be taken into account as well; i.e., a type of double layer is set up on adsorption. Such considerations show that chemisorption of an electronegative adatom can result in either an increase or decrease in the work function depending on the natures of the atom and metal. Presumably similar considerations hold for admolecules. Most likely, then, the cluster systems studied here do correctly model the charge-transfer aspects of alkyne adsorption on metal surfaces in accord with intuitive chemical concepts of electronegativity differences between carbyne carbons and transition metals. In addition, it seems clear from this work that the greater the number of transition-metal atoms that can be associated with a carbyne carbon at a given metal site, the greater the net charge transfer to the carbyne carbon atom.

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**Registry No.**  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ , 100-41-4;  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ , 100-46-9;  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ , 100-51-6;  $\text{C}_6\text{H}_5\text{CH}_3$ , 108-88-3;  $\text{HCCH}$ , 74-86-2;  $\text{C}_6\text{H}_5\text{CCH}$ , 536-74-3;  $\text{Co}_2(\text{CO})_8(\text{C}_2\text{H}_2)$ , 12264-05-0;  $\text{Co}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{CCH})$ , 12154-91-5;  $\text{Co}_3(\text{CO})_9\text{CH}$ , 15664-75-2;  $\text{Co}_3(\text{CO})_9\text{CC}_6\text{H}_5$ , 13682-08-6;  $\text{Co}_4(\text{CO})_{10}(\text{C}_2\text{H}_2)$ , 12282-40-5;  $\text{Co}_4(\text{CO})_{10}(\text{C}_6\text{H}_5\text{CCH})$ , 12568-53-5;  $\text{Co}_2(\text{CO})_8\text{C}_2(\text{Ph})_2$ , 14515-69-6.

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## Complexes of $(\text{C}_6\text{F}_5)_2\text{Co}$ and $(\text{C}_6\text{F}_5)_2\text{Ni}$ . Synthesis of $(\eta^6\text{-Arene})\text{bis}(\text{pentafluorophenyl})\text{cobalt(II)}$ Using Cobalt Atoms. Reactions, $\eta^6\text{-Arene} \text{Lability}$ , and Use in Synthesis of Tetrahedral $(\text{C}_6\text{F}_5)_2\text{Co}(\text{L})_2$

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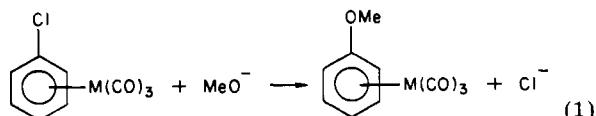
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The high lability of the  $\eta^6\text{-arene}$  ligand in  $(\text{C}_6\text{F}_5)_2\text{Co}(\eta^6\text{-arene})$  has been used to advantage to prepare new  $(\text{C}_6\text{F}_5)_2\text{Co}(\text{L})_2$  and  $(\text{C}_6\text{F}_5)_2\text{Co}(\text{L-L})$  complexes ( $\text{L}$  = tetrahydrofuran, tetrahydrothiophene, and pyridine and  $\text{L-L}$  = bipyridine). According to spectral and magnetic data these are tetrahedral compounds. Similar  $\pi$ -arene displacements on  $(\text{C}_6\text{F}_5)_2\text{Ni}(\eta^6\text{-arene})$  have yielded square-planar *trans*- $(\text{C}_6\text{F}_5)_2\text{Ni}(\text{L})_2$  and square-planar *cis*- $(\text{C}_6\text{F}_5)_2\text{Ni}(\text{L-L})$ . The starting cobalt-arene complex induced the polymerization of norbornadiene and propyne. Thermolysis of the starting complex led to free radical decomposition, which is contrasted by nonradical reductive coupling with the nickel analogue.  $\eta^6\text{-Arene}$ -exchange equilibria for the cobalt- and nickel-arene complexes indicated the order of preference for  $\eta^6\text{-arenes}$  as mesitylene  $>$  toluene  $>$  benzene  $>$  anisole for cobalt and mesitylene  $>$  toluene  $\approx$  anisole  $>$  benzene for nickel. A literature background regarding monoarene complexes is presented.

### Background

The first mono(arene)metal complexes were reported in 1958.<sup>1-4</sup> Upon complexation, the properties of the arene change significantly. For example, some nucleophilic displacements became facile (e.g., eq 1). The potential



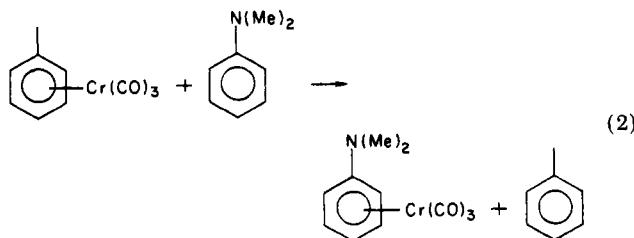
synthetic utility of this reaction prompted investigations of ways of cleaving the M-arene bond to release the new arene. Pyridine and phosphines worked well,<sup>4</sup> but the products were not easily converted back to arenes such that M could be reused. Natta and co-workers<sup>2</sup> and Nicholls and Whiting<sup>3,4</sup> reported greater than 60% yields of  $(\eta^6\text{N,N-dimethylaniline})\text{Cr}(\text{CO})_3$  from the reaction of  $(\eta^6$

(1) Fischer, E. O.; Öfele, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* 1958, 13B, 458.

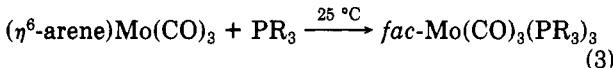
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toluene)Cr(CO)<sub>3</sub> and *N,N*-dimethylaniline (eq 2).

Over the years several papers describing  $\pi$ -arene displacement by  $\sigma$ -donor ligands have appeared.<sup>5-10</sup> Basolo and co-workers<sup>5</sup> studied the rate of phosphine displacement of arene from  $(\eta^6\text{-arene})Mo(CO)_3$  complexes (eq 3).



The facial isomer was formed exclusively, and the rate was directly proportional to the nucleophilicity of the incoming ligand and inversely proportional to the donor strength of the arene. The derived rate expression was first order in arene complex and first order in phosphine. Stepwise loss of arene was proposed. Pidcock, Smith, and Taylor<sup>6,7</sup> studied phosphite displacement of substituted arenes in  $(\eta^6\text{-arene})Mo(CO)_3$  and found that the facility of displacement was *o*-xylene > *p*-xylene > *m*-xylene > mesitylene > hexamethylbenzene, in basic agreement with Basolo.<sup>5</sup> Oxygen and nitrogen donor ligands also displace  $\pi$ -bound arenes on molybdenum, and this is a reversible reaction at reflux temperatures.<sup>8</sup>

The most labile  $\eta^6$ -arene is contained in  $(\eta^6\text{-arene})Ni(C_6F_5)_2$ .<sup>9-11</sup> Treatment of the toluene complex with an excess of PEt<sub>3</sub> in toluene produced *trans*- $(C_6F_5)_2Ni(PEt_3)_2$  in high yield. The reaction was complete in seconds at room temperature. Similarly, addition of THF to crystals of  $(\eta^6\text{-toluene})Ni(C_6F_5)_2$  produced the bis(ether) complex  $(THF)_2Ni(C_6F_5)_2$  immediately. The reaction is not reversible at room temperature. In fact, arene solvents are an ideal medium for recrystallization.<sup>12</sup>

The first  $\pi$ -arene exchange was reported by Natta and co-workers<sup>2</sup> in 1958, and they used the reaction for the preparation of group 6 metal-arene carbonyl complexes not available from direct reaction.

A number of studies of the exchange process have been reported, and several mechanisms have been implicated.<sup>13-17</sup> Furthermore, substituents on the coordinated arene have profound effects both on coordination preference and on reactivity of the metal-arene bond.<sup>18,19</sup>

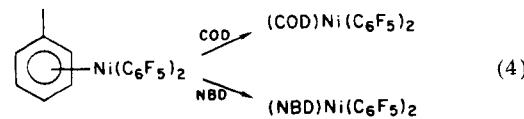
Mahaffy and Pauson<sup>17</sup> reported a detailed study of arene-exchange equilibria for (arene)tricarbonylchromium complexes. Even though catalysts were employed (dibutyl ether or benzonitrile), equilibration times of 20 h at 140 °C were needed, showing the robust nature of the M-arene bond.

We have reported equilibrium exchange data on  $(\eta^6\text{-mesitylene})Ni(C_6F_5)_2$ .<sup>11</sup> The displacing arene was present in 30-fold excess in chloroform solution at room temperature. No catalyst was used and the reactions were complete in minutes. Here it was found that toluene and anisole were favored over benzene and benzene was favored over fluorobenzene, (trifluoromethyl)benzene, and hexafluorobenzene.

Muetterties and co-workers<sup>20</sup> reported exchange reactions of  $(\eta^6\text{-arene})Mo(CO)_3$ , and trends were the same as Mahaffy and Pauson<sup>17</sup> found.  $(\eta^6\text{-C}_6H_6)Ru(COD)$  (COD = 1,5-cyclooctadiene) was found to be inert to exchange in the absence of a catalyst. Addition of 3 equiv of acetonitrile catalyzed a self-exchange which was 22% complete in 204 h at 50 °C. The isoelectronic  $[(\eta^6\text{-C}_6H_6)Ir(COD)]^+$  complex was very unreactive, with only a trace of product detectable after 700 h.<sup>20</sup>

Iron-arene complexes  $(\eta^6\text{-arene})Fe(L\text{-}L)$ , where L-L = diphos or bipyridine, have been found to be inert to arene exchange, even in the presence of catalysts.<sup>21</sup>

Only highly reactive metal-arene bonds undergo exchange reactions with added dienes. A reversible reaction was observed for  $[(\text{diene})_2Rh]^+$ ,<sup>22</sup> whereas irreversible and synthetically useful reactions were observed for  $(\eta^6\text{-toluene})Ni(C_6F_5)_2$  (eq 4).<sup>11</sup>



COD = 1,5-cyclooctadiene; NBD = norbornadiene

## Objective

The complexes  $(\eta^6\text{-arene})M(C_6F_5)_2$ , where M = Co or Ni, represent a unique class of compounds. There are no other examples of neutral isostructural arene complexes with different metals from the same periodic row.<sup>20,23</sup>

The present study was initiated for several reasons: first and foremost, to attempt preparation of new compounds; second, to directly compare aspects of reactivity between the isostructural Co and Ni complexes. Information gained may provide evidence on the nature of bonding interactions.<sup>24</sup>

## Results and Discussion

The metal atom syntheses of  $(\eta^6\text{-arene})M(C_6F_5)_2$  (M = Co, Ni) complexes has been discussed previously.<sup>9,11,25</sup> We

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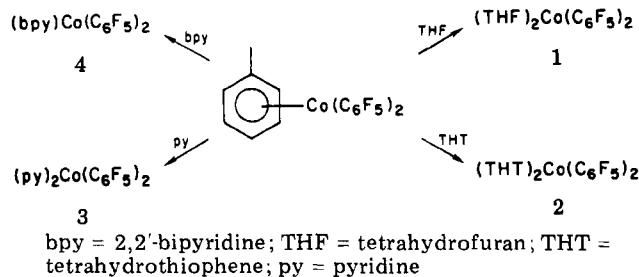
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would only point out here that we have attempted classical solution procedures (Grignard reagents, active metal powders, etc.) for their preparation without success.<sup>26</sup> Indeed, we would predict little success for the solution methods since we now know that any donor solvent displaces the  $\pi$ -arene ligand, and ether or other donor solvents are invariably required in at least one step for Grignard or organolithium reactions or for solution phase active metals preparations.

**A. Arene Displacements by  $\sigma$ -Donor Molecules. Preparation of  $(C_6F_5)_2CoL_2$  and Comparisons with Analogous Nickel Compounds.** The  $\pi$ -arene ligand in  $(\pi\text{-arene})Co(C_6F_5)_2$  is easily and completely replaced by essentially all  $\sigma$ -donor ligands. Thus, addition of neat THF, pyridine (py), or a toluene solution of bipyridine (bpy) to the complex dissolved in toluene produces 1, 3, and 4, respectively. Color change was instantaneous.



Addition of pentane caused the precipitation of 1 and 3, whereas 4 was insoluble in toluene and precipitated during addition of the bpy solution. Preparation of the THT complex was done in methylene chloride since it would not precipitate properly from a toluene-pentane solution. 1, 2, and 3 are blue microcrystalline solids that melt sharply and without decomposition in a sealed capillary tube. However, they are extremely air sensitive and somewhat pressure sensitive. Decomposition will slowly occur in a stream of argon gas or if the solids are subjected to low pressure ( $10^{-3}$  torr) for several hours. They are storeable in a nitrogen-filled ampules indefinitely, however. All three of these complexes are soluble in aromatic solvents and methylene chloride but are insoluble in alkanes and decompose in chloroform.

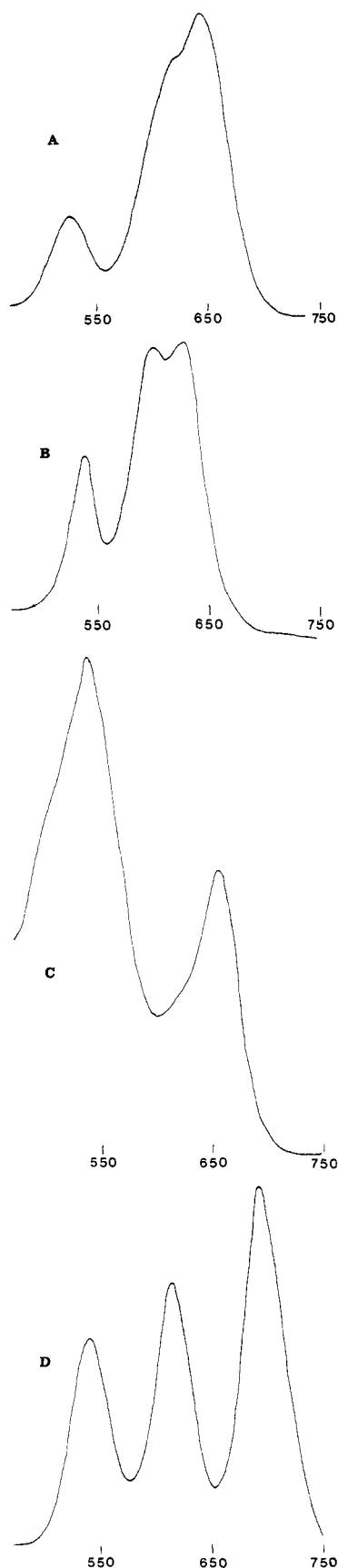
The bpy complex 4 is a turquoise solid and is less air sensitive. Decomposition occurred upon melting, and solubilization in methylene chloride produced a red-violet solution. Removal of the solvent yielded a red-violet solid that turned turquoise on warming to room temperature, indicating solvation-complexation by methylene chloride; 4 is insoluble in aromatic solvents and decomposed in chloroform.

**Spectra of 1-4. Visible.** The visible spectra of tetrahedral cobalt(II) compounds is dominated by the  $^4A_2(F) \rightarrow ^4T_1(P)$  transition. High-energy doublet states of the correct symmetry mix with the  $^4T_1(P)$  state which produces a complex envelope for the transition. Extinction coefficients of approximately 300-900 are expected.<sup>27</sup>

Figure 1 illustrates the visible spectra obtained for 1-4 in methylene chloride. All of the complexes obey Beer's law, and their color and spectra agree with that predicted for tetrahedral complexes. Thus, 1-3 are blue (it should be noted that octahedral cobalt(II) complexes are generally red or pink) and exhibit three bands with the expected extinction coefficients for tetrahedral systems. On the

(26) For lead articles for active metals preparations see: Rieke, R. D. *Acc. Chem. Res.* 1977, 10, 301 and ref 37.

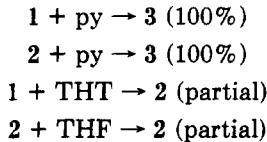
(27) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980.



**Figure 1.** Visible spectra of 1-4 (nm) ( $\epsilon, M^{-1} \text{cm}^{-1}$ ): A, 645 ( $\epsilon$  485), 620 ( $\epsilon$  411), 525 ( $\epsilon$  153); B, 635 ( $\epsilon$  706), 605 ( $\epsilon$  703), 537 ( $\epsilon$  425); C, 665 ( $\epsilon$  642), 528 ( $\epsilon$  1105); D, 704 ( $\epsilon$  676), 625 ( $\epsilon$  519), 556, ( $\epsilon$  400).

other hand, 4 exhibits a somewhat different visible spectrum with just two bands with slightly higher extinction coefficients. In general, the data agree with the expectation of 1-4 being tetrahedral in structure.

Since the spectra are sufficiently different, we investigated qualitative ligand lability by using the visible spectra as our detector of change. Thus, a small excess of pyridine quantitatively displaced both THF and THT. However, THT did not cleanly displace THF nor did THF cleanly displace THT at room temperature. Ligand redistribution appears to occur partially, and the visible spectra were not superpositions of the spectra of the starting complexes. The bpy complex 4 did not react with py, THF, or THT. Thus, the THF and THT ligands are labile in 1 and 2, and py and bpy ligands are preferred.



**Infrared.** Coordinated pentafluorophenyl moieties exhibit several diagnostic vibrational modes in the mid-infrared region. Bands at ca. 1500, 1050, and 950  $\text{cm}^{-1}$  indicate coordination. A band at 800  $\text{cm}^{-1}$  has been used to confirm *cis*, *trans* isomers of several square-planar mono- and bis(pentafluorophenyl)palladium and mono- and bis(pentafluorophenyl)platinum complexes. The band splits into two for *cis* complexes, a single band is observed for mono(pentafluorophenyl), and no band is present for *trans* complexes.<sup>28</sup> Compounds 1–4 all possess intense bands at approximately 1500, 1050, and 950  $\text{cm}^{-1}$ . No absorption occurs at 800  $\text{cm}^{-1}$ . In light of the weight of evidence and basic bonding theory<sup>27</sup> that these are tetrahedral complexes, we concluded that the 800- $\text{cm}^{-1}$  band is not applicable to the  $\sigma$ -pentafluorophenyl ligands in a tetrahedral geometry. Considering the analogous square-planar nickel complexes, a split band is observed at about 800  $\text{cm}^{-1}$  for the bpy complex, which is consistent with prior reports.<sup>28</sup> However, analogously prepared THF, THT, and py adducts for Ni exhibit a single band near 800  $\text{cm}^{-1}$  which is inconsistent with prior work on Pd and Pt, since we believe these complexes are *trans*.<sup>27</sup>

Other infrared bands generally support the formulation for these complexes. The mid-infrared region for the cobalt and nickel derivatives are virtually identical. This is not surprising since very small frequency shifts are generally observed for a molecule upon complexation to a metal center.<sup>30</sup> The spectra often are mere superpositions of the individual ligands. For the THT complex a significant shift was observed though. Thus the C-S ring stretch of THT occurs at  $683\text{ cm}^{-1}$  for the free molecule and shifts to  $660\text{--}670\text{ cm}^{-1}$  upon coordination.<sup>31</sup> In agreement, the spectrum of **2** has a weak band at  $670\text{ cm}^{-1}$  which is assigned to the perturbed ring stretch.

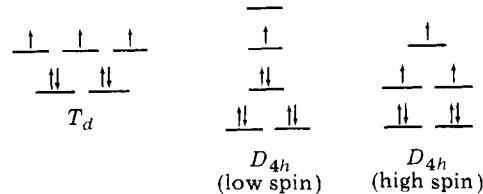
Metal-ligand vibrations were studied further by using far IR. Complexes 1-4 exhibited very similar spectra in this region. Similar results were observed for the analogous Ni analogues, although the Co and Ni derivatives differ from each other. It is likely that these bands are due to the  $C_6F_5$  group and not M-L vibrations. The variant geometries of the Co (tetrahedral) and Ni (square planar) could account for the differences observed. At any rate,

Table I. Magnetic Susceptibilities of  
 $(C_6F_5)_2CoL_2$  Complexes

	$\mu_{\text{eff}}$ , $\mu_{\text{B}}$	solv/ext std
$(\text{C}_6\text{F}_5)_2\text{Co}(\text{THF})_2$	3.23	$\text{C}_6\text{D}_6/\text{Me}_2\text{Si}$
$(\text{C}_6\text{F}_5)_2\text{Co}(\text{THT})_2$	3.96	$\text{C}_6\text{D}_6/\text{Me}_2\text{Si}$
$(\text{C}_6\text{F}_5)_2\text{Co}(\text{py})_2$	3.48	$\text{C}_6\text{D}_6/\text{Me}_2\text{Si}$
$(\text{C}_6\text{F}_5)_2\text{Co}(\text{bpy})$	3.84	$\text{CH}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$

no quantitative information was obtained about M-L bond strengths from the far IR study (cf. Experimental Section for a list of bands observed).

**Magnetic Measurements.** Two geometries are possible for four-coordinate  $d^7$  metal centers: tetrahedral and square planar.<sup>27</sup>



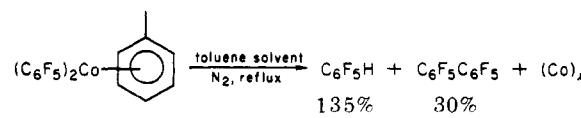
Tetrahedral compounds always contain three unpaired electrons, and square planar contain one (low spin), although three unpaired electrons are theoretically possible but are not generally observed. Use of the angular overlap model<sup>32</sup> shows no geometric stabilization of square-planar high spin over tetrahedral for a  $d^7$  case. The valence shell electron pair repulsion model predicts the ligands will move as far apart as possible (i.e.  $T_d$  is favored). Therefore, the magnetic susceptibility is very strong evidence for  $T_d$  vs.  $D_{4h}$  geometry.

Magnetic susceptibilities were obtained for the Co aducts by the Evans NMR method,<sup>33,34</sup> and the results are tabulated in Table I. Diamagnetic corrections were applied,<sup>35</sup> and all compounds were assumed to obey the Curie law. The results are consistent for Co(II) compounds with  $T_d$  geometry. Cotton and Holm<sup>36</sup> obtained similar values for bis(halogen)bis(isocyanide)Co(II) compounds.

In conclusion, all the results are consistent with (1) facile replacement of the  $\pi$ -toluene ligand in  $(C_6F_5)_2Co(\pi\text{-toluene})$  by L, yielding  $(C_6F_5)_2CoL_2$  (L = THF, THT, py) and  $(C_6F_5)_2Co(L_2)$  (L<sub>2</sub> = bpy). All these compounds are tetrahedral with three unpaired electrons. They are reactive, labile, and air sensitive, much more so than the corresponding square-planar, diamagnetic  $(C_6F_5)_2NiL_2$  complexes (see Experimental Section for properties).

**B. Thermal Decomposition of  $(C_6F_5)_2Co(\pi\text{-toluene})$ . Evidence for Homolytic Lability of the  $Co-C_6F_5$  Bond.** Pyrolysis of crystals of the cobalt-toluene complex at about 150 °C caused the reductive elimination of decafluorobi-phenyl (93%), release of toluene (100%), and formation of Co particles.

Under nitrogen in refluxing toluene the cobalt-toluene complex slowly decomposed. After 3 days GLC analysis showed



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Table II. Arene-Exchange Equilibria

		% displacement
$(C_6F_5)_2Co(\eta^6\text{-toluene})$	+ 1C <sub>6</sub> D <sub>6</sub>	26
	+ 10C <sub>6</sub> D <sub>6</sub>	48
	+ 10C <sub>6</sub> F <sub>6</sub>	0
	+ 10C <sub>6</sub> H <sub>5</sub> F	0
	+ 10C <sub>6</sub> F <sub>5</sub> H	0
	+ 1C <sub>6</sub> D <sub>6</sub>	68
	+ 10C <sub>6</sub> D <sub>6</sub>	84
	+ toluene	85
	+ 10toluene	100
	+ imesitylene	100
	+ 10C <sub>6</sub> F <sub>6</sub>	0
	+ 10C <sub>6</sub> F <sub>5</sub> H	0
	+ 10sym-C <sub>6</sub> H <sub>3</sub> (CF <sub>3</sub> ) <sub>3</sub>	0
	+ 10C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	0
	+ 10p-C <sub>6</sub> H <sub>4</sub> (CF <sub>3</sub> ) <sub>2</sub>	0
$(C_6F_5)_2Ni(\eta^6\text{-toluene})$	+ 1C <sub>6</sub> D <sub>6</sub>	29
	+ 10C <sub>6</sub> D <sub>6</sub>	50
	+ 20C <sub>6</sub> D <sub>6</sub>	67
	+ 30C <sub>6</sub> F <sub>6</sub>	0
	+ 10sym-C <sub>6</sub> H <sub>3</sub> (CF <sub>3</sub> ) <sub>3</sub>	0
	+ 10C <sub>6</sub> F <sub>5</sub> H	0
	+ 20C <sub>6</sub> H <sub>5</sub> F	0
$(C_6F_5)_2Ni(\eta^6\text{-anisole})$	+ toluene	48
	+ 2toluene	85

Comparisons with the Ni analogue indicates that the two compounds have similar thermal stabilities but that the Ni system decomposes much more cleanly to decafluorobiphenyl: only 7% C<sub>6</sub>F<sub>5</sub>H and 73% C<sub>6</sub>F<sub>5</sub>C<sub>6</sub>F<sub>5</sub>.<sup>11</sup>

Apparently homolytic cleavage of the Co-C<sub>6</sub>F<sub>5</sub> bond is more favorable than for Ni-C<sub>6</sub>F<sub>5</sub>. The C<sub>6</sub>F<sub>5</sub> radical could then scavenge H from toluene. The Ni and Co complexes are isostructural with the Co-C<sub>6</sub>F<sub>5</sub> bond 1.931 Å and the Ni-C<sub>6</sub>F<sub>5</sub> bond 1.891 Å,<sup>23,24</sup> which supports the idea that the Co-C<sub>6</sub>F<sub>5</sub> bond is more homolytically labile. It is also of interest to note that C<sub>6</sub>F<sub>5</sub>-Ni-C<sub>6</sub>F<sub>5</sub> cleanly reductively eliminates C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub> apparently with very little C<sub>6</sub>F<sub>5</sub> free radical intermediacy. This would suggest a straightforward intramolecular elimination mechanism.

**C. Reaction of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Co(η<sup>6</sup>-toluene) with Organic Dienes and Alkynes.** Reactions of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ni-(η<sup>6</sup>-toluene) with norbornadiene (NBD) and 1,5-cyclooctadiene produced novel diene complexes (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ni-diene.<sup>11</sup> However, no similar Co(II)-diene or, for that matter, any Co(II) diene complexes are known. Reasons for this are not available in the literature.

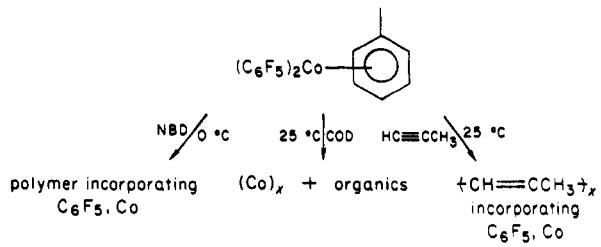
Reaction of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Co(η<sup>6</sup>-toluene) with NBD produced a black, polymeric solid. Extraction of the solid with toluene followed by GLC analysis showed no free NBD, indicating complete polymerization. Some pentafluorobenzene (16%) was detected. The polymer contained carbon-fluorine bonds (infrared).

Reaction with COD caused decomposition with the formation of metallic cobalt, and the reaction mixture was not analyzed further.

Reaction with propyne resulted in polymer formation, pentafluorobenzene (22%), and small amounts of propyne trimers (1,2,4-trimethylbenzene, 13%; 1,3,5-trimethylbenzene, 5%, based on complex). Infrared analysis of the polymer indicated the presence of carbon-fluorine bonds.

**D. Arene-Exchange Reactions.** Structural studies of (C<sub>6</sub>F<sub>5</sub>)M(π-arene)<sup>23</sup> (M = Co, Ni) show that the Co analogue has a shorter Co-π-arene bond. We anticipated that this short bond length would lead to less π-arene ability vs. the Ni analogue.<sup>11</sup> However, this has not been found to be the case, as the following data indicate.

Bis(pentafluorophenyl)(η<sup>6</sup>-arene)cobalt(II) is a paramagnetic complex, and a result of this is the absence of



a detectable <sup>1</sup>H NMR signal in the range of δ -20 to +30, which proved to be advantageous for studying arene exchange. The appearance of free arene signals could be monitored after addition of a displacing arene. The major limitation was that the complexed ring had to have a significantly different chemical shift than the displacing arene.

Equation 5 shows coordinated anisole displacement by benzene-d<sub>6</sub>. Cyclohexane or methylene chloride was used as an internal standard.

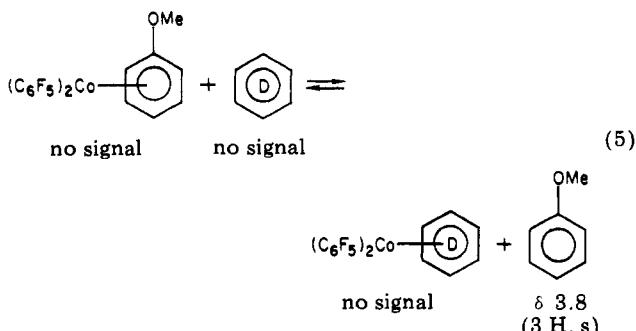


Table II summarizes data for toluene and anisole exchange. Time between injection of the reactant and recording the spectrum was about 20 s (32 °C probe temperature). Equilibrium was attained in this time period. The results correlate surprisingly well with that reported by Mahaffy and Pauson<sup>17</sup> for (CO)<sub>3</sub>Cr(π-arene), considering the vastly higher lability of the present system. Note the apparent destabilizing effect of a methoxy substituent.

No dissociation of the cobalt-arene complex in CDCl<sub>3</sub> (in the absence of displacing arene) was detected. Earlier we had reported partial dissociation of the nickel-arene complex in CDCl<sub>3</sub>.<sup>11</sup> In that work we had used well-formed crystals of the complex, which apparently contained some incorporated excess arene since repeat of this work with carefully vacuum-dried powder showed no sign of dissociation in CDCl<sub>3</sub>. Due to this error we repeated some of the exchange work with the nickel-arene system. Table II summarizes this work, and the same trends were found as reported previously,<sup>11</sup> but the differences are (1) no dissociation occurred in the absence of displacing arene, (2) fluorinated or other electron-demanding arenes did not displace toluene or anisole even if used in large excess, and (3) equilibrium was attained rapidly for toluene and anisole displacements.

The data indicate that the Co and Ni complexes are both extremely labile and have very similar substituent preferences. Thus, methylated arenes are greatly preferred with mesitylene > toluene ≈ anisole > benzene. The resonance hybrid of anisole, with a large contribution of the mesomeric form leading to diene-like character for complexed anisole, has been used to explain rate data<sup>6,7</sup> and could be used in this case. That is, diene complexes of Co(II) are unknown, whereas for Ni(II) they are quite stable. (Recall that with (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ni(η<sup>6</sup>-toluene)

Table III. Infrared ( $\text{cm}^{-1}$ ) and NMR Data for  $(C_6F_5)_2M(L)_2$  and  $(C_6H_5)_2M(L-L)$  Derivatives

Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II) (KBr, Nujol)
1632 m, 1535 m, 1502 vs, 1450 vs, 1375 m, 1330 m, 1285 w, 1255 m, 1180 m, 1066 s, 1055 vs, 1020 s, 955 vs, 870 s, 770 m, 730 m, 715 w, 600 w, 482 m, 354 s, 345 m, 270 m, 244 s, 220 m
Bis(pentafluorophenyl)bis(tetrahydrothiophene)cobalt(II) (Nujol)
1638 m, 1603 w, 1582 vw, 1517 vw, 1500 vs, 1450 vs, 1375 m, 1365 m, 1320 m, 1308 vw, 1272 w, 1258 m, 1250 m, 1200 vw, 1187 vw, 1122 vw, 1062 s, 1050 vs, 995 vw, 950 vs, 880 w, 850 vw, 815 w, 765 m, 710 w, 670 w, 600 w, 590 w, 517 w, 483 w, 390 vw, 356 s, 346 m, 280 w, 250 s, 238 s, 220 m
Bis(pentafluorophenyl)bis(pyridine)cobalt(II) (Nujol/Fluorolube)
1630 m, 1605 s, 1580 w, 1530 w, 1492 vs, 1450 vs, 1420 s, 1377 m, 1365 m, 1325 m, 1280 w, 1248 m, 1218 m, 1155 w, 1090 vw, 1070 s, 1050 vs, 1013 m, 950 vs, 945 vs, 835 vw, 822 vw, 800 w, 755 s, 720 vw, 697 vs, 639 w, 600 w, 483 vw, 425 s, 390 vw, 356 s, 346 w, 280 w, 251 s, 238 m, 220 w
(2,2'-Bipyridine)bis(pentafluorophenyl)cobalt(II) (Nujol)
1630 m, 1610 w, 1605 m, 1575 vw, 1566 vw, 1535 vw, 1497 vs, 1475 m, 1450 vs, 1375 m, 1335 w, 1324 m, 1255 m, 1177 m, 1160 m, 1068 s, 1050 vs, 1020 m, 950 vs, 900 vw, 768 vs, 745 m, 482 m, 420 s, 390 vw, 361 s, 350 m, 280 s, 272 m, 235 s, 210 m, 130 m, 108 m
Bis(pentafluorophenyl)bis(tetrahydrofuran)nickel(II) <sup>13</sup> (Nujol/Fluorolube)
1658 w, 1520 sh, 1504 vs, 1460 vs, 1375 s, 1365 sh, 1352 w, 1325 vw, 1275 m, 1255 m, 1228 w, 1115 vw, 1100 w, 1058 vs, 1035 vs, 1012 w, 952 vs, 917 w, 895 vs, 880 vs, 822 vw, 785 vs, 738 w, 724 w, 610 w, 578 vw, 485 w, 395 m, 375 m, 356 w, 310 s, 293 s, 273 w, 248 w, 230 s; <sup>1</sup> H NMR ( $\text{CDCl}_3$ ) $\delta$ 3.73 (m, 4 H), 1.73 (m, 4 H)
Bis(pentafluorophenyl)bis(tetrahydrothiophene)nickel(II) (Nujol/Fluorolube)
2967 w, 2937 sh, 2860 vw, 1635 m, 1613 sh, 1578 vw, 1545 vw, 1500 vs, 1453 vs, 1435 sh, 1375 vs, 1343 m, 1336 w, 1324 w, 1311 w, 1273 m, 1265 sh, 1238 vw, 1207 vw, 1125 vw, 1061 s, 1047 s, 954 vs, 886 w, 811 w, 780 s, 743 vw, 726 w, 661 w, 514 m, 445 vw, 390 m, 330 vw, 300 m, 275 vw, 240 m; <sup>1</sup> H NMR ( $\text{CDCl}_3$ ) $\delta$ 1.9 (m, 4 H), 2.37 (m, 2 H), 2.75 (m, 2 H)
Bis(pentafluorophenyl)bis(pyridine)nickel(II) <sup>37</sup> (Nujol)
1635 w, 1606 m, 1585 vw, 1503 vs, 1455 vs, 1450 vs, 1380 sh, 1375 m, 1370 sh, 1355 m, 1350 sh, 1345 m, 1275 m, 1230 w, 1215 w, 1210 w, 1150 w, 1095 w, 1050 vs, 1038 w, 1015 w, 945 vs, 825 vw, 815 vw, 787 m, 777 s, 760 sh, 756 s, 735 w, 720 vw, 700 m, 692 s, 645 w, 550 w, 465 vw, 465 s, 450 w, 390 w, 318 m, 300 m, 230 sh, 224 s
(2,2'-Bipyridine)bis(pentafluorophenyl)nickel(II) <sup>38</sup> (Nujol)
1630 m, 1605 m, 1567 w, 1546 w, 1530 vw, 1498 vs, 1375 m, 1365 sh, 1352 m, 1342 sh, 1330 vw, 1317 m, 1220 w, 1258 m, 1220 w, 1170 w, 1162 m, 1125 vw, 1120 vw, 1110 vw, 1100 vw, 1062 vs, 1045 sh, 1030 w, 1018 w, 975 sh, 950 vs, 900 s, 875 w, 782 vs, 772 vs, 730 s, 700 w, 675 vw, 665 w, 642 w, 580 vw, 465 w, 465 s, 418 s, 326 m, 312 w, 275 vw, 247 m, 233 sh, 225 m, 164 m, 158 m

dienes irreversibly displace the  $\pi$ -toluene.<sup>11</sup> So the diene character of anisole apparently aids stabilization of the nickel-anisole complex.

We conclude that the cobalt- and nickel-arene complexes both are similarly and extremely labile with respect to arene displacement. Both prefer electron-rich arenes. A "backside arene displacement" has been implicated as a mechanistic step, but further, very careful kinetic analyses are needed to clearly establish the true mechanism. We are currently undertaking such studies.

## Experimental Section

**Preparation of  $(C_6F_5)_2M(\eta^6\text{-arene})$  ( $M = \text{Co, Ni}$ ).** Synthesis of toluene complexes of both Co and Ni was accomplished by using the metal vapor technique which has been previously described.<sup>9,11,25</sup> Complexes containing anisole, toluene- $d_8$ , benzene, and benzene- $d_6$  were prepared by dissolving crystals of the toluene complexes with a large excess of the appropriate dry, deoxygenated arene. Vacuum evaporation of excess arene left the desired derivative in quantitative yield. See Table IV for properties and spectra.

**General Manipulations, Analyses, Purifications, and Instruments.** The preparation and handling of all compounds was under an inert atmosphere of nitrogen. A Vacuum Atmospheres inert-atmosphere box was used extensively in this work. Manipulations outside the inert-atmosphere box were accomplished by using standard Schlenk glassware and a dual manifold inert line with nitrogen and vacuum connections.

Instruments employed: Beckman IR-12, IBM I/R 98 FT-IR, Varian T-60 <sup>1</sup>H NMR, Varian XL-100 NMR (<sup>1</sup>H and <sup>19</sup>F), Cahn/Ventron Faraday balance, Finnegan CI/EI mass spectrometer, Perkin-Elmer Coleman 124 UV-vis spectrophotometer, and Varian Aerograph Series 1400 gas chromatograph using a 5 ft  $\times$   $1/8$  in. 30% SE-30/Chromosorb P column.

Elemental and molecular weight analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Samples were manipulated under nitrogen.

All fluorinated compounds were purchased from PCR Chemical Co. and freeze-thaw degassed prior to use. Anhydrous 2,2'-bipyridine was used as received. Solvents and arenes were purified by distillation from the appropriate reagent: benzene, toluene, pentane, and THF from benzophenone ketyl/reflux under nitrogen; tetrahydrothiophene from lithium aluminum hydride; pyridine from barium oxide/reflux under nitrogen; methylene chloride from  $P_2O_5$ /reflux under nitrogen; chloroform from molecular sieves; Nujol over sodium wire.

### I. Arene Displacement Reactions by $\sigma$ -Donor Ligands.

**A. Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II).** Bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II) (0.10 g, 0.2 mmol) was dissolved with dry, deoxygenated toluene (1 mL) and filtered into a Schlenk tube (within the inert-atmosphere box). Several drops of dry, deoxygenated tetrahydrofuran were added. The red-brown colored solution instantly turned to a deep blue. Dry, deoxygenated pentane (ca. 5 mL) was added to precipitate the product. The colorless supernate was removed and the blue microcrystalline solid washed twice with 5-mL aliquots of pentane. The supernate and washes were discarded. The Schlenk tube was removed from the drybox, connected to a vacuum line, and evacuated. The blue solid was dried for ca. 5 min. Extended vacuum drying (ca. 20 min) or drying with a nitrogen purge decomposed the product. The product is soluble in aromatics, methylene chloride, and tetrahydrofuran and insoluble in alkanes and decomposes in chloroform. It is stable indefinitely as a solid in a sealed vial under nitrogen and stable for several hours in solution. Decomposition is instant upon exposure to air. Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II): 0.107 g, 100%; mp 123.5 °C, sealed capillary. Anal. Calcd: C, 44.72; H, 3.00. Found: C, 44.23; H, 3.08.

**B. Bis(pentafluorophenyl)bis(tetrahydrothiophene)cobalt(II).** Bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II) (0.10 g, 0.2 mmol) was dissolved with dry, deoxygenated methylene chloride (1 mL) and filtered into a Schlenk tube (within the inert-atmosphere box). Several drops of dry, deoxygenated tetrahydrothiophene were added to the filtrate. The color of the solution changed from red-brown to dark blue. The Schlenk tube was removed from the inert-atmosphere box and connected to a vacuum line. Solvent and excess substrate were removed by reduced pressure evaporation. The blue microcrystalline residue

Table IV. Properties and Spectra of New  $\eta^6$ -Arene Complexes of Co and Ni

	mp, °C	NMR <sup>a</sup>	IR (vs, s, m only) <sup>c</sup>	
(benzene)Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	146 dec	7.14 (s)	1506 s, 963 vs, 800 s, 775 s 1500 s, 1284 s, 1060 s, 960 s, 790 m, 435 m, 343 m, 260 m	yellow-brown
(benzene- <i>d</i> <sub>6</sub> )Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>			1502 vs, 1060 s, 926 vs, 794 s 1560 s, 1536 s, 1520 vs, 1257 s, 1274 vs, 1063 s, 959 vs, 790 vs, 435 m, 340 m, 275 m	yellow-brown
(toluene- <i>d</i> <sub>8</sub> )Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	118 dec	3.78 (s, 3 H), 6.6-7.5 (m, 5 H) <sup>b</sup>	1503 s, 1051 ms, 951 s, 780 s, 435 m, 340 m, 260 m	orange-brown
(anisole)Ni(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>			1503 vs, 1053 m, 953 s, 783 m 1503 vs, 1056 s, 950 vs, 778 s, 631 m	red-brown
(benzene)Co(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	150 dec		1542 s, 1495 vs, 1267 s, 1055 s, 1024 m, 950 s, 819 m, 780 s, 435 m, 345 m, 278 m	yellow-brown
(benzene- <i>d</i> <sub>6</sub> )Co(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>			1503 s, 1053 m, 953 s, 783 m 1503 vs, 1056 s, 950 vs, 778 s, 631 m	yellow-brown
(toluene- <i>d</i> <sub>8</sub> )Co(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>			1503 vs, 1056 s, 950 vs, 778 s, 631 m	orange-brown
(anisole)Co(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	120 dec			red-brown

<sup>a</sup> CDCl<sub>3</sub> solvent, δ vs. Me<sub>4</sub>Si. <sup>b</sup> CD<sub>2</sub>Cl<sub>2</sub> solvent. <sup>c</sup> Nujol mull, KBr; cm<sup>-1</sup>.

was washed twice with 5-mL aliquots of dry, deoxygenated pentane and then dried in vacuo for 5 min. Exposure to reduced pressure or nitrogen purge for extended periods of time (ca. 20 min) decomposed the sample. The product is extremely air sensitive. It is soluble in aromatics, methylene chloride, and tetrahydrothiophene and insoluble in alkanes and decomposes in chloroform. The product is stable indefinitely in the solid state when sealed in a vial filled with nitrogen and stable for several hours in deoxygenated solvents. Bis(pentafluorophenyl)bis(tetrahydrothiophene) cobalt(II): 0.113 g, 99%; mp 86 °C, sealed capillary. Anal. Calcd: C, 42.2; H, 2.83; S, 11.26. Found: C, 41.93; H, 3.10; S, 11.08.

**C. Bis(pentafluorophenyl)bis(pyridine)cobalt(II).** The procedure for preparation of bis(pentafluorophenyl)bis(pyridine)cobalt(II) is identical with the preparation of the tetrahydrofuran derivative except dry, deoxygenated pyridine was used instead of tetrahydrofuran. Stability and solubilities are similar. A reaction of 0.1 g (0.2 mmol) of bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II) produced bis(pentafluorophenyl)bis(pyridine)cobalt(II): 0.104 g, 95%; mp 152 °C, sealed capillary. Anal. Calcd: C, 47.9; H, 1.83; N, 5.08. Found: C, 47.25; H, 2.02; N, 5.34.

**D. (2,2'-Bipyridine)bis(pentafluorophenyl)cobalt(II).** Bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II) (0.10 g, 0.2 mmol) was dissolved with dry, deoxygenated toluene (2 mL) and filtered into a Schlenk tube. This operation was performed in a nitrogen-filled drybox. Anhydrous 2,2'-bipyridine (0.032 g, 0.2 mmol) was dissolved in dry, deoxygenated toluene (ca. 1 mL) and slowly added to the filtrate. The red-brown solution turned opaque green. A turquoise solid precipitated. The brown supernate was removed by using a syringe. The supernate was evaporated to dryness via vacuo, yielding a trace amount of red material. The residue was not analyzed. The turquoise precipitate was washed twice with dry, deoxygenated toluene (5 mL) and then twice with dry, deoxygenated pentane (5 mL). The Schlenk tube was removed from the dry box, connected to a vacuum line, and evacuated. The turquoise product is air sensitive. The product is soluble in methylene chloride producing a red-violet solution. It is insoluble in aromatics and decomposes in chloroform. Solutions are stable under nitrogen for days, and the solid is stable indefinitely when sealed in a vial filled with nitrogen. (2,2'-Bipyridine)bis(pentafluorophenyl)cobalt(II): 0.101 g, 92%; mp 156-175 °C dec, sealed capillary. Anal. Calcd: C, 48.11; H, 1.47; N, 5.10. Found: C, 48.22; H, 1.69; N, 5.26.

**E. Bis(pentafluorophenyl)(L)<sub>2</sub>nickel(II) (L = Tetrahydrothiophene, Pyridine; L<sub>2</sub> = 2,2'-Bipyridine).** Bis(pentafluorophenyl)( $\eta^6$ -toluene)nickel(II) (0.1 g, 0.2 mmol) was dissolved with dry, deoxygenated toluene (ca. 1 mL) and filtered into a Schlenk tube (within the inert-atmosphere box). Several drops of dry, deoxygenated tetrahydrothiophene or pyridine were added. In the case of bipyridine, a stoichiometric quantity was dissolved in a minimum amount of toluene, and the resulting solution was added. Within 1 min a yellow precipitate formed. The supernate was removed and saved for a second crop. The product was washed with dry deoxygenated pentane. The Schlenk tube was

then connected to a vacuum line and the product dried by vacuum evaporation. All yields were quantitative. The complexes are very stable yellow solids. They can be handled in air for several minutes. They are slightly soluble in aromatics, soluble in chloroform and methylene chloride, and insoluble in alkanes. The complexes were prepared for an infrared study. The pyridine and bipyridine derivatives have previously been reported by Rieke<sup>37</sup> and Stone<sup>38</sup> respectively. Bis(pentafluorophenyl)bis(tetrahydrothiophene)nickel(II): mp 125 °C dec. Anal. Calcd: C, 42.4; H, 2.83; S, 11.26. Found: C, 41.99; H, 2.95; S, 11.02.

**II. Arene-Exchange Reactions.** The following procedure, up to the time of NMR analysis, was carried out in inert-atmosphere box using dry, deoxygenated solvents and reagents.

Bis(pentafluorophenyl)( $\eta^6$ -arene)cobalt(II), where arene = toluene or anisole, was weighed into a 2-mL volumetric flask. Cyclohexane was added as an internal standard. The flask was filled with CDCl<sub>3</sub>. The final concentration of arene complex was 0.1 M. The concentration of cyclohexane was 0.25 M. After the solutions were mixed 0.5-mL aliquots were transferred into NMR tubes by syringe. The NMR tubes were then capped by rubber septums. The tubes were placed into a NMR spectrometer and scanned. The tubes were removed and injected with a known amount of a displacing arene. A GC syringe was used to accomplish this. The tubes were inverted several times and then placed into the spectrometer. Spectra were recorded and the signals integrated.

Solutions of bis(pentafluorophenyl)( $\eta^6$ -anisole)nickel(II) were made analogously. An internal standard was not necessary. Toluene was injected in various amounts. Peaks corresponding to complexes and uncomplexed toluene were integrated to determine percent displacement.

**III. Reactions with Dienes and Propyne. A. Reactions with Norbornadiene.** ( $\eta^6$ -Toluene)bis(pentafluorophenyl)cobalt(II) (0.125 g, 0.25 mmol) was dissolved in toluene (ca. 6 mL) and then filtered under an inert atmosphere. The solution was cooled to 0 °C, and 0.1 mL (1.0 mmol) distilled, deoxygenated norbornadiene was added dropwise. No color change took place. After 1 h of stirring at 0 °C, the solution formed a gel. Vacuum was applied, and the volatiles were analyzed by GLC with an appropriate internal standard and correction factors. Pentafluorobenzene (16%, 0.04 mmol) was present. No decafluorobiphenyl was detected. The black residue was extracted with toluene, giving a red-brown solution. The solution was decomposed by exposure to air and then analyzed by GLC. Norbornadiene was not detected. The black polymeric solid was not analyzed.

**B. Reaction with 1,5-Cyclooctadiene.** ( $\eta^6$ -Toluene)bis(pentafluorophenyl)cobalt(II) (0.05 g, 0.1 mmol) was dissolved in toluene (3 mL) and filtered under an inert atmosphere. Cyclooctadiene (1 mL) was added to the solution. No visible change was observed. The solution was stirred for 5 h at room tem-

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perature. During this time considerable decomposition occurred, precipitating metallic cobalt. The volatiles were not analyzed.

**C. Reaction with Propyne.** ( $\eta^6$ -Toluene)bis(pentafluorophenyl)cobalt(II) (0.05 g, 0.1 mmol) was dissolved with methylene chloride (1.5 mL) and then filtered into a Schlenk tube in an inert atmosphere. The Schlenk tube was attached to a vacuum line and the solution freeze-thaw degassed. A 625-torr sample of degassed propyne was introduced over the solution. The color changed from red-brown to dark red. After the mixture was stirred for 90 min, volatiles were removed and analyzed by GLC with methylcyclohexane as an internal standard. Toluene (90%) and pentafluorobenzene (22%) were present. On the basis of the amount of starting arene complex, mesitylene (4.5%) and 1,2,4-trimethylbenzene (12.8%) also were present (identified by GC-MS and retention time). The polymeric residue was not analyzed.

**IV. Pyrolysis of Bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II).** Bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II) (0.099 g, 0.2 mmol) was transferred into a Schlenk tube under an inert atmosphere. The Schlenk tube was evacuated and then placed into an oil bath preheated to 150 °C. The red-brown solid melted and turned black. Clear liquid began refluxing on the walls of the tube. After 15 min of heating, the Schlenk tube was removed from the bath and allowed to cool to room temperature. The vessel was then pressurized with dry nitrogen and opened. The residue was extracted with methylene chloride several times, and the washes were combined. Methylcyclohexane was added as an internal standard, and the mixture was analyzed by GLC. Toluene (100%) and decafluorobiphenyl (93%) were present.

**V. Solution Decomposition of Bis(pentafluorophenyl)( $\eta^6$ -toluene)cobalt(II).** Bis(pentafluorophenyl)( $\eta^6$ -

toluene)cobalt(II) (0.108 g, 0.22 mmol) was dissolved with toluene and then filtered under an inert atmosphere. The filtrate was syringed into a one-neck, 50-mL round-bottom flask equipped with a reflux condenser. The condenser was topped with a stopcock for connection to a nitrogen line. The apparatus was then connected to a nitrogen supply. Constant pressure was maintained with a mineral oil bubbler and continuous nitrogen purge. The solution was refluxed for 72 h until colorless. Methylcyclohexane was added as an internal standard and the solution analyzed by GLC. Pentafluorobenzene (135%, 0.3 mmol) and decafluorobiphenyl (29.6%, 0.06 mmol) were present.

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**Registry No.** 1, 71589-04-3; 2, 86197-37-7; 3, 86197-38-8; 4, 86197-39-9; ( $C_6F_5$ )<sub>2</sub>Ni(THF)<sub>2</sub>, 74153-74-5; ( $C_6F_5$ )<sub>2</sub>Ni(THT)<sub>2</sub>, 86197-40-2; ( $C_6F_5$ )<sub>2</sub>Ni(py)<sub>2</sub>, 86258-55-3; ( $C_6F_5$ )<sub>2</sub>Ni(bpy), 38192-72-2; BNi( $C_6F_5$ )<sub>2</sub> (B = benzene), 86217-13-2; BNi( $C_6F_5$ )<sub>2</sub> (B = benzene- $d_6$ ), 74167-02-5; BNi( $C_6F_5$ )<sub>2</sub> (B = toluene- $d_6$ ), 74167-00-3; BNi( $C_6F_5$ )<sub>2</sub> (B = anisole), 74167-01-4; BCo( $C_6F_5$ )<sub>2</sub> (B = benzene), 86197-41-3; BCo( $C_6F_5$ )<sub>2</sub> (B = benzene- $d_6$ ), 86197-42-4; BCo( $C_6F_5$ )<sub>2</sub> (B = toluene- $d_6$ ), 86197-43-5; BCo( $C_6F_5$ )<sub>2</sub> (B = anisole), 86197-44-6; BCo( $C_6F_5$ )<sub>2</sub> (B = toluene), 60528-58-7; BNi( $C_6F_5$ )<sub>2</sub> (B = toluene), 66197-14-6; NBD, 121-46-0; COD, 111-78-4; pentafluorobenzene, 363-72-4; propyne, 74-99-7; mesitylene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6; decafluorobiphenyl, 434-90-2.

## Further Studies on the Metal to Metal Migration Processes. The Steric Influence of the Phosphorus Ligands on the Oxidative Addition of Dihydrogen and of Hexafluoro-2-butyne to $[\text{Ir}(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{P(O-}t\text{-Bu)}_3)]_2$

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The sterically hindered  $[\text{Ir}(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{P(O-}t\text{-Bu)}_3)]_2$  diiridium(I) complex reacts reversibly with molecular hydrogen to yield 1:1 and 2:1 adducts, identified as  $[(\text{H}_2(\text{P(O-}t\text{-Bu)}_3)(\text{CO})\text{Ir}^{\text{III}}(\mu\text{-S-}t\text{-Bu})_2\text{Ir}^{\text{I}}(\text{CO})(\text{P(O-}t\text{-Bu)}_3)]$  and  $[\text{Ir}^{\text{III}}(\text{H}_2)(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{P(O-}t\text{-Bu)}_3)]_2$ , by chemical and spectroscopic evidence. With hexafluoro-2-butyne, an unsymmetrical and a symmetrical 1:1 adduct,  $[(\text{CO})(\text{P(O-}t\text{-Bu)}_3)\text{Ir}^{\text{I}}(\mu\text{-S-}t\text{-Bu})_2\text{Ir}^{\text{III}}(\text{CO})(\text{P(O-}t\text{-Bu)}_3)(\eta^2\text{-C}_4\text{F}_6)]$  and  $[\text{Ir}^{\text{II}}(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{P(O-}t\text{-Bu)}_3)_2(\mu\text{-}\eta^1\text{-C}_4\text{F}_6)(\text{Ir-}\text{Ir})$  were obtained.  $[(\text{H}_2(\text{P(O-}t\text{-Bu)}_3)(\text{CO})\text{Ir}^{\text{III}}(\mu\text{-S-}t\text{-Bu})_2\text{Ir}^{\text{I}}(\text{CO})(\text{P(O-}t\text{-Bu)}_3)]$  reacts with  $\text{C}_4\text{F}_6$  and  $[(\text{CO})(\text{P(O-}t\text{-Bu)}_3)\text{Ir}^{\text{I}}(\mu\text{-S-}t\text{-Bu})_2\text{Ir}^{\text{III}}(\text{CO})(\text{P(O-}t\text{-Bu)}_3)(\eta^2\text{-C}_4\text{F}_6)]$  reacts with  $\text{H}_2$  to yield quantitatively in both cases  $[(\text{H}_2)(\text{CO})(\text{P(O-}t\text{-Bu)}_3)\text{Ir}^{\text{III}}(\mu\text{-S-}t\text{-Bu})_2\text{Ir}^{\text{III}}(\text{P(O-}t\text{-Bu)}_3)(\text{CO})(\eta^2\text{-C}_4\text{F}_6)]$ . In the context of bimetallic activation processes, the bulkiness of the ligand  $\text{P(O-}t\text{-Bu)}_3$  appears as an effective reactivity modulator, probably through its influence on the flexibility of the bimetallic  $\text{Ir}_2\text{S}_2$  core.

### Introduction

Continuing studies in this laboratory have focused on the interaction of  $[\text{Ir}(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{PR}_3)]_2$  ( $\text{R} = \text{OMe, Ph, NMe}_2, \text{Me}$ ) with small molecules. These dimeric Ir(I) complexes undergo facile and irreversible oxidative addition of a variety of substances including molecular hydrogen,<sup>1</sup> iodine,<sup>2</sup> and hexafluoro-2-butyne.<sup>3</sup> The products

are symmetrical 1:1 adducts with Ir-Ir single bonds as shown in Scheme I.

From our point of view, these reactions exemplify some specific types of behavior of polynuclear entities<sup>4</sup> including

(4) (a) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* 1982, 21, 146-156. (b) Poilblanc, R. *Inorg. Chim. Acta* 1982, 62, 75-86 and references.

(5) Our hypothesis was partially supported by the fact that the symmetrical dihydridoiridium(II) complexes react irreversibly in solution with hexafluoro-2-butyne to yield a diiridium(III) species in which both hydrides are found on the same iridium atom while the alkyne is bound to the other iridium atom.<sup>6</sup> Moreover, this result strongly suggested the existence of an equilibrium between the symmetrical  $(\text{H})\text{Ir-}\text{Ir}(\text{H})$  and the unsymmetrical  $(\text{H})_2\text{Ir-}\text{Ir}$  dihydrido complexes.

(1) Bonnet, J.-J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* 1979, 101, 5940-5948.

(2) Bonnet, J.-J.; Kalck, P.; Poilblanc, R. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 551-552.

(3) Devillers, J.; Bonnet, J.-J.; de Montauzon, D.; Galy, J.; Poilblanc, R. *Inorg. Chem.* 1980, 19, 154-159.