THE CHEMISTRY OF BIS(PENTAFLUOROPHENYL)(η^6-TOLUENE)COBALT(II):

ARENE DISPLACEMENTS AND EXCHANGE REACTIONS

by

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A MASTERS THESIS

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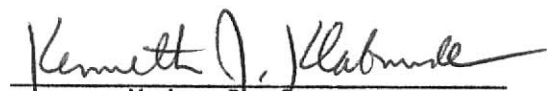requirements of the degree

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Introduction

The first monoarene complexes were reported in 1958 by several laboratories.[1,2,3,4] The reaction was a carbonyl displacement by an aromatic ring:

$$M(CO)_6 + arene \rightleftharpoons (\eta^6\text{-arene})M(CO)_3 + 3\ CO$$

$$M = Cr,\ Mo,\ W$$
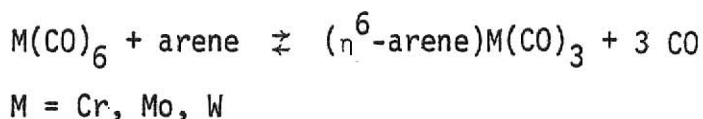
The reaction was reversible and yields were improved by carbon monoxide removal. A wide variety of ring systems were suitable for direct preparation by this method.

Properties of the π-complexed aromatic rings changed drastically. Nucleophilic substitution was a facile reaction:
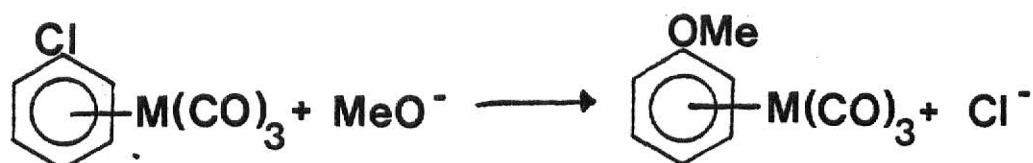
Because of possible synthetic utility as the above reaction describes it was natural to search for a method of cleaving the metal-arene bond. Pyridine and phosphines worked well,[4] but the products were not easily converted back to arenes. Natta et al.,[2] then Nicholls and Whiting[4] reported greater than 60% yield of $(\eta^6\text{-N,N-dimethylaniline})$ Cr(CO)$_3$ from the reaction of $(\eta^6\text{-toluene})$Cr(CO)$_3$ and N,N-dimethylaniline:
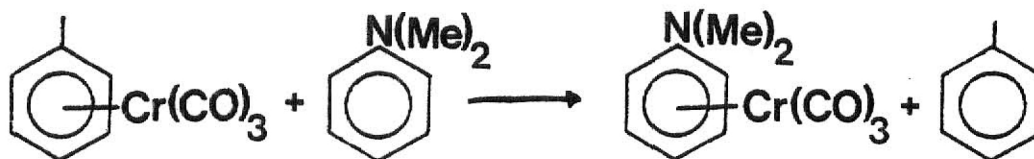
Thus in the time span of one year, two new and mechanistically obscure reactions were discovered. Several important observations were noted during the course of events. . .

1. electron rich rings produced higher yields and more thermally stable complexes than rings containing electron withdrawing substituents.

2. <u>tert</u>-butylbenzene reacted at a rate much slower than toluene.

3. <u>m</u>-xylene formed a more stable complex than did either <u>o</u>- or <u>p</u>-xylene.

I. Arene Displacement with σ- Donor Ligands

Very little work has been published on the mechanism of displacement of arene by sigma donor ligands. What is known deals exclusively with Group VI metals.

Basolo <u>et al.</u>[5] studied the rate of phosphine displacement of arene from $(\eta^6$-arene)Mo(CO)$_3$ complexes.

$$(\eta^6\text{-arene})\text{Mo(CO)}_3 + \text{PR}_3 \xrightarrow{25°C} \underline{fac}\text{-Mo(CO)}_3(\text{PR}_3)_3$$
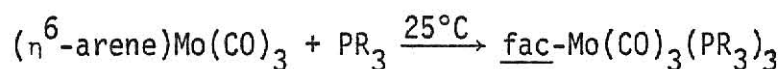
The <u>facial</u> isomer was formed exclusively. The rate of product formation decreased with the following arene ligands:
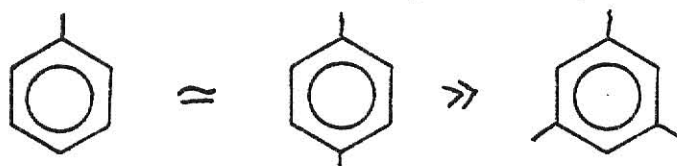
The rate was also dependent on the displacing ligand:

$$\text{P}(\underline{n}\text{-Bu})_3 \gg \text{P}\phi\text{Cl}_2 > \text{PCl}_3$$
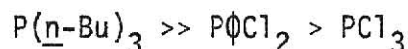
The results show the rate is directly proportional to the nucleophilicity of incoming ligand and inversely proportional to donor strength of arene. All reactions were carried out pseudo first order with a ten fold excess of phosphine ligand. Second order constants were estimated and found to be linear. The derived rate expression was first order in arene complex and first order in phosphine.

As CO and arene are kinetically inert at the temperature used and only the <u>facial</u> isomer is formed, it is reasonable to assume coordinated

arene is not lost in one step. A mechanism was proposed:[5]
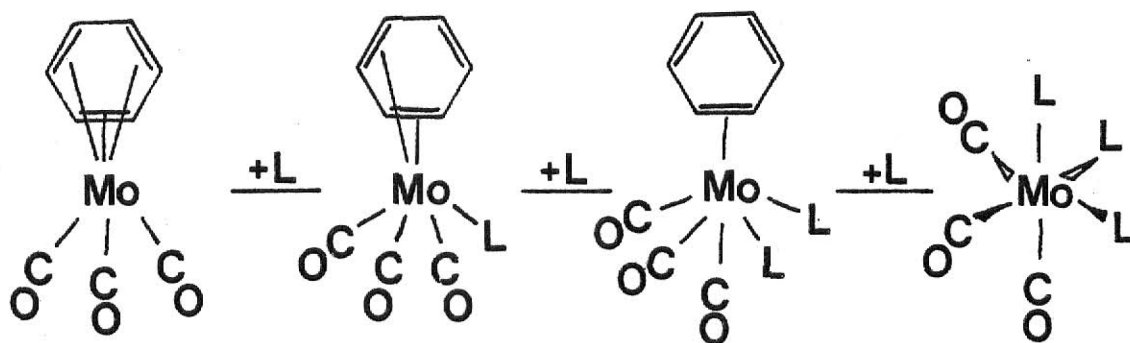
The proposed mechanism is considered viable today.

Carter, McPhail and Sim[6] found the conformation of a substituted arene complex was dependent on the nature of the substituent. The concept of "octahedral valencies" was used. If one views the $M(CO)_3$ fragment along the C_3 axis, it is clear the remaining orbitals from the metal are staggered relative to the M-CO bonding orbitals.
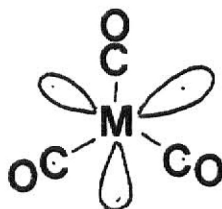
Alkyl substituents enhance the π-electron density at adjacent positions in the ring, e.g.

● = positions of greatest π-electron density

Greatest overlap will occur when the positions of high electron density in the arene coincide with the metal fragments "octahedral valence" orbitals. Thus, in (η^6-mesitylene)$M(CO)_3$, one would predict

an eclipsed conformation of methyl groups and carbonyl ligands. This was confirmed by structural analysis. The concept is readily extended to substituents other than alkyl. Alkoxy, for instance, is an <u>ortho-</u>, <u>para</u> director. The anisole derivative is predicted and found to be eclipsed. A simple ester function is a <u>meta</u> director and should exist staggered. Again, the prediction is correct by analysis.[5]

Carbonyl stretching frequencies were found to vary inversely with electron donating substituents in the arene complex.[5,7,8]

	$\Delta(CO)$ cm^{-1}
$(\eta^6$-dimethylaniline)Mo(CO)$_3$	1970
$(\eta^6$-anisole)Mo(CO)$_3$	1970
$(\eta^6$-mesitylene)Mo(CO)$_3$	1975
$(\eta^6$-$\underline{p}$-xylene)Mo(CO)$_3$	1979
$(\eta^6$-toluene)Mo(CO)$_3$	1984

This data suggests electron donating substituents increase the strength of metal-arene bonding.

Pidcock, Smith and Taylor[9,10] used the above data and the "octahedral valency" argument to rationalize their kinetic data. The following reaction was studied:

$$(\eta^6\text{-arene})Mo(CO)_3 + P(OMe)_3 \rightarrow \underline{fac}\text{-Mo(CO)}_3[P(OMe)_3]_3 + \text{arene}$$
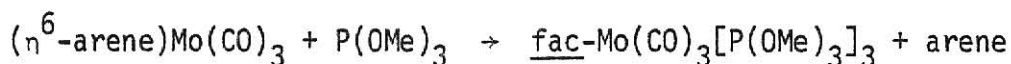
The rate of displacement of substituted arenes by phosphite was

$$\underline{o}\text{-xylene} > \underline{p}\text{-xylene} > \underline{m}\text{-xylene} \gg \text{mesitylene} > \text{HMB}$$
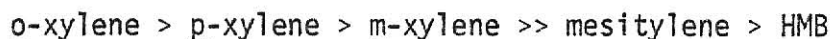
$$\text{HMB} = \text{hexamethylbenzene}$$

The results were in agreement with that of Basolo and co-workers.[5]

The ordering of the xylenes is straightforward. <u>Meta</u>-xylene has three activated positions in C_3 symmetry, <u>para</u>-xylene has two and <u>ortho</u>-xylene has one. Therefore, one would predict an ordering of bond strength to be the same as the rate of displacement. Hexamethylbenzene is thought to be both thermodynamically and sterically controlled. In either conformation, staggered or eclipsed, an incoming ligand will be hindered by the methyl groups:

------- = octahedral valance

⟶ = approaching ligand
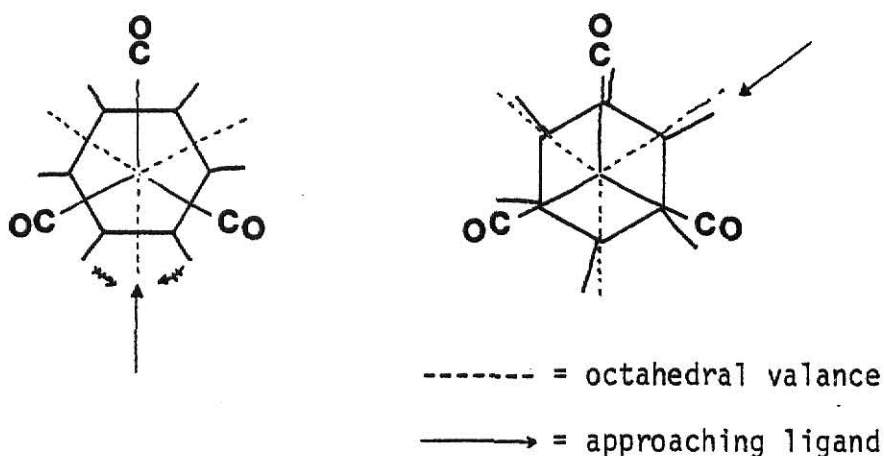
Two anomalies arose from this investigation.
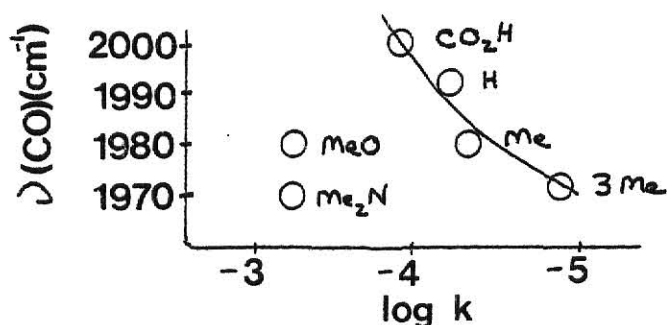
Coordinated anisole and dimethylaniline were displaced at a rate greater than even that of benzene. The graph above is a measure of arene donor strength. A resonance model was tentatively advanced:
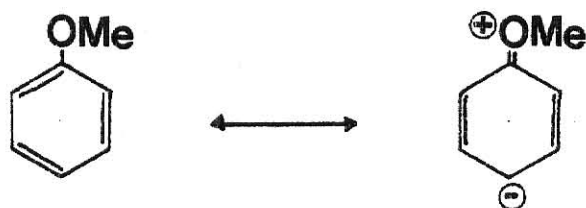
The zwitterionic contribution to the resonance hybrid could stabilize a diene type activated complex. This would reduce the systems energy if the first intermediate in arene displacement is $[(\eta^4\text{-arene})Mo(CO)_3L]$ as Basolo[5] proposed.

Stability of Group VI arene complexes is great. Molybdenum was used in the above kinetic investigations because its complexes are the most reactive. $(\eta^6\text{-arene})Mo(CO)_3$ is displaced at a rate two orders of magnitude greater than tungsten. Tungsten arenes are, in turn, two orders of magnitude faster than the chromium analogs. Using a 10 fold excess of phosphorus donor and 50°C still requires several hours for certain molybdenum arenes.

Adducts with oxygen and nitrogen donor ligands are also available by arene displacement[11]:

$$(\eta^6\text{-benzene})Mo(CO)_3 \xrightarrow[\text{reflux}]{\text{solvent L}} (L)_3Mo(CO)_3$$
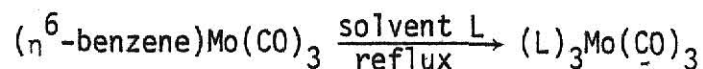
The arene complex is simply refluxed in a donor solvent. The reaction is reversible. Regeneration of the arene complex is accomplished by the same procedure.

$$(L)_3Mo(CO)_3 \xrightarrow[\text{reflux}]{\text{benzene}} (\eta^6\text{-}\phi H)Mo(CO)_3$$
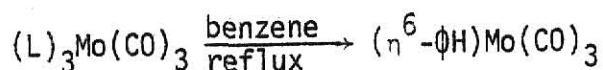
$[(\eta^6\text{-arene})M(CO)_3]^+$, where M = Mn, Re, also possess displaceable arenes.[12] Tris-acetonitrile complexes can be prepared from both metal complexes.

$$[(\eta^6\text{-arene})M(CO)_3]^+ + CH_3CN \xrightarrow[\Delta]{CH_3CN} [(CH_3CN)_3M(CO)_3]^+$$
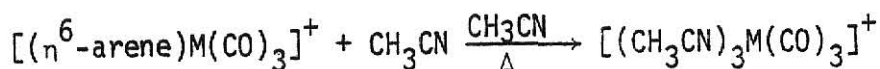
Rhenium reacts ca. 23,000 times faster than manganese. Product formation taking minutes with Rhenium will take days for manganese. Formation of a tris-acetone adduct illustrates the reactivity difference:

$$[(\eta^6\text{-arene})M(CO)_3]^+ + CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_3 \rightarrow [(\text{acetone})_3M(CO)_3]^+ + \text{arene}$$
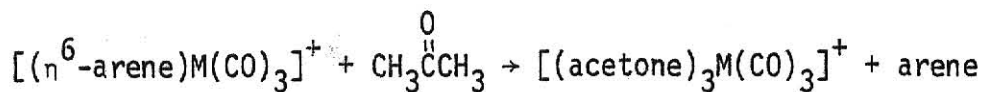
M = Re   several hours

M = Mn   no reaction in months

$(\eta^6\text{-arene})Ni(\phi_f)_2$ contains the most labile arene-metal bond known to date.[13,14,15] Treatment of the toluene complex with excess triethylphosphine in toluene solvent produces trans-Bis(triethylphosphine)bis-(pentafluorophenyl) Ni(II) in high yield. More significant is that the reaction is complete in seconds.

$$(\eta^6\text{-toluene})Ni(\phi_f)_2 + PEt_3 \xrightarrow{\phi Me} \underline{trans}\text{-}(PEt_3)_2Ni(\phi_f)_2$$
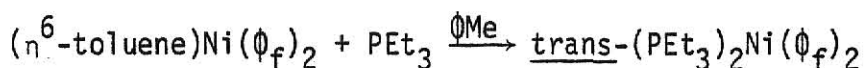
Addition of neat tetrahydrofuran to crystals of $(\eta^6\text{-toluene})Ni(\phi_f)_2$ produces the bis-ether adduct. Reaction is complete in seconds at room temperature.[15]

Unlike $(THF)_3Mo(CO)_3$ which can be converted back to an arene complex (simple equilibrium concepts), $(THF)_2Ni(\phi_f)_2$ is slightly soluble in arene solvents. In fact, arene solvents are an ideal medium for recrystallization.[16]

II. Arene Displacement by Arenes

Arene displacement by aromatic rings is commonly referred to as arene exchange. The exchange reaction was first reported by Natta et al.[2] in 1958. The reaction was used exclusively for the preparation of Group VI metal-arene carbonyl complexes not available from direct reaction.
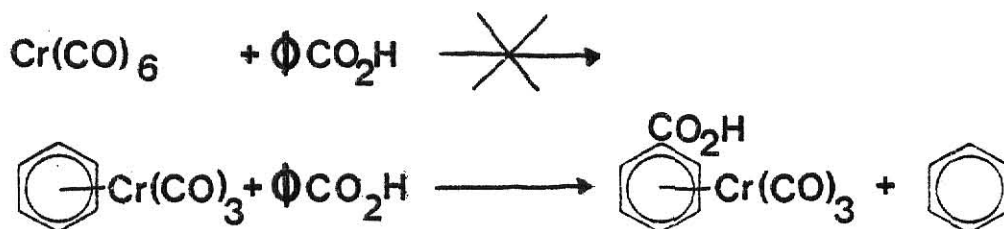
Strohmeier and co-workers[17,18,19] conducted the first mechanistic study of this unknown process. Using ^{14}C labelled benzene and $(\eta^6$-benzene$)Cr(CO)_3$, the production of labelled complex was monitored.

$$\overset{*}{\bigcirc} + \bigcirc\!\!-Cr(CO)_3 \xrightarrow{160°C} \overset{*}{\bigcirc}\!\!-Cr(CO)_3 + \bigcirc$$
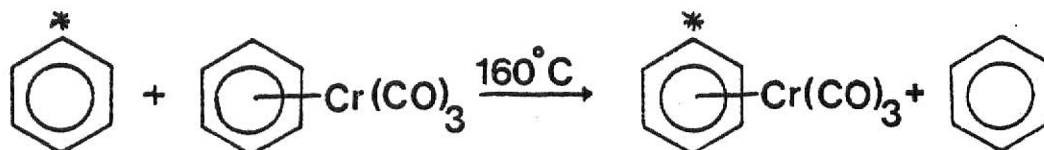
The rate expression obtained was second order in complex and one-third order in benzene. Two mechanisms were proposed to be operating simultaneously.

1

$$2\bigcirc\!\!-Cr(CO)_3 \longrightarrow \left[\bigcirc\!\!-Cr\cdots\bigcirc\cdots Cr-CO \right] \longrightarrow \bigcirc +$$

$$\bigcirc\!\!-Cr(CO)_3 + \text{"}Cr(CO)_3\text{"} \xrightarrow{\overset{*}{\bigcirc}} \overset{*}{\bigcirc}\!\!-Cr(CO)_3$$

2

$$2\bigcirc\!\!-Cr(CO)_3 + \overset{*}{\bigcirc} \longrightarrow \left[\bigcirc\!\!-Cr\cdots\bigcirc\cdots Cr\cdots\overset{*}{\bigcirc} \right] \longrightarrow$$

$$\overset{*}{\bigcirc}\!\!-Cr(CO)_3 + \bigcirc\!\!-Cr(CO)_3 + \bigcirc$$
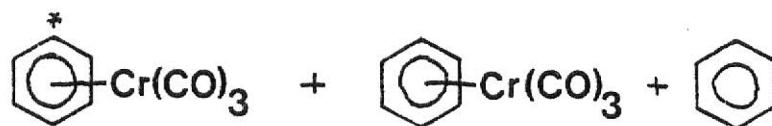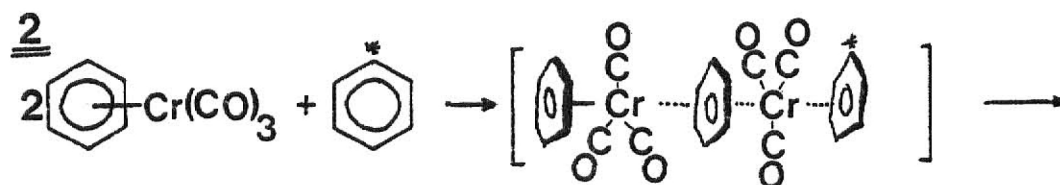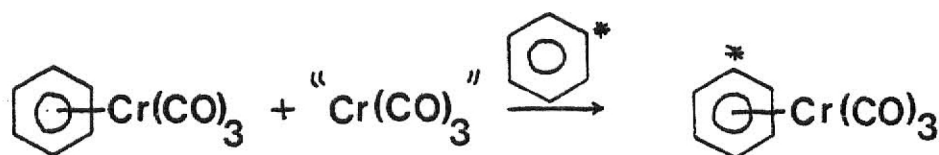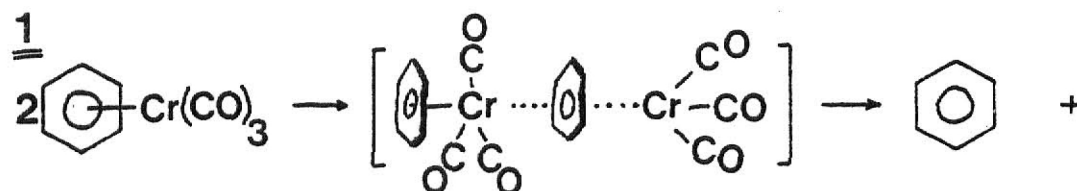
If a chiral aromatic ring were to be used, the ring should undergo the equivalent of a Walden inversion. No further work by Strohmeier is available.

Several years later, Jackson et al.,[20] tested the two mechanisms proposed by Strohmeier using a chiral aromatic arene system.

Arene chromium tricarbonyl derivatives were prepared directly from the hexacarbonyl and 1-methylindane:
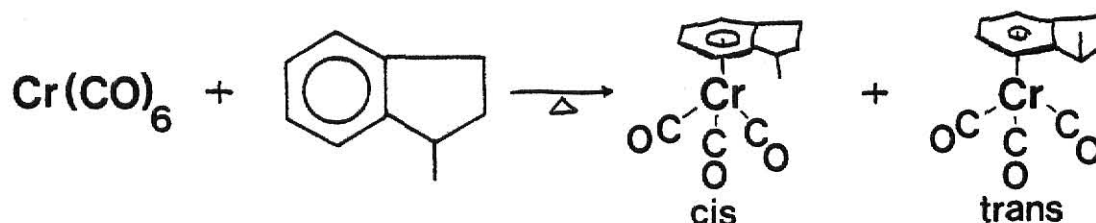
The cis and trans isomers were formed in equal amounts and were readily separated by GLC. Each pure isomer was dissolved in inert solvent and heated. No isomerization took place. Therefore, Mechanism 1 (vide supra) does not appear to be correct as exchange must take place in the absence of added arene. Next, a pure isomer was dissolved and a small amount of 1-methylindane was added. Isomerization occurred yielding the 50:50 mixture thus Mechanism 2 was supported.

Conclusive evidence against Mechanism 2 was obtained by Mahaffy and Pauson.[21] The exchange reaction of mesitylene and trans-(1-methylindane)chromium tricarbonyl was monitored by ^{1}H NMR.
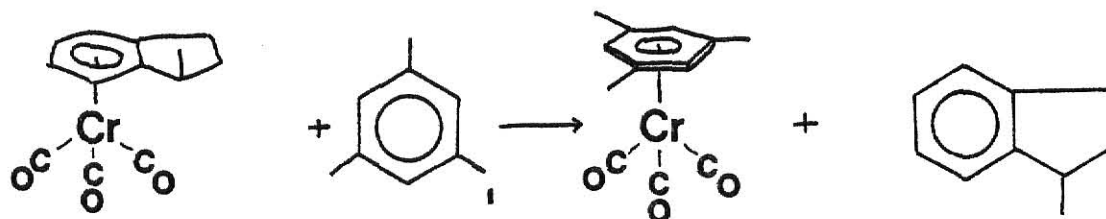
During early stages of the reaction, only the trans complex was present. The cis isomer only appeared late in the reaction after the concentration of free 1-methylindane became appreciable. Collapse of the intermediate in Mechanism 2, going to product, must produce an inversion. This

was not observed.
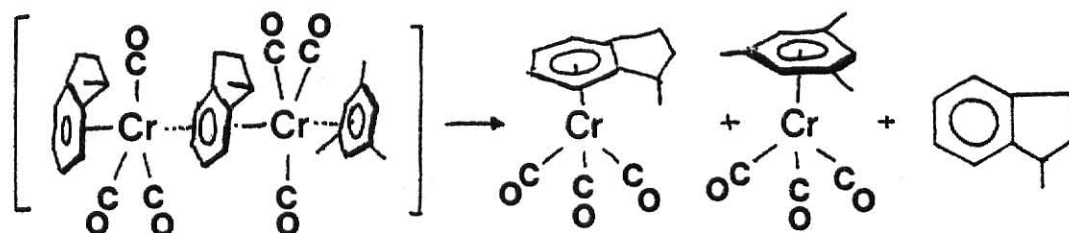
In the absence of catalyst, Mahaffy and Pauson favor a disproportionation reaction:
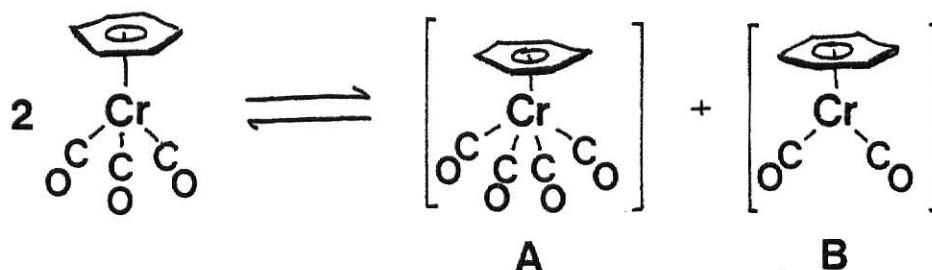
A and/or B could be the reactive species. The intermediate is more plausible than a very high energy fragment such as $[Cr(CO)_3]$. The mechanism is consistent with the second order dependence observed by Strohmeier.

Klabunde et al.,[15] reported a kinetic study involving (η^6-arene)Ni $(\phi_f)_2$. Coordinated vs free mesitylene could be detected by ^{1}H NMR. The addition of toluene-d_8 caused displacement of coordinated mesitylene. The reverse reactions were also studied. 50% exchange was attained in the range of minutes at 55°C to hours at 25°C. The process appeared to be first order in complex and first order in added arene. The complex was reported to dissociate ca. 10% in $CDCl_3$ solution. This is not considered correct following further experimentation (see Experimental and Results and Discussion sections) so this data is of questionable

mechanistic value.

Substituents on the coordinated arene, as mentioned before, exhibit profound effects on reactivity of the metal-arene bond. Ofule and co-workers[22] obtained information on several substituted napthalene derivatives. The complexes were made by direct reaction. Numbers inside the rings indicate percent coordination by $Cr(CO)_3$.
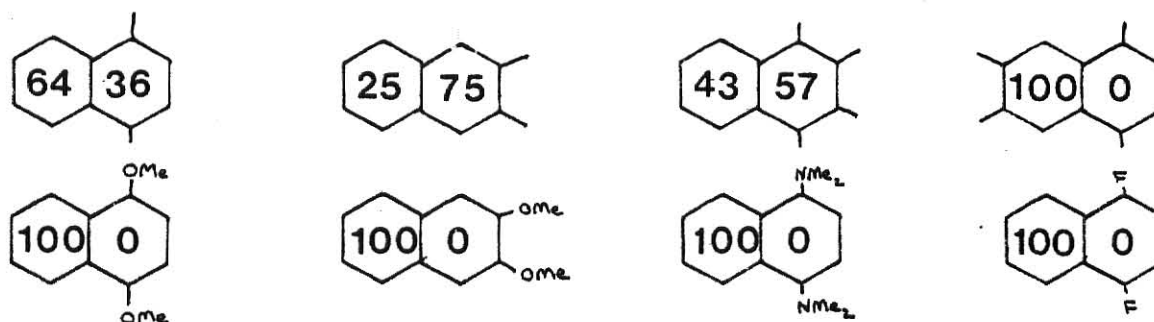
The preference of coordination is remarkable. Clearly, methoxy is a destabilizing substituent. This effect was seen by Pidcock[9] (vide supra) on displacement rates of arenes by phosphite. Why 2,3-dimethyl-napthalene is favored over the 1,4-isomer is not understood. The effect is real and maximized in the case of 1,4,6,7-tetramethylnapthalene.

A very complete study of arene exchange equilibria has been reported by Mahaffy and Pauson[21] for arene tricarbonyl chromium complexes. The reactants were mixed in a one to one ratio. A catalyst was employed to speed equilibration. Dibutyl ether and benzonitrile (catalyst) in an 80:20 mixture was the medium.
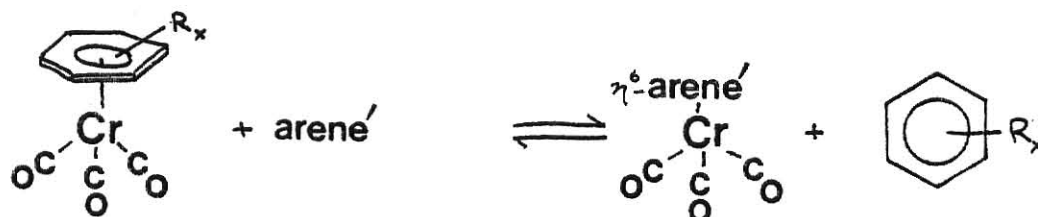
Even though a catalyst was employed, conditions were strenuous.

Temperatures of 140°C and equilibration times of 20 hours were needed.

The first series of exchange reactions were designed to yield information concerning alkyl substituents. Complexed mesitylene was displaced by a variety of monosubstituted rings:
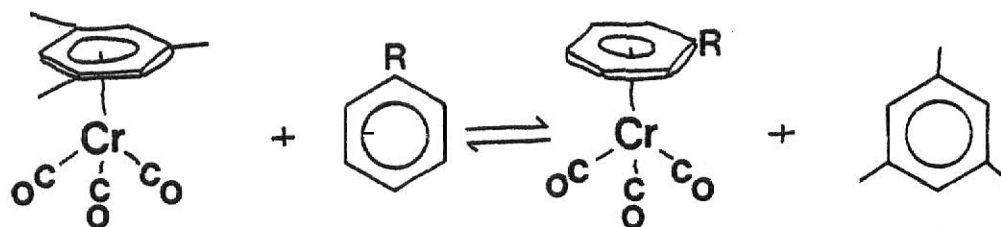
R	% exchange
Me	13.5
Et	6.5
n-Pr	1
i-Pr	1

Clearly the equilibrium constant is depressed as substituents become larger. Methyl substitution appears to be the most effective group. The data is supported by early reports that t-butylbenzene reacted at a slower rate than toluene in arene formation reactions[4] (vide supra).

The second set of exchange reactions varied number and position of alkyl substituents.

$$(\text{arene-A})Cr(CO)_3 + \text{arene B} \underset{2}{\overset{1}{\rightleftharpoons}} (\text{arene B})Cr(CO)_3 + \text{arene A}$$
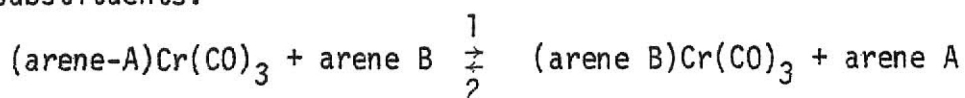
Arene A	Arene B	% exchange (1)
p-xyl	benzene	27
p-xyl	φMe	29
p-xyl	mesitylene	66
φMe	mesitylene	78

Benzene and toluene displacement of p-xylene are within experimental error. This is in agreement with metal-arene bond energies obtained in microcalorimetric studies by Connors et al. [23]

Next, heteroatoms were introduced as substituents.

$$(arene\ A)Cr(CO)_3 + arene\ B \underset{2}{\overset{1}{\rightleftharpoons}} (arene\ B)Cr(CO)_3 + arene\ A$$

Arene A	Arene B	% exchange (1)
ϕH	$\phi CO_2 Me$	14
ϕH	ϕOMe	23
ϕH	$\phi\overset{O}{\overset{\|}{C}}Me$	24
ϕH	ϕF	0
ϕNMe_2	ϕH	21
ϕNMe_2	p-xyl	46

The destabilizing effect of methoxy is clear. The same effect was seen by Pidcock[9,10] and Öfele.[22] Interestingly, benzene displaces p-xylene and dimethylaniline to the same extent. The dimethylaniline:p-xylene reaction provides support for the data, being a 50:50 mixture. This is in conflict with displacement rates Pidcock obtained.[9,10] No rationale has been given for the difference.

Klabunde and co-workers[15] have reported equilibrium exchange data for (η^6-mesitylene)Ni(ϕ_f)$_2$. Displacing arene was in thirty fold excess. The reactions were carried out in chloroform at room temperature and were not catalyzed. The following data was reported:
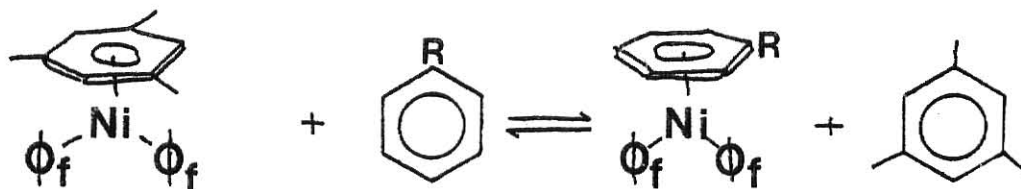
ΦR	% exchange
blank	10
toluene	38
anisole	38
benzene	27
ΦCF$_3$	16
ΦF	16
Φ$_f$F	12

Values obtained for fluorine are low as would be expected. Anamolies for toluene, anisole and benzene are seen in light of Mahaffy and Pauson's data. In this case there is no apparent destabilizing effect for anisole. In fact, a net stabilization is seen when comparisons are made to toluene and benzene.

Muetterties[24] reported qualitative observations of exchange reactions on (η^6-arene)Mo(CO)$_3$. Trends were the same as Mahaffy and Pauson found. (ΦH)Ru(COD) was found to be inert to exchange in an uncatalyzed reaction. Addition of 3 equivalents of acetonitrile catalyzed a self exchange reaction. The process was 22% complete in 204 hours at 50°C.
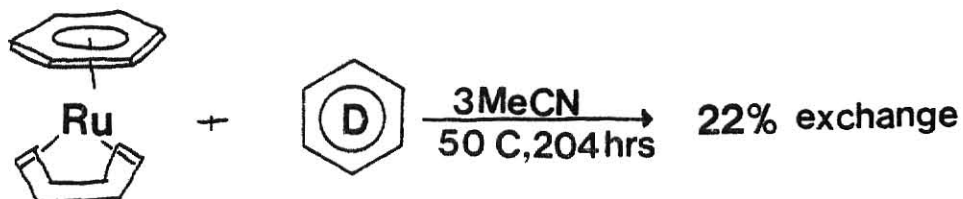
The isoelectronic iridium complex was also quite unreactive.[24] Products were detectable only after 700 hours.
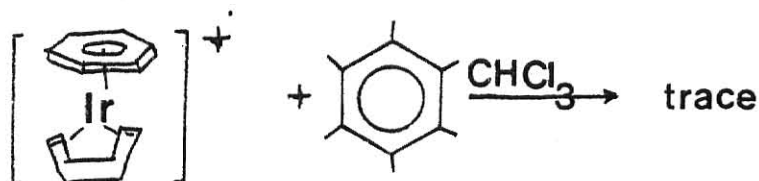
The reaction is anion dependent. Possible intermediates with tetrafluoroborate could be:

$$(COD)Ir\diamond BF_2 \quad or \quad (COD)Ir-FBF_3$$
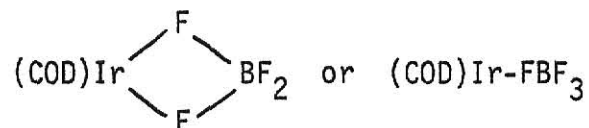
Reaction rate is accelerated one order of magnitude by acetone catalysis.

III. Displacement of Arenes by Dienes

To the knowledge of this investigator the only arene complex known to undergo arene displacement by dienes is $(\eta^6$-arene$)Ni(\phi_f)_2$.[15] Treatment of the complex with excess COD in toluene solvent produces 73% isolated yield of $(COD)Ni(\phi_f)_2$.
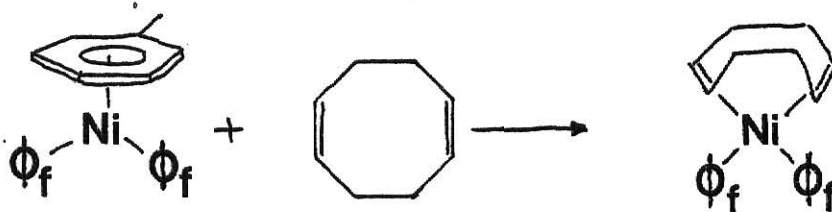
NBD will react with $(\eta^6$-arene$)Ni(\phi_f)_2$ to produce 10% yield of (NBD)-$Ni(\phi_f)_2$ and a high polymer of NBD. The reaction is exothermic.
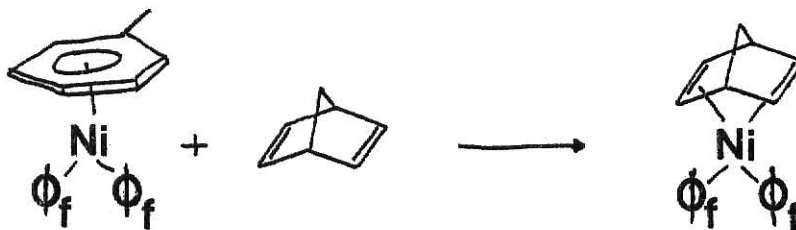
Experimental

Preparation of Bis(pentafluorophenyl)(η^6-arene)M; M = Co, Ni

Synthesis of toluene complexes of both cobalt and nickel was accomplished using the metal vapor technique which has previously been described.[25,26] Complexes containing anisole, toluene-d_8, benzene and benzene-d_6 were prepared by simply dissolving crystals of toluene complex with the appropriate dry, deoxygenated arene. Vacuum evaporation of excess arene produced the desired derivative in quantitative yield.

The preparation and handling of all compounds was under an inert atmosphere of nitrogen. A Vacuum Atmospheres Company dry box was used extensively in this work. Manipulations outside the dry box were accomplished using standard schlenkware and a dual manifold inert line with nitrogen and vacuum connections.

Instruments

1. Beckman IR-12 infrared spectrophotometer

2. IBM I/R 98 FT IR

3. Varian T-60 'H NMR

4. Varian XL-100 NMR ('H, ^{19}F)

5. Cahn/Ventron Faraday balance

6. Finnegan CI/EI mass spectrometer

7. Perkin Elmer Coleman 124 UV-VIS spectrophotometer

8. Varian Aerograph Series 1400 gas-liquid chromatograph using a 5 ft. 30% SE-30/Chromosorb P column

Elemental and Molecular Weight Analysis

All analyses were carried out under nitrogen and were performed by Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside, New York 11377-2495.

Reagents and Solvents

All fluorinated compounds were purchased from PCR Chemical Co. and degassed prior to use. Anhydrous 2,2'-bipyridine was used as received. The following is a list of solvents and reagents and the method of purification.

toluene	benzophenone ketyl/reflux under nitrogen
benzene	benzophenone ketyl/reflux under nitrogen
pentane	benzophenone ketyl/reflux under nitrogen
tetrahydrofuran	benzophenone ketyl/reflux under nitrogen
tetrahydrothiophene	lithium aluminum hydride
pyridine	barium oxide/reflux under nitrogen
methylene chloride	phosphorus pentoxide/reflux under nitrogen
chloroform	molecular sieves
Nujol	sodium wire

I. Arene Displacement Reactions by Sigma Donor Ligands

Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II)

Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (0.10g, 0.2mmol), was dissolved with dry, deoxygenated toluene (1 mL) and filtered into a schlenk tube. This was performed in a dry box. Several drops of dry, deoxygenated tetrahydrofuran was added. The red-brown colored solution instantly turned to a deep blue color. 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 dry box, connected to a vacuum line and evacuated. The blue solid was dried for ca. 5 minutes. Extended

vacuum drying (ca. 20 minutes) or drying with a nitrogen purge decompose
the product. The product is soluble in aromatics, methylene chloride
and tetrahydrofuran. The product is 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(tetrahydro-
furan)cobalt(II), (0.107g, 100%), (mp 123.5°C, sealed capillary).
Elemental analysis: found C 44.23%, H 3.08%; calculated C 44.72%, H 3.00%.
Spectral data is reported in the Results and Discussion section.

Bis(pentafluorophenyl)bis(tetrahydrothiophene)cobalt(II)

Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (0.10g, 0.2mmol) ,was
dissolved with dry, deoxygenated methylene chloride (1 mL) and filtered
into a schlenk tube. This was performed in a dry box filled with
nitrogen. 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 dry box and connected
to a vacuum line. Solvent and excess substrate were removed by reduced
pressure evaporation. The blue microcrystalline residue was washed
twice with 5 mL aliquots of dry, deoxygenated pentane then dried via
vacuo for 5 minutes. Exposure to reduced pressure or nitrogen purge
for extended periods of time (ca. 20 minutes) decomposes the sample. The
product is extremely air sensitive. It is soluble in aromatics,
methylene chloride, tetrahydrothiophene and insoluble in alkanes. The
product 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), (0.113g, 99%), (mp 86°C, sealed

capillary). Elemental analysis: found C 41.93%, H 3.10%, S 11.08%; calculated C 42.2%, H 2.83%, S 11.26%. Spectral data is reported in the Results and Discussion sections.

Bis(pentafluorophenyl)bis(pyridine)cobalt(II)

The procedure for preparation of Bis(pentafluorophenyl)bis(pyridine) cobalt(II) is identical to the preparation of the tetrahydrofuran derivative except dry, deoxygenated pyridine is used instead of tetra- hydrofuran. Stability and solubilities are similar. 0.1g (0.2 mmol), Bis(pentafluorophenyl)(η^6-toluene)cobalt(II) produced Bis(pentafluoro- phenyl)bis(pyridine)cobalt(II), (0.104g, 95%), (m.p. 152°C, sealed capillary). Elemental analysis: found C 45.34%, H 1.79%, N 5.01%; calculated C 47.9%, H 1.83%, N 5.08%. Spectral data is reported in the Results and Discussion section.

(2,2'-bipyridine)bis(pentafluorophenyl)cobalt(II)

Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (0.10g, 0.2mmol),was dissolved with dry, deoxygenated toluene (2 mL) and filtered into a schlenk tube. This operation was performed in a nitrogen filled dry box. Anhydrous 2,2'-bipyridine, (0.032g,0.2mmol),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 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) 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 colored product is air sensitive. The product is soluble in methylene chloride producing a

red-violet colored 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), (0.101g, 92%), (m.p. 156-175 dec, sealed capillary). Elemental analysis: found C 48.22%, H 1.69%, N 5.26%; calculated C 48.11%, H 1.47%, N 5.10%. Spectral data is reported in the Results and Discussion section.

Reaction with Carbon Monoxide

Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (0.15g, 0.3mmol),was dissolved with dry, deoxygenated methylene chloride (4 mL) and filtered into a schlenk tube. The filtration was carried out in a nitrogen filled dry box. The schlenk tube was removed from the box, connected to a vacuum line and freeze-thaw degassed. After the solution warmed to room temperature, 630 mm Hg of research grade carbon monoxide was allowed to stand over the solution. Within minutes the solution turned from red-brown to dark brown. The volatiles were removed via vacuo leaving a thick brown oil. Infra red analysis of the neat oil indicated decafluorobiphenyl, terminal and bridging coordinated carbon monoxide and no pentafluorophenyl-cobalt bands. Spectral data is reported in the Results and Discussion section.

Bis(pentafluorophenyl)(L)$_2$nickel(II)

L = tetrahydrothiophene, pyridine

L$_2$= 2,2'-bipyridine

Bis(pentafluorophenyl)(η^6-toluene)nickel(II), (0.1g, 0.2mmol),was dissolved with dry, deoxygenated toluene (ca. 1 mL) and filtered into a schlenk tube. This procedure was carried out in a nitrogen filled dry 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 one minute 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 infra red study. The pyridine and bipyridine derivatives have previously been reported by Rieke[27] and Stone[28] respectively. Bis(pentafluorophenyl)bis(tetrahydro-thiophene)nickel(II) (m.p. 125°dec.). Elemental analysis: found C 41.99%, H 2.95%, S 11.02%; calculated C 42.4%, H 2.83%, S 11.26%. Spectral data is reported in the Results and Discussion section.

II. Arene Exchange Reactions

The following procedure, up to the time of NMR analysis, was carried out in a nitrogen filled dry box using dry, deoxygenated solvents and reagents.

Bis(pentafluorophenyl)(η^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 $CDCl_3$. The final concentration of arene complex was 0.1M. The concentration of cyclohexane was 0.25M. After mixing, 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 known amount of a displacing

arene. A GC syringe was used to accomplish this. The tubes were inverted several times then placed into the spectrometer. Thermal equilibration was assumed to occur instantly. The spectrum was recorded and the signals integrated.

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

III. Reactions with Dienes

Reaction with Norbornadiene

0.125g(.25mmol)(η^6-toluene)bis(pentafluorophenyl)cobalt(II) 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 (1.0mmol) distilled, deoxygenated norbornadiene was added dropwise. No color change took place. After one hour of stirring at 0°C the solution formed a gel. Vacuum was applied and the volatiles analyzed by GLC with appropriate internal standard and correction factors. Pentafluorobenzene (16%,0.04mmol) 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 then analyzed by GLC. Norbornadiene was not detected. The black polymeric solid was not analyzed.

Reaction with 1,5-cyclooctadiene

0.05g(.1mmol)(η^6-toluene)bis(pentafluorophenyl)cobalt(II) 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 hours at room temperature.

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

Reaction with propyne

0.05g (.1mmol)(η^6-toluene)bis(pentafluorophenyl)cobalt(II) was dissolved with methylene chloride (1.5 mL) 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. 625 mm Hg of degassed propyne was introduced over the solution. The color changed from red-brown to dark red. After stirring for 90 minutes, volatiles were removed and analyzed by GLC with methylcyclohexane as an internal standard. Toluene (90%) and pentafluorobenzene (22%) were present. Based on the amount of starting arene complex: mesitylene (4.5%) and 1,2,4-trimethylbenzene (12.8%) were present. The polymeric residue was not analyzed.

Pyrolysis of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II)

   Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (0.099g, 0.2mmol),was
transferred into a schlenk tube under an inert atmosphere. The schlenk
tube was evacuated, 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 minutes of heating, the schlenk
tube was removed from the bath and let 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
combined. Methylcyclohexane was added as an internal standard then
the mixture was analyzed by GLC. Toluene (100%) and decafluorobiphenyl
(93%) were present.

Solution Decomposition of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II)

   Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (0.108g, 0.22mmol),was
dissolved with toluene then filtered under an inert atmosphere. The
filtrate was syringed into a one neck, 50 mL roundbottom 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 hours until colorless. Methylcyclohexane was added
as an internal standard and the solution analyzed by GLC. Penta-
fluorobenzene (135%,.3mmol)and decafluorobiphenyl (29.6%,.06mmol) were
present.

Reaction with Cyclopentadiene: Preparation of $Cp_3Co_2(\phi_f)_2$

All manipulations were carried out with dry, deoxygenated solvents and reagents.

Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), (.205g, .42mmol), was dissolved in methylene chloride (5 mL) and filtered. The filtrate was cooled to 0°C using an ice bath. Freshly cracked cyclopentadiene (51μL, .6mmol) was slowly syringed into the cold solution. A color change, from red-brown to green-red, occurred during the addition. The solution was stirred for several minutes then all volatiles were pumped into a trap cooled with liquid nitrogen. Methylcyclohexane was added to the volatiles as an internal standard. GLC analysis showed the presence of toluene (85%) and pentafluorobenzene (50%, .4mmol). The black residue was washed several times with toluene (5 mL aliquots). The black residue made up the major amount of product. The residue was dissolved with a minimum amount of methylene chloride and filtered. The solution was dark brown. Solvent was slowly evaporated leaving air stable black microcrystals of $Cp_3Co_2(\phi_f)_2$. (.12g, 60%), (m.p. 212,dec) sealed capillary). Elemental analysis; found: C 49.52%, H 2.19%, F 30.19%; calculated: C 50.00%, H 2.48%, F 29.30%.

Magnetic Susceptibilities

The Evans NMR Method[29] was used to determine μ_{eff} for several compounds. Density-volume corrections pointed out by Cohen[30] were employed for accurate concentration determinations at the probe temperature of the NMR.

A Faraday balance was used for variable temperature susceptibility measurements on $Cp_3Co_2(\phi_f)_2$.[31]

OBJECTIVE

Bis(pentafluorophenyl)(η^6-arene)M, where M = Co, Ni, represents a unique class of arene complexes. There are no other examples of neutral isostructural arene complexes with different metals from the same periodic row.

Previous work by Klabunde et al.[15] has shown the nickel species to possess an extremely reactive metal-arene bond (see Introduction). Displacement and exchange processes occur at room temperature, are usually complete in minutes, and are uncatalysed. This unique complex also provided the first example of arene displacement by dienes.

The study reported herein was initiated for several reasons: first and foremost, to attempt preparation of new complexes; second, to directly compare all aspects of reactivity between the two isostructural complexes. Information gained may provide evidence on the nature of bonding interactions, especially regarding the arene-metal bond in the cobalt and nickel complexes.

I. Arene Displacements by σ-Donor Molecules

A. Preparation of Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II) <u>1</u>

Bis(pentafluorophenyl)bis(tetrahydrothiophene)cobalt(II) <u>2</u>

Bis(pentafluorophenyl)bis(pyridine)cobalt(II) <u>3</u>

(2,2'-bipyridine)bis(pentafluorophenyl)cobalt(II) <u>4</u>

Addition of neat THF, py or a toluene solution of bipy to Bis(penta-fluorophenyl)(n^6-toluene)cobalt(II) dissolved in toluene produces <u>1</u>, <u>3</u>, and <u>4</u> respectively. Color change is instantaneous. <u>1</u> and <u>3</u> can be precipitated with the addition of pentane. <u>4</u> is insoluble in toluene and precipitates during addition of bipy. Preparation of <u>2</u> must be carried out in methylene chloride since it will not precipitate from a toluene-pentane solution, and vacuum evaporation of a toluene solution produces an impure oil. <u>1</u>, <u>2</u>, and <u>3</u> are blue colored microcrystalline solids. Melting points taken in a sealed capillary tube are sharp and occur without decomposition. Thus the compounds have good thermal stability.

<u>1</u>, <u>2</u>, and <u>3</u> are very air sensitive. Decomposition will also occur in a stream of dry argon gas or if the solids are subjected to low pressure (10^{-3} torr) for several hours. This feature made accurate elemental analysis difficult. <u>1</u>, <u>2</u>, and <u>3</u> can be stored in sealed nitrogen filled ampoules for several months without significant decomposition. Possibly a partial pressure of donor ligand is needed for a stable atmosphere.

These compounds will decompose in a dry box if left in an open container. The solids turn grey on the surface in 24 hours. The grey residue is insoluble in all common organic solvents and was not analyzed. <u>1</u>, <u>2</u>, and <u>3</u> are soluble in aromatic solvents and methylene chloride, insoluble in alkanes and decompose in chloroform.

4 is a turquoise solid and also air sensitive, but to a lesser extent (qualitative judgement). Decomposition occurs before melting producing a light brown solid. The complex is soluble in methylene chloride producing a red-violet colored solution. If this solvent is removed via vacuo, a red-violet solid begins to form on the cold walls of the schlenk tube. As the walls warm, the color returns to turquoise. This indicates solvation by methylene chloride. 4 is insoluble in aromatic solvents and decomposes in chloroform.

Repeated attempts to obtain crystals suitable for single crystal x-ray diffraction studies failed for all four compounds.

The table below summarizes properties not covered above.

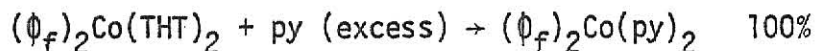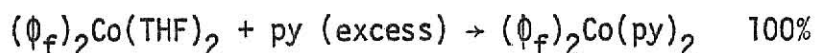| cmpd	m. pt. (°C)	color	solvent for prep.	solubility
1	124	blue	tol	tol, THF, CH_2Cl_2
2	86	blue	CH_2Cl_2	tol, THT, CH_2Cl_2
3	152.5	blue	tol	tol, py, CH_2Cl_2
4	156(dec)	turquoise	tol	CH_2Cl_2

Yields for all four compounds were > 90%.

Visible Spectra

High spin d^7 systems have no crystal field stabilization energy advantage between octahedral and tetrahedral geometries. Octahedral complexes usually have extinction coefficients two orders of magnitude less than tetrahedral complexes. Octahedral complexes generally are red or pink whereas tetrahedral complexes are intense blue. 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 ca. 300 to 900 are expected.[32]

The spectra were obtained in methylene chloride. All four complexes obey Beer's Law. The spectra are reproduced in Figure I(A-D) and values tabulated in Table 1. As can be seen, the experimental results correlate well with theoretical prediction.

A qualitative experiment was possible because of the large spectral differences between compounds 1, 2 and 3. Several drops of pyridine were added to solutions of 1 and 2 (carried out in a dry box). The visible spectrum was scanned and showed quantitative formation of 3, the bis(pyridine) adduct. Thus the adducts themselves possess very labile ligands.

$$(\phi_f)_2Co(THF)_2 + py \text{ (excess)} \rightarrow (\phi_f)_2Co(py)_2 \quad 100\%$$

$$(\phi_f)_2Co(THT)_2 + py \text{ (excess)} \rightarrow (\phi_f)_2Co(py)_2 \quad 100\%$$

Addition of THF to solutions of $(\phi_f)_2Co(THT)_2$ and THT to solutions of $(\phi_f)_2Co(THF)_2$ did not yield information on oxygen vs sulfur binding preference. In both cases the resulting spectrum was not a superposition of the spectra of either starting complex.

Ligand redistribution may occur but the difficulty (impossibility) of preparing authentic samples makes this very tentative.
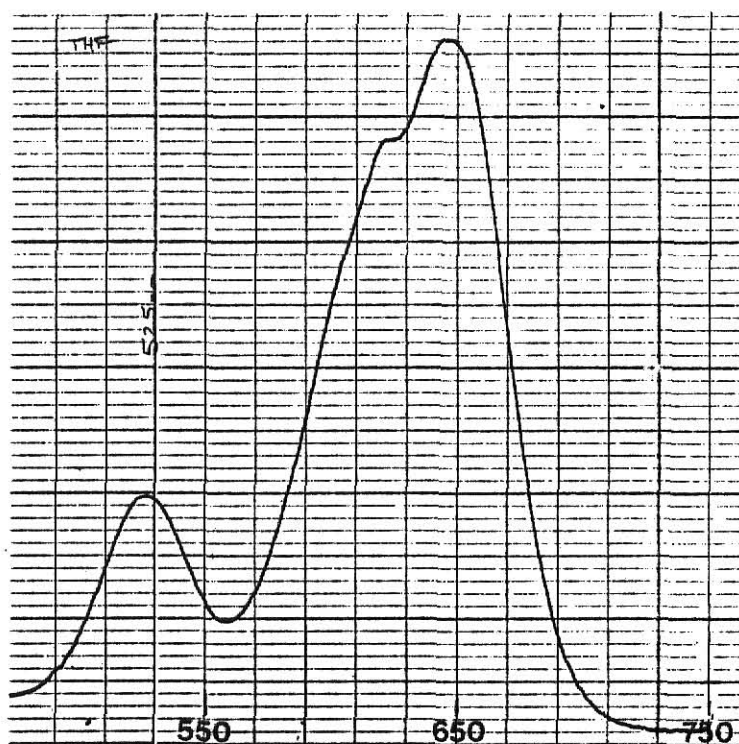
Fig. 1-A Visible Spectrum of Bis(pentafluorophenyl)
bis(tetrahydrofuran)cobalt(II)

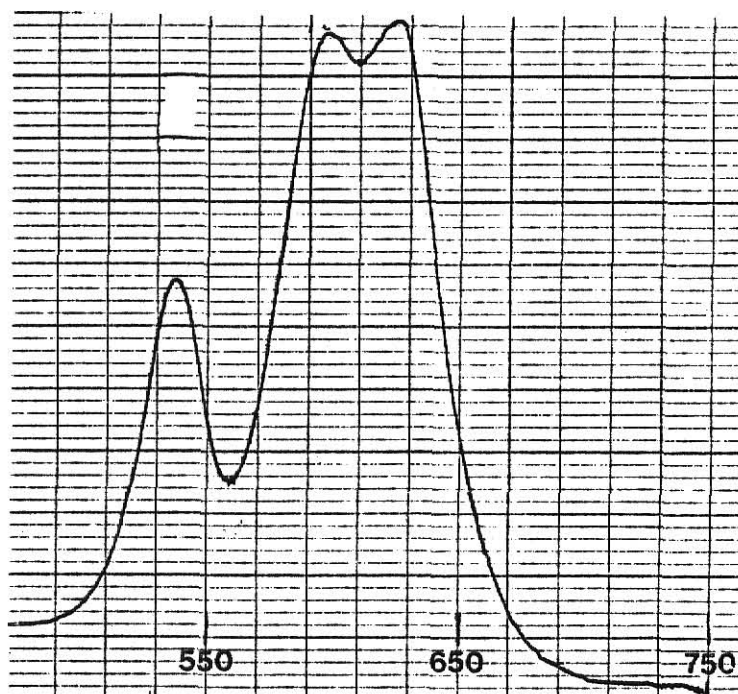Fig. 1-B Visible Spectrum of Bis(pentafluorophenyl)
bis(pyridine)cobalt(II)

Fig. 1-D Visible Spectrum of Bis(pentafluoro-
phenyl)bis(tetrahydrothiophene)cobalt(II)
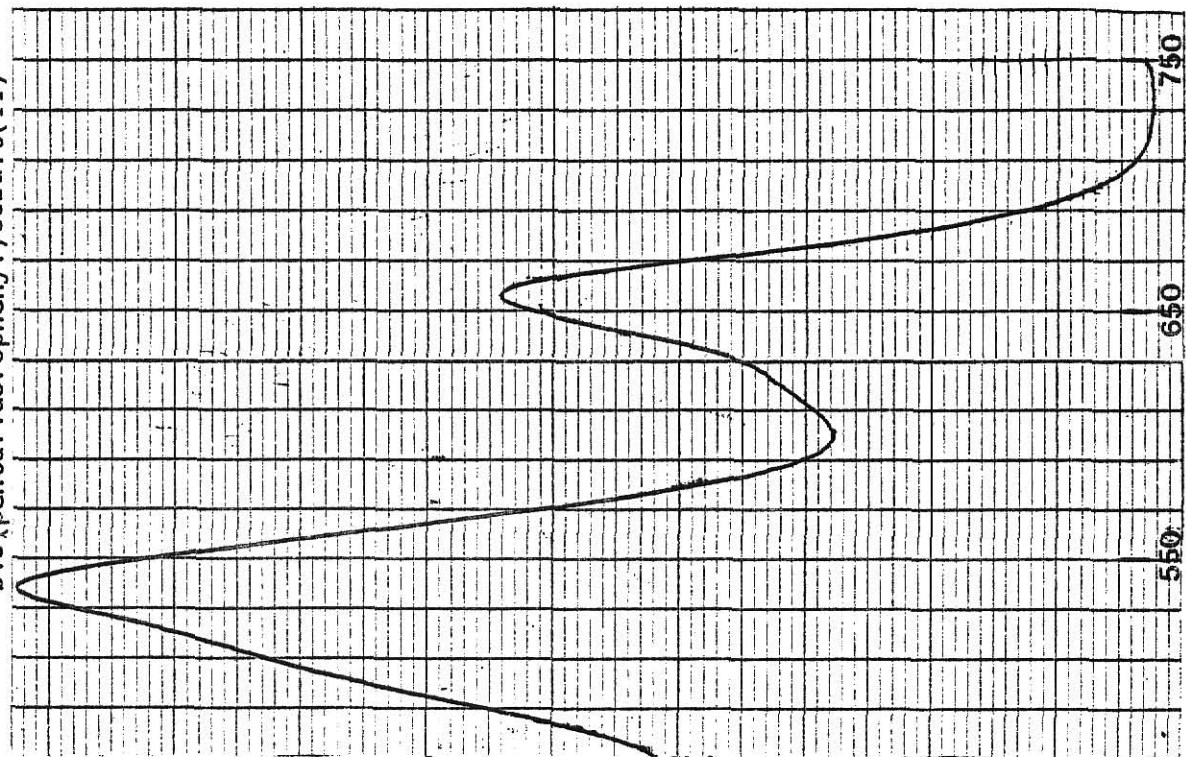
Fig. 1-C Visible Spectrum of (2,2'-bipyridine)
bis(pentafluorophenyl)cobalt(II)
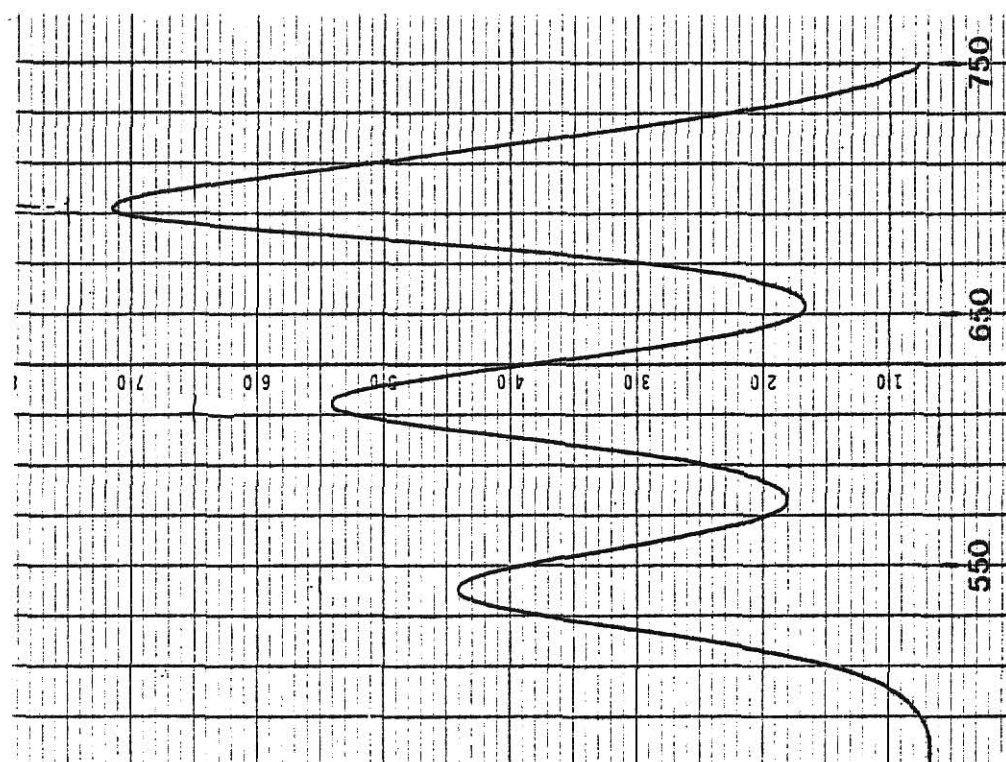
Table 1 Visible Spectra[a] (nm) $\varepsilon = M^{-1}cm^{-1}$

Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II)

     645 nm (ε = 485)

     620 nm (ε = 411)

     525 nm (ε = 153)

Bis(pentafluorophenyl)bis(pyridine)cobalt(II)

     635 nm (ε = 706)

     605 nm (ε = 703)

     537 nm (ε = 425)

Bis(pentafluorophenyl)bis(tetrahydrothiophene)cobalt(II)

     704 nm (ε = 676)

     625 nm (ε = 519)

     556 nm (ε = 400)   .

(2,2'-bipyridine)bis(pentafluorophenyl)cobalt(II)

     665 nm (ε = 642)

     538 nm (ε = 1105)

[a]CH_2Cl_2 solvent

Infrared Spectra

Coordinated pentafluorophenyl moieties exhibit several diagnostic vibrational modes in the mid infrared region. Bands at ca. 1500, 1050 and 950 cm^{-1} indicate coordination. A band at 800 cm^{-1} has been used to confirm cis, trans isomers of several mono- and bis-pentafluorophenyl palladium and platinum complexes which are square planar. The band splits into two for cis complexes; a single band is observed for mono-pentafluorophenyl and no band is present for trans complexes.[33] Compounds 1, 2, 3, and 4 all possess intense bands at ca. 1500, 1050, and 950 cm^{-1} (Fig. 2A-D). No absorption occurs at 800 cm^{-1}. In light of elemental analysis, the visible spectra and basic bonding theory[32] (vide supra), we must conclude the diagnostic value of the 800 cm^{-1} band is not applicable to bis pentafluorophenyl ligands in a tetrahedral geometry.

The C-S ring stretch of tetrahydrothiophene occurs at 683 cm^{-1} for the free molecule and shifts to 660 - 670 cm^{-1} upon coordination.[34] The infrared spectrum of bis(pentafluorophenyl)bis(tetrahydrothiophene) cobalt(II) (Fig. 2-C) has a weak band at 670 cm^{-1} which is assigned to the perturbed ring stretch. Infrared spectra are included for the nickel analogs (Fig. 3A-D).

The mid infrared region for the cobalt and nickel derivatives are virtually identical. Frequently , very small frequency shifts are observed for a molecule upon complexation to a metal center.[35] The spectra usually are mere superpositions of the individual ligands. One major difference should be pointed out. Nickel complexes are square planar and exhibit absorption at ca. 800 cm^{-1}. A single band appears near 800 cm^{-1} for bis-THF, THT and py adducts. This is not expected as all three compounds appear to be trans. An incomplete structural analysis on the THF complex

indicates a <u>trans</u> configuration.[36] A split band is present at 800 cm^{-1}

in the spectrum of the bipy derivative. Since bipy can only be bound

<u>cis</u>, this result is consistent.

The spectral results are tabulated in Table 2.

Fig. 2-A Infrared Spectrum of Bis(pentafluorophenyl)bis(tetrahydrofuran)
cobalt(II) (KBr)

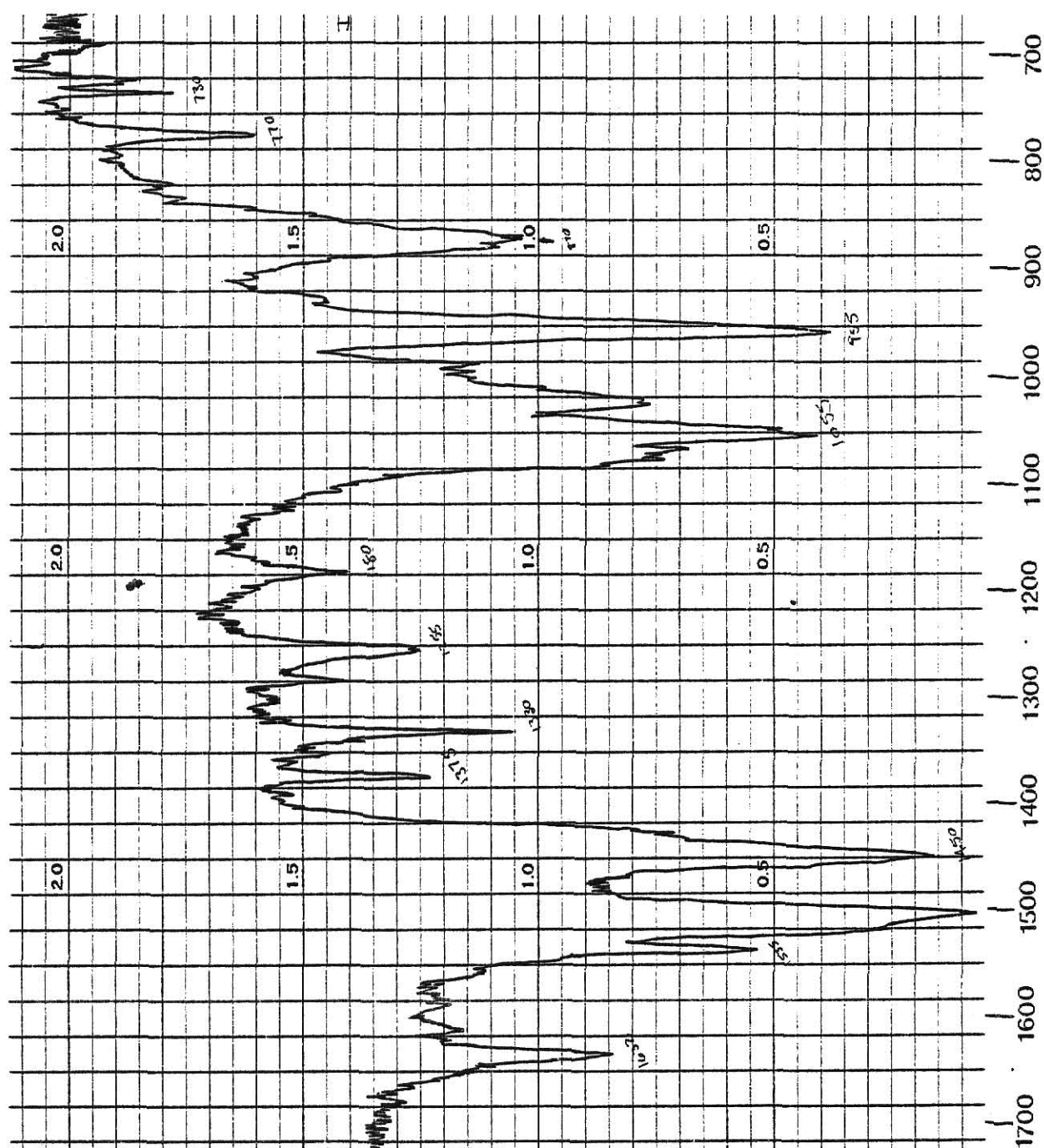Fig. 2-B Infrared Spectrum of Bis(pentafluorophenyl)bis(pyridine)
cobalt(II), (Nujol)

38

Fig. 2-C   Infrared Spectrum of Bis(pentafluorophenyl)bis(tetrahydrothiophene) cobalt(II), (Nujol)

Fig. 2-D Infrared Spectrum of (2,2'-bipyridine)bis(pentafluorophenyl)
cobalt(II), (Nujol)

Fig. 3-A   Infrared Spectrum of Bis(pentafluorophenyl)bis(tetrahydrofuran)
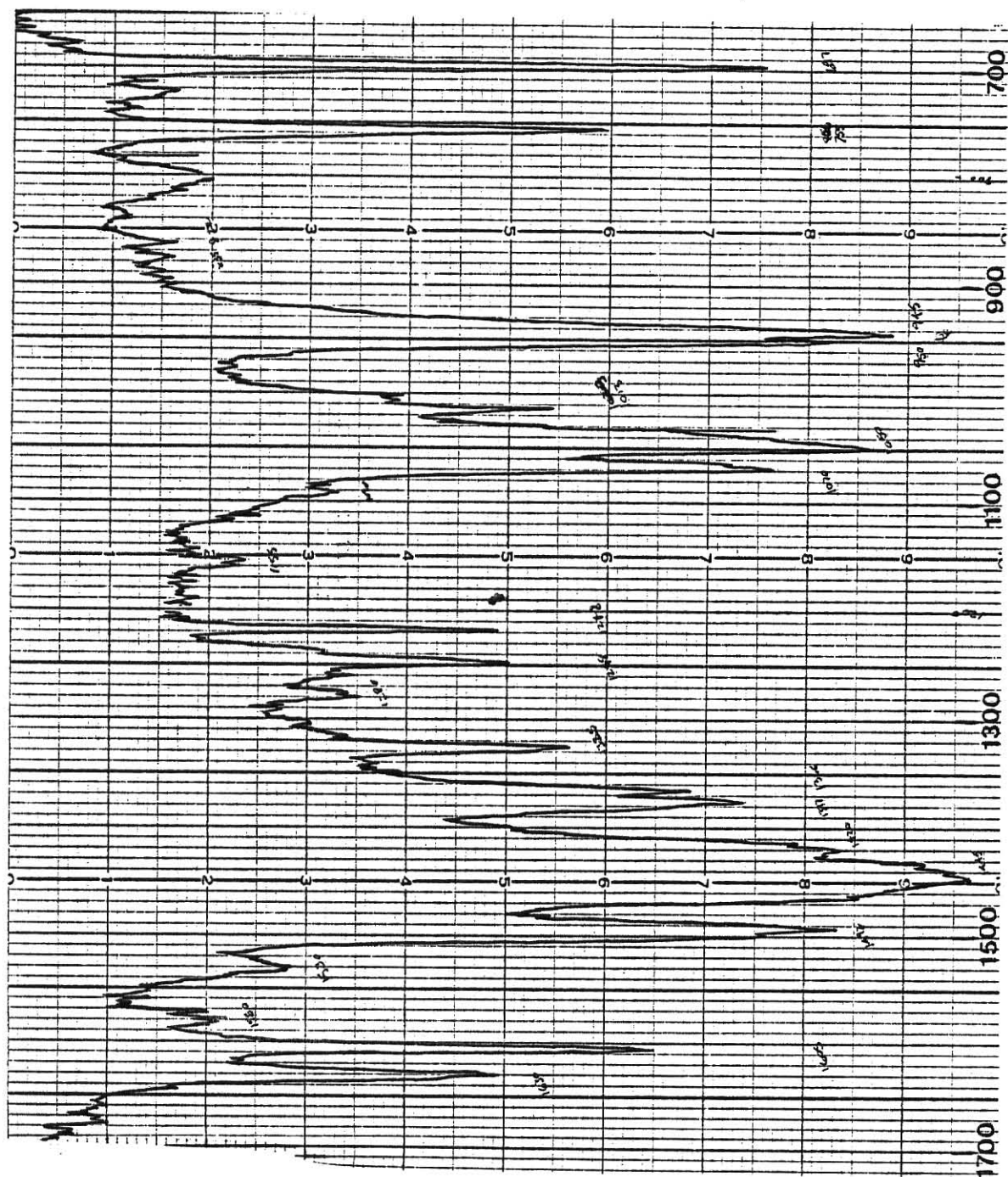nickel(II), (Nujol)

Fig. 3-B   Infrared Spectrum of Bis(pentafluorophenyl)bis(pyridine)nickel
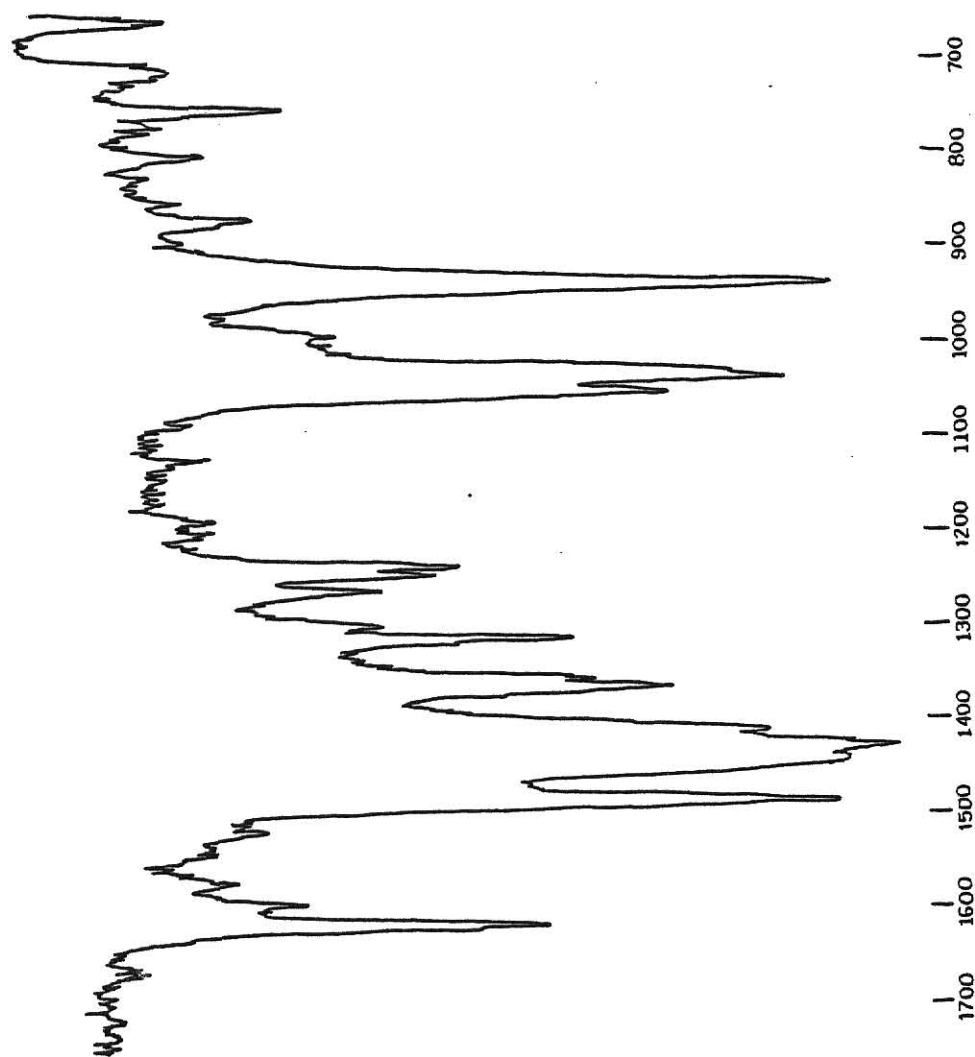(II), (Nujol)

Fig. 3-C Infrared Spectrum of Bis(pentafluorophenyl)bis(tetrahydrothiophene) nickel(II), (Nujol)
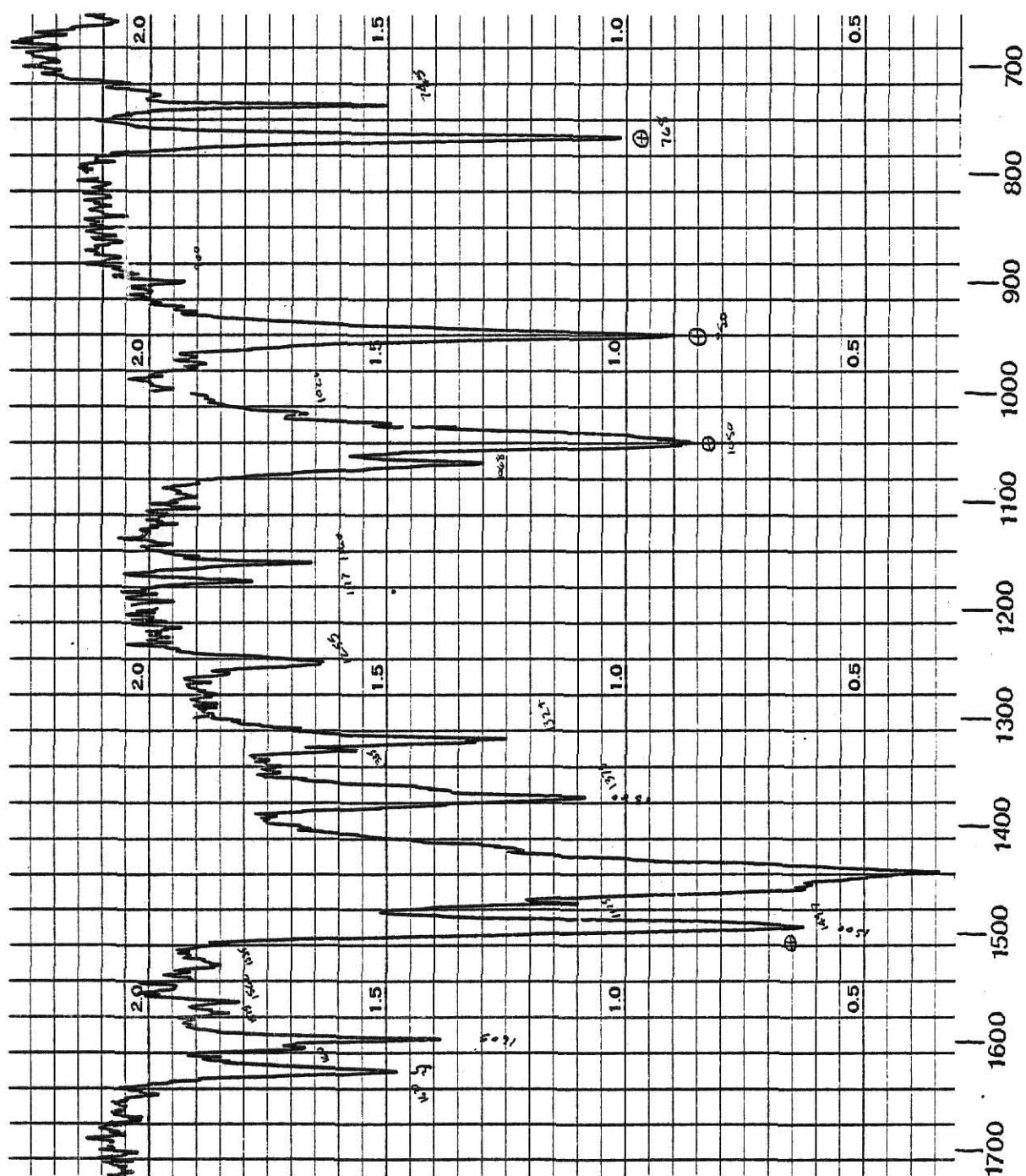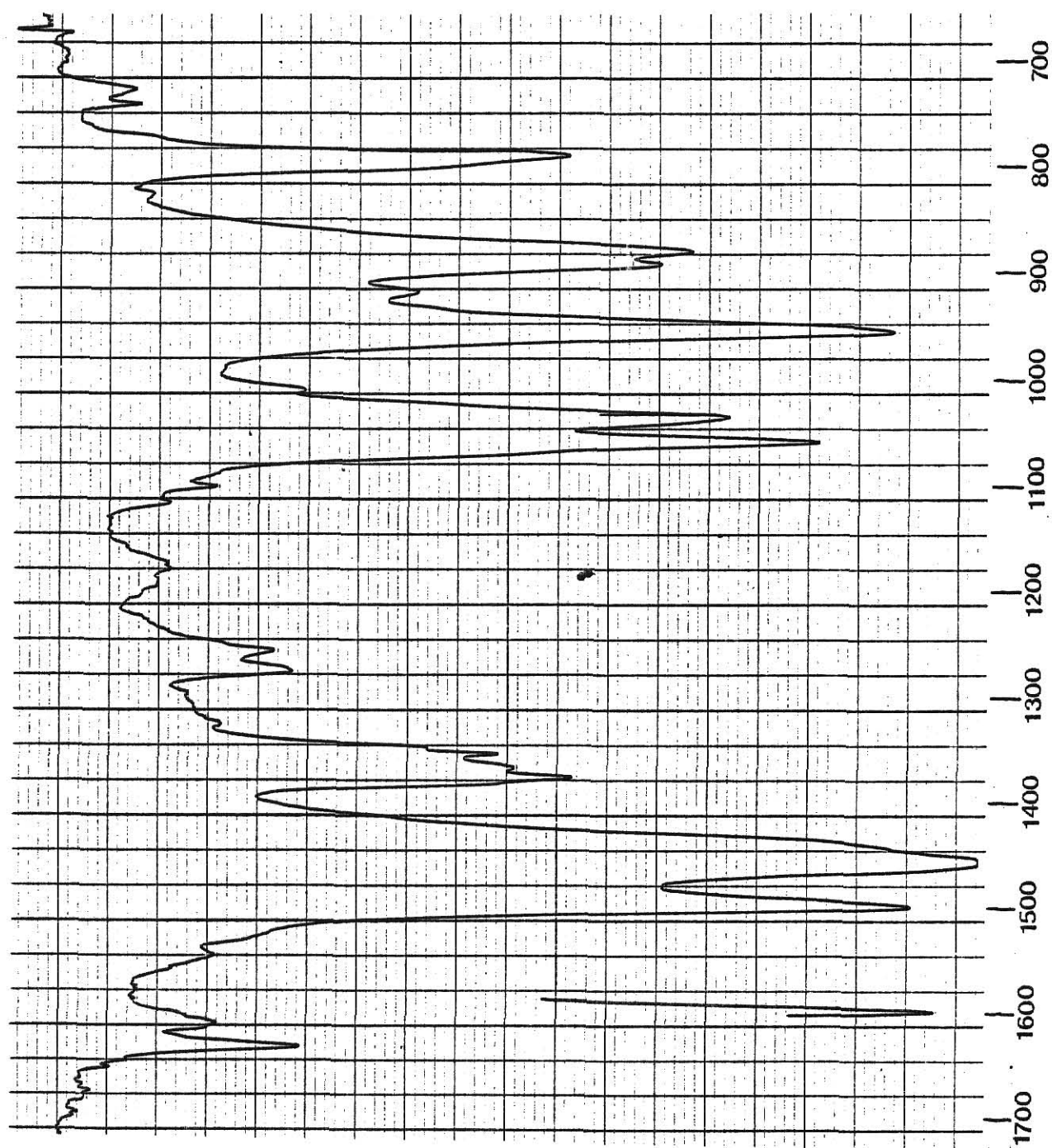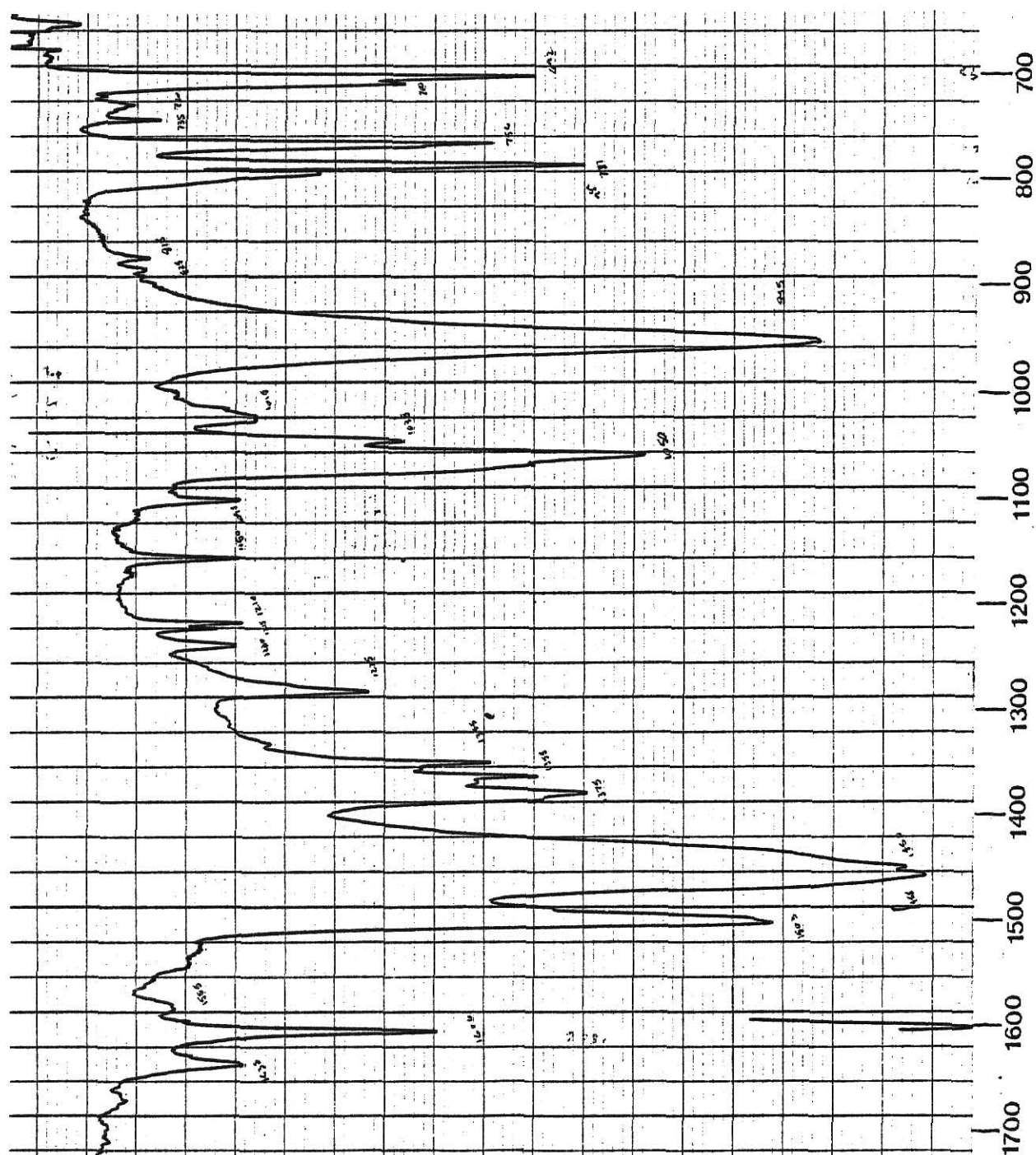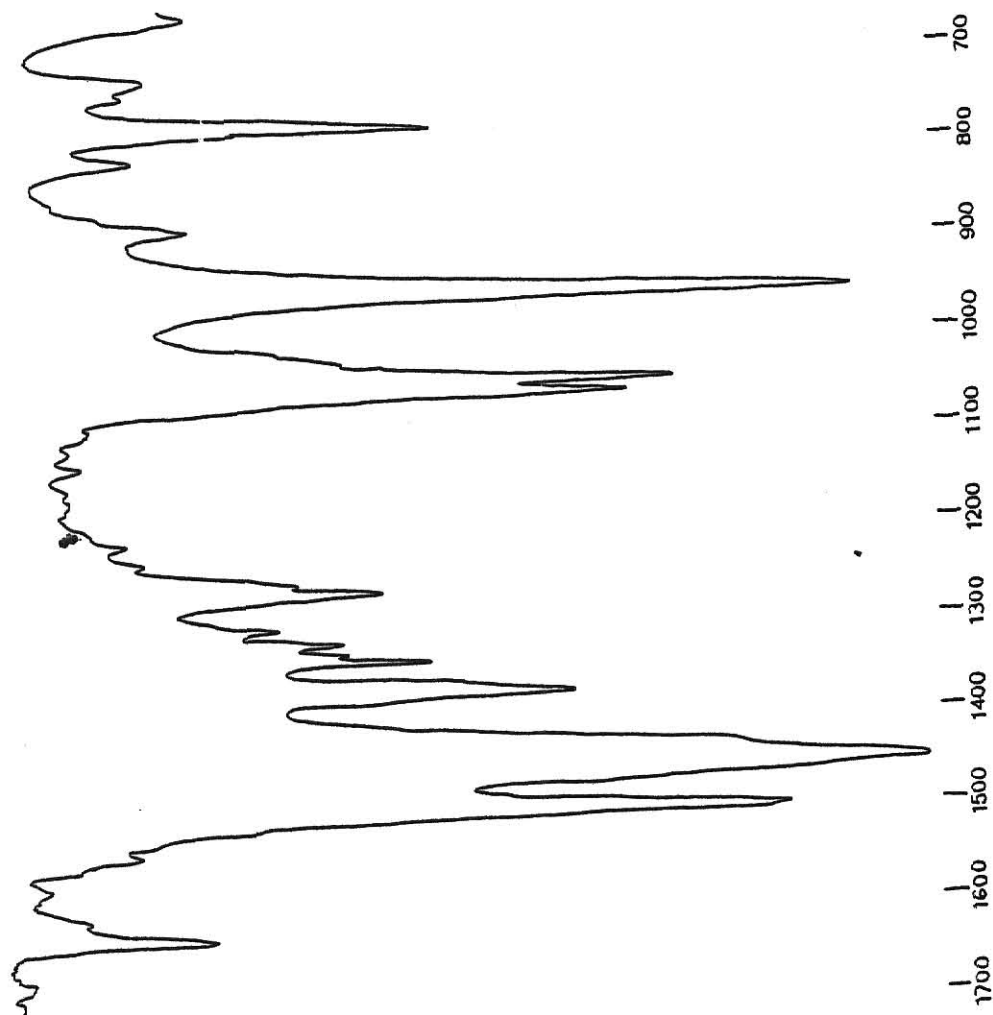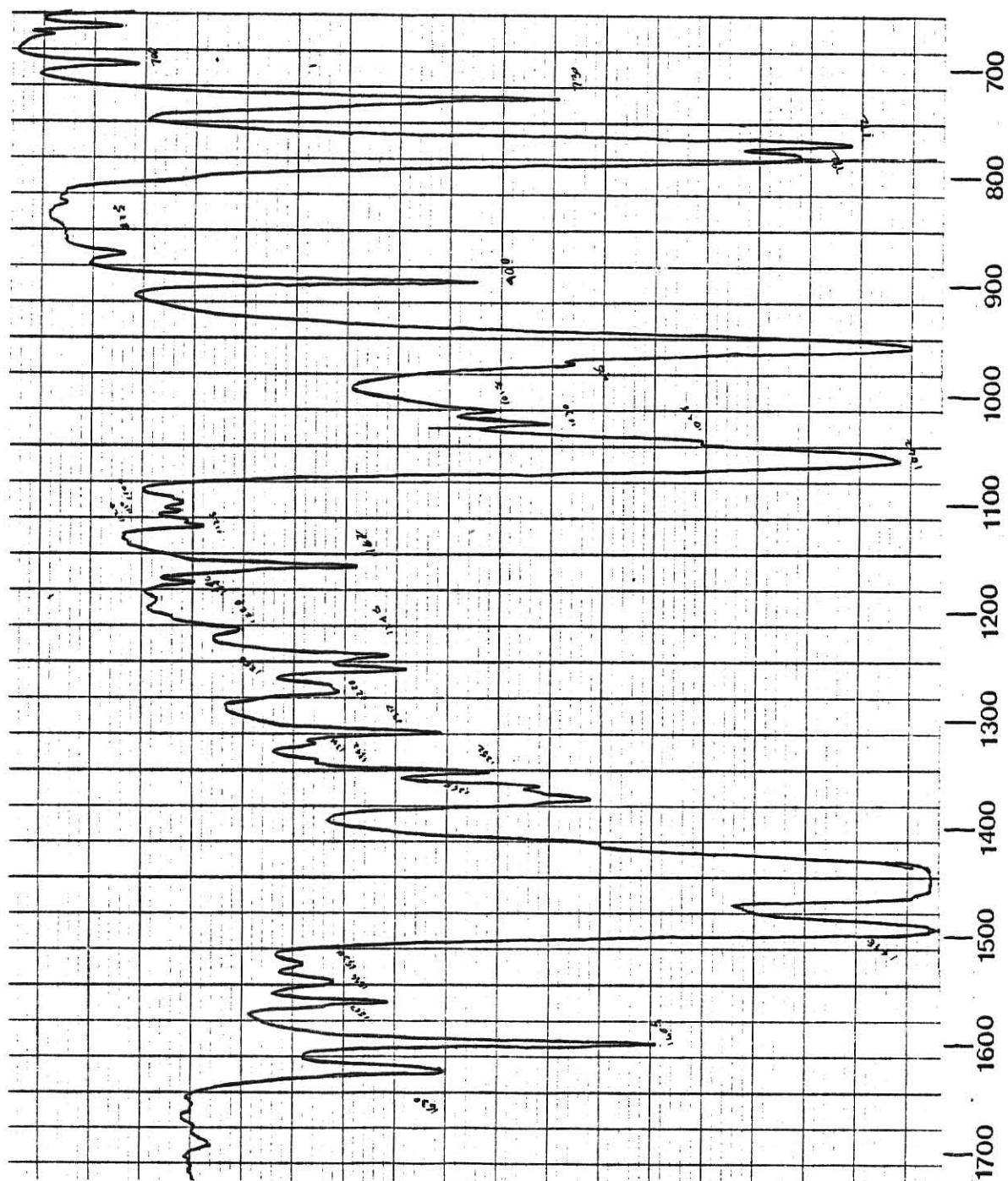
Fig. 3-D Infrared Spectrum of (2,2'-bipyridine)bis(pentafluorophenyl) nickel(II), (Nujol)

Table 2 Infrared Spectra of Cobalt and Nickel Derivatives (in cm^{-1})

Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II), (KBr)

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.

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.

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.

(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.

Bis(pentafluorophenyl)bis(tetrahydrofuran)nickel(II)[15], (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.

Bis(pentafluorophenyl)bis(tetrahydrothiphene)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.

Bis(pentafluorophenyl)bis(pyridine)nickel(II),[27] (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 m, 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.

(2,2'-bipyridine)bis(pentafluorophenyl)nickel(II),[28] (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.

Far Infrared Spectra

Stability differences between the cobalt and nickel compounds being discussed are great. The cobalt compounds are very air sensitive whereas the nickel analogs are very air stable. In fact, the ether and thioether nickel adducts may be handled in air for several hours. The nitrogen donor adducts of nickel are indefinitely air and moisture stable.

We obtained far infrared data in hopes of identifying metal ligand vibrations to quantify differences in bond strength. The spectra are reproduced in Fig. 4A-H and tabulated in Table 3.

For A_2B_2M complexes, group theory predicts the following number of infrared active metal ligand stretches.[37]

cmpd	Geometry	(M-A)	(M-B)
trans-A_2B_2M	sq. pl.	1	1
cis-A_2B_2M	sq. pl.	2	2
A_2B_2M	tetrahedral	2	2

The similarity of all cobalt derivatives was unexpected. Variations of intensity are seen but all bands occur at nearly the same frequency. The same result was obtained for the nickel derivatives. This strongly suggests the bands are ligand vibrations. Activation of infrared inactive bands can occur upon complexation.[38] One can immediately see from the complexity of the spectra that no pure metal-ligand vibration is obvious. Metal-aryl vibrations are very weak and rarely seen.[35] Bromopentafluoro-benzene has infrared absorptions as low as 218 cm^{-1}. Thus the penta-fluorophenyl ligand could be the cause of the complex spectra.

Comparison between cobalt and nickel compounds yields no information helpful to band assignment. The spectra of nickel adducts is in general less complex than cobalt. Assembling molecular models is instructive.

The square planar geometry possessed by the nickel derivatives allows the planes passing through the ligands to be perpendicular to the metal ligand bond vectors. Steric interactions are minimized. However, the cobalt analogs are very crowded. The model is so complex that this author refrains from attempting to draw them. The crowding of the ligands in a tetrahedral arrangement may activate modes of ligand vibration which square planar arrangements do not.

Bipyridine derivatives of nickel and cobalt exhibit bands below 200 cm^{-1} (Fig. 4I,J). Nickel and cobalt _tris_-bipy complexes have metal-nitrogen vibrations _ca_ 250 cm^{-1}.[38] Possibly a very low energy mode has been shifted into the infrared region; the rotational mode as the rings try to become perpendicular as an example. Interestingly the nickel derivative has significantly higher energy absorptions which indicates the mode(s) is affected by complex stability.

Useful information was obtained in the case of nitrogen adducts. A band at 404 cm^{-1} for free pyridine and bipyridine shifts to _ca_. 425 cm^{-1} upon coordination through nitrogen.[35] The shift was observed and confirms metal-nitrogen bonding (opposed to a heteroatom arene metal bond).

48
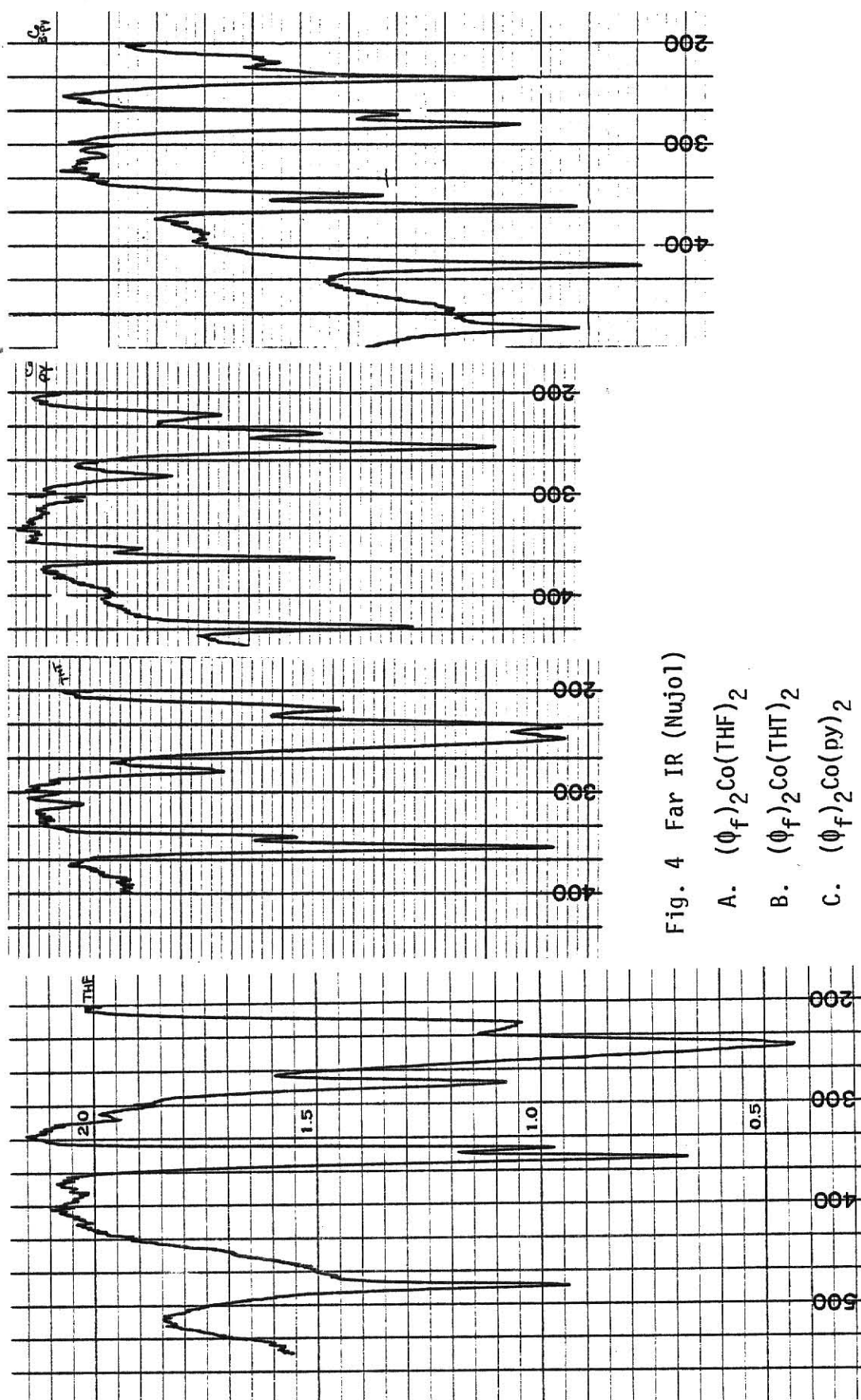
Fig. 4 Far IR (Nujol)

A. $(\phi_f)_2Co(THF)_2$

B. $(\phi_f)_2Co(THT)_2$

C. $(\phi_f)_2Co(py)_2$

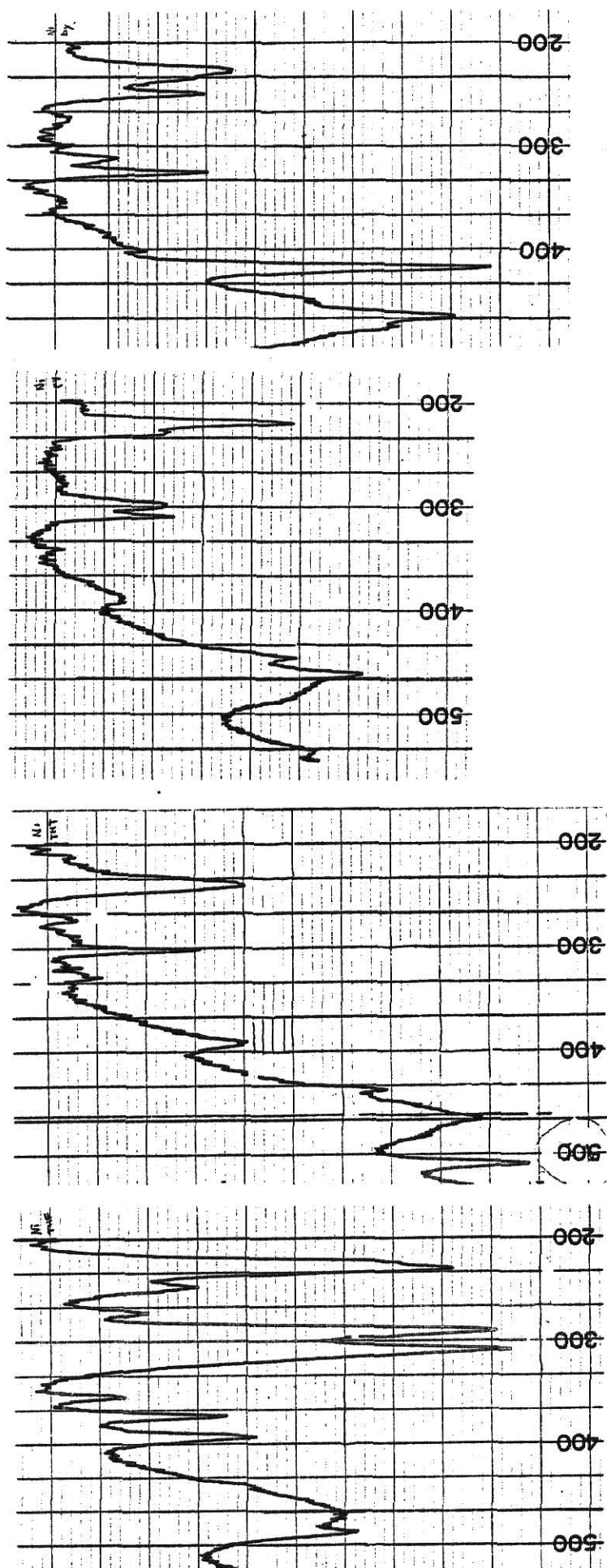D. $(\phi_f)_2Co(bipy)$

Fig. 4 cont. Far IR (Nujol)

E. $(\phi_f)_2Ni(THF)_2$

F. $(\phi_f)_2Ni(THT)_2$

G. $(\phi_f)_2Ni(py)_2$

H. $(\phi_f)_2Ni(bipy)$

Table 3 Far Infrared Spectra of Cobalt and Nickel Derivatives

Bis(pentafluorophenyl)bis(tetrahydrofuran)cobalt(II), (Nujol)

     600 w, 482 m, 354 s, 345 m, 270 m, 244 s, 220 n.

Bis(pentafluorophenyl)bis(tetrahydrothiophene)cobalt(II), (Nujol)

     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)

     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)

     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), (Nujol)

     395 m, 375 m, 356 w, 310 s, 293 s, 273 w, 248 w, 230 s.

Bis(pentafluorophenyl)bis(tetrahydrothiophene)nickel(II), (Nujol)

     514 m, 445 vw, 390 m, 330 vw, 300 m, 275 vw, 240 m.

Bis(pentafluorophenyl)bis(pyridine)nickel(II),[27] (Nujol)

     465 s, 450 w, 390 w, 318 m, 300 m, 230 sh, 224 s.

(2,2'-bipyridine)bis(pentafluorophenyl)nickel(II),[28] (Nujol)

     465 s, 418 s, 326 m, 312 w, 275 vw, 247 m, 233 sh, 225 m, 164 m,
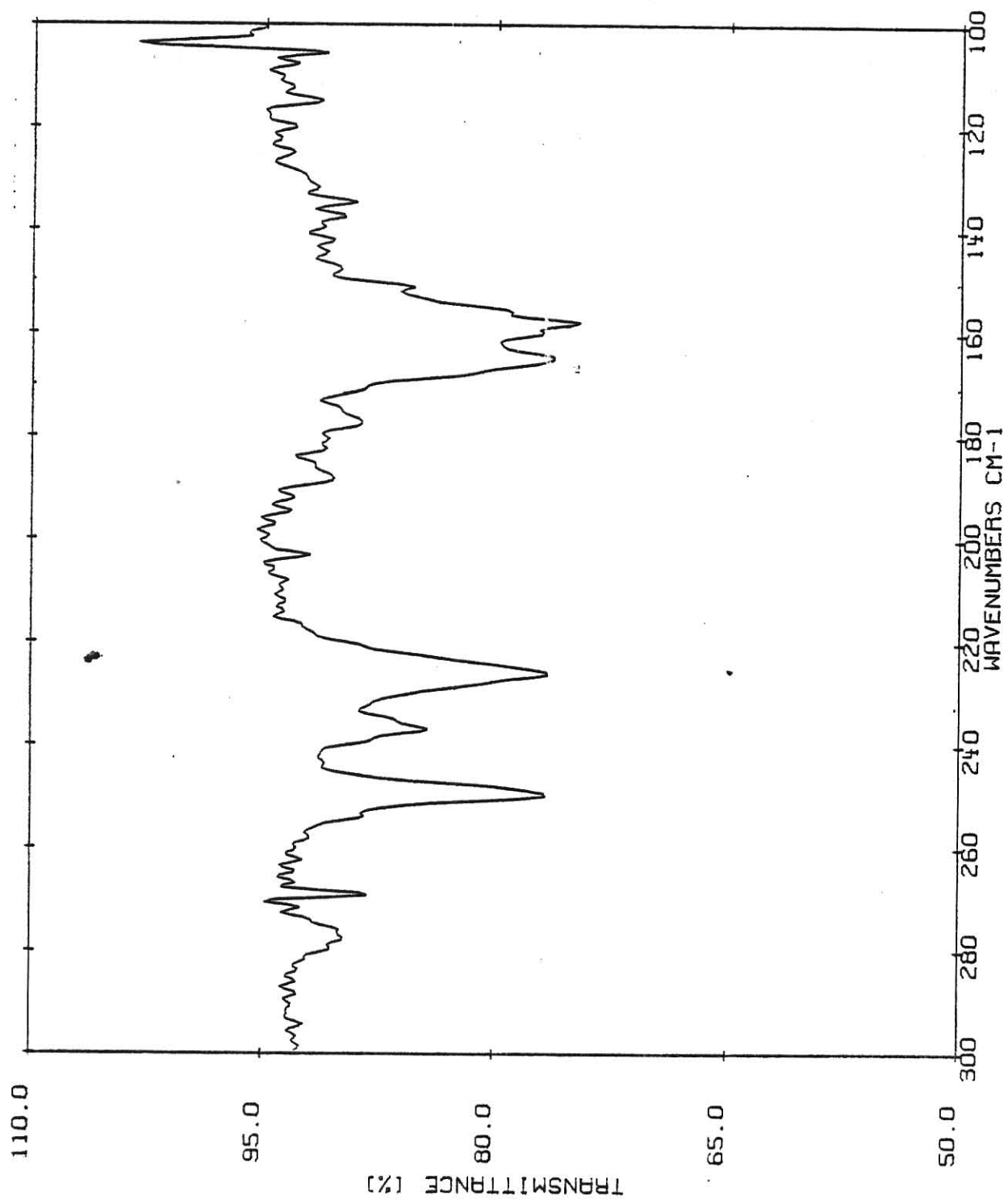158 m.

Fig. 4-I Far Infrared Spectrum of (2,2'-bipyridine)bis(pentafluorophenyl)
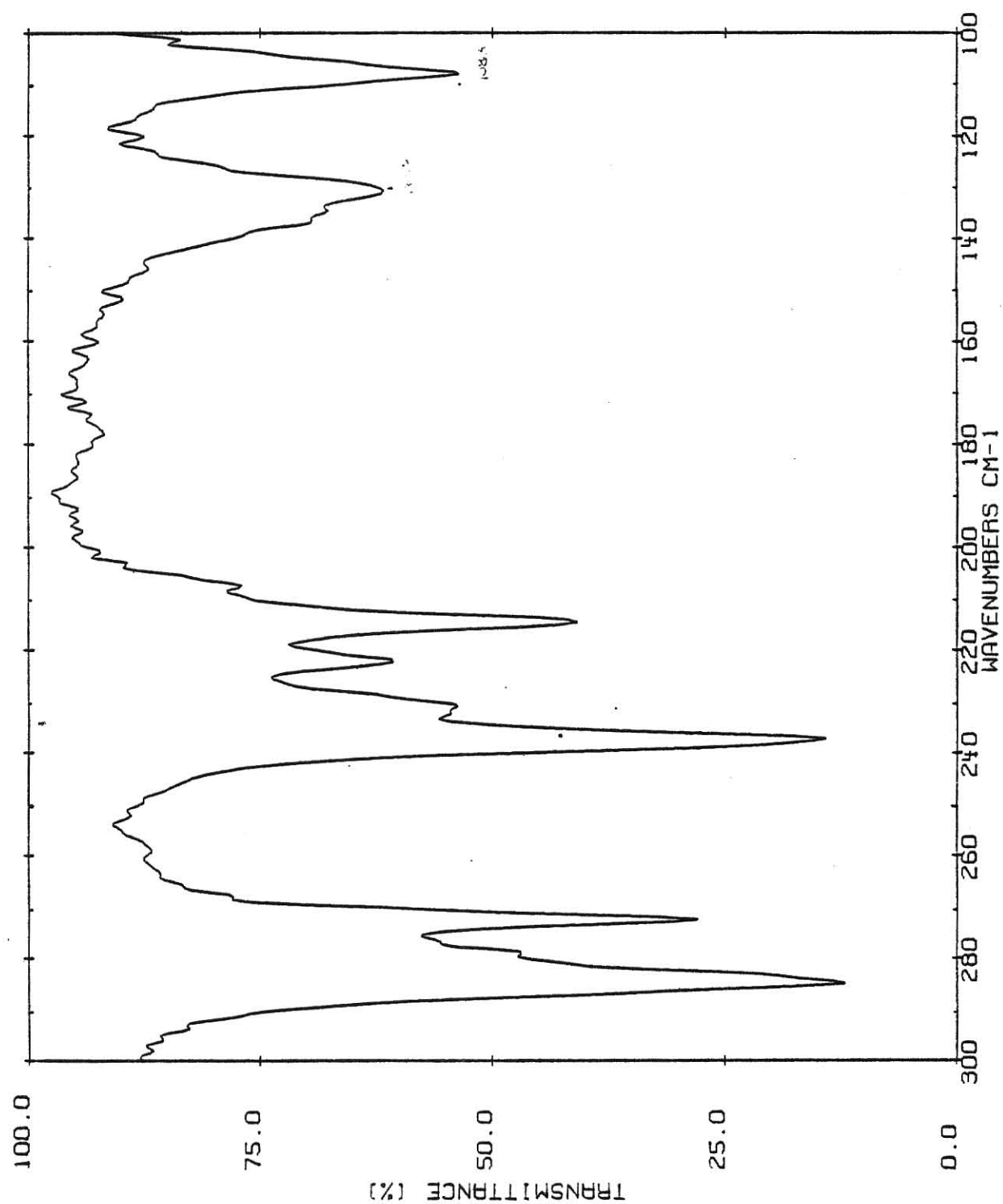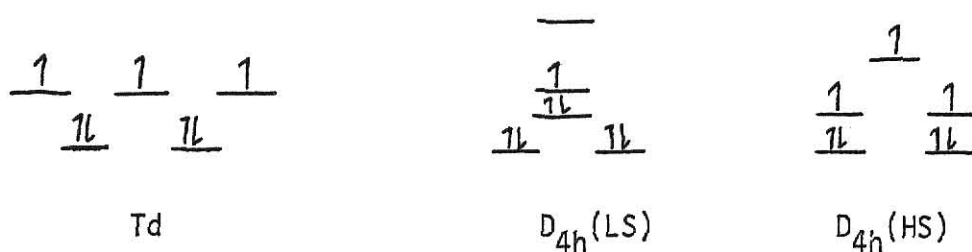nickel(II), (Nujol)

Fig. 4-J Far Infrared Spectrum of (2,2'-bipyridine)bis(pentafluorophenyl)
cobalt(II), (Nujol)

Magnetic Measurements

Two geometries are possible for four coordinate d^7 metal centers: tetrahedral and square planar[32] eg.

Tetrahedral compounds are redundant for high spin-low spin assignments. There are always three unpaired electrons. Square planar compounds on the other hand have the possibility to exist in high spin or low spin configurations. High spin square planar compounds are not known. Use of the Angular Overlap Model[39] 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). This is always found true. Therefore, the magnetic susceptibility is very strong evidence for T_d vs D_{4h} geometry. One unpaired electron gives values ca. 2 BM while three unpaired electrons give values greater than 3 BM and usually close to 4 BM.

Magnetic susceptibilities were obtained for cobalt donor adducts by the Evans NMR Method.[29] The results are tabulated in Table 4.

Table 4

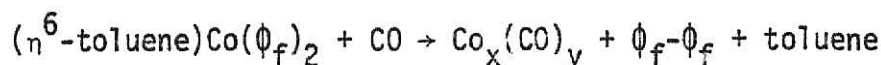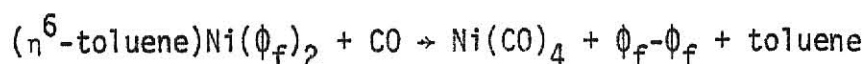| compound	μ_{eff}(BM)	solvent/external standard
$(\phi_f)_2Co(THF)_2$	3.23	C_6D_6/TMS
$(\phi_f)_2Co(THT)_2$	3.96	C_6D_6/TMS
$(\phi_f)_2Co(py)_2$	3.48	C_6D_6/TMS
$(\phi_f)_2Co(bipy)$	3.84	CH_2Cl_2/CH_2Cl_2

Diamagnetic corrections were applied.[31] All compounds were assumed to obey the Curie Law. The results are consistent for cobalt(II) compounds with T_d geometry. Cotton and Holm[40] obtained similar values for bis(halogen)-bis(isocyanide)cobalt(II) compounds.

Figure 5 shows a typical experimental result. The contact shift induced by solute paramagnetism is measured, in hertz, from the external standard. Accurate concentrations must be known, therefore the solution volume is corrected for the temperature difference between ambient and probe temperature.[30] The measured value, in hertz, is used to calculate μ_{eff}.[29]

Faraday measurements failed because of the sensitivity of the compounds to air and moisture.

B. Reaction with Carbon Monoxide

Reaction of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), in solution or solid state, with carbon monoxide cause complete reductive elimination of the pentafluorophenyl ligands producing decafluorobiphenyl and cobalt carbonyl clusters. The reaction is similar to the nickel species:[15]

$$(\eta^6\text{-toluene})Ni(\phi_f)_2 + CO \rightarrow Ni(CO)_4 + \phi_f\text{-}\phi_f + \text{toluene}$$

$$(\eta^6\text{-toluene})Co(\phi_f)_2 + CO \rightarrow Co_x(CO)_y + \phi_f\text{-}\phi_f + \text{toluene}$$

Infrared analysis of the reaction product (thick brown oil) showed $\nu(CO)$ bands at 2065 vs, 2045 vs, 2030 broad vs corresponding to terminally bound CO and a strong broad band at 1860 cm^{-1} corresponding to bridging CO. The spectrum also confirmed the absence of coordinated pentafluorophenyl ligands (i.e. no bands at 1050 cm^{-1}, 950 cm^{-1} or 800 cm^{-1}). Because of the variety of cluster compounds formed by cobalt and the problem of separating them from each other and trapped decafluorobiphenyl, the oil was not characterized.
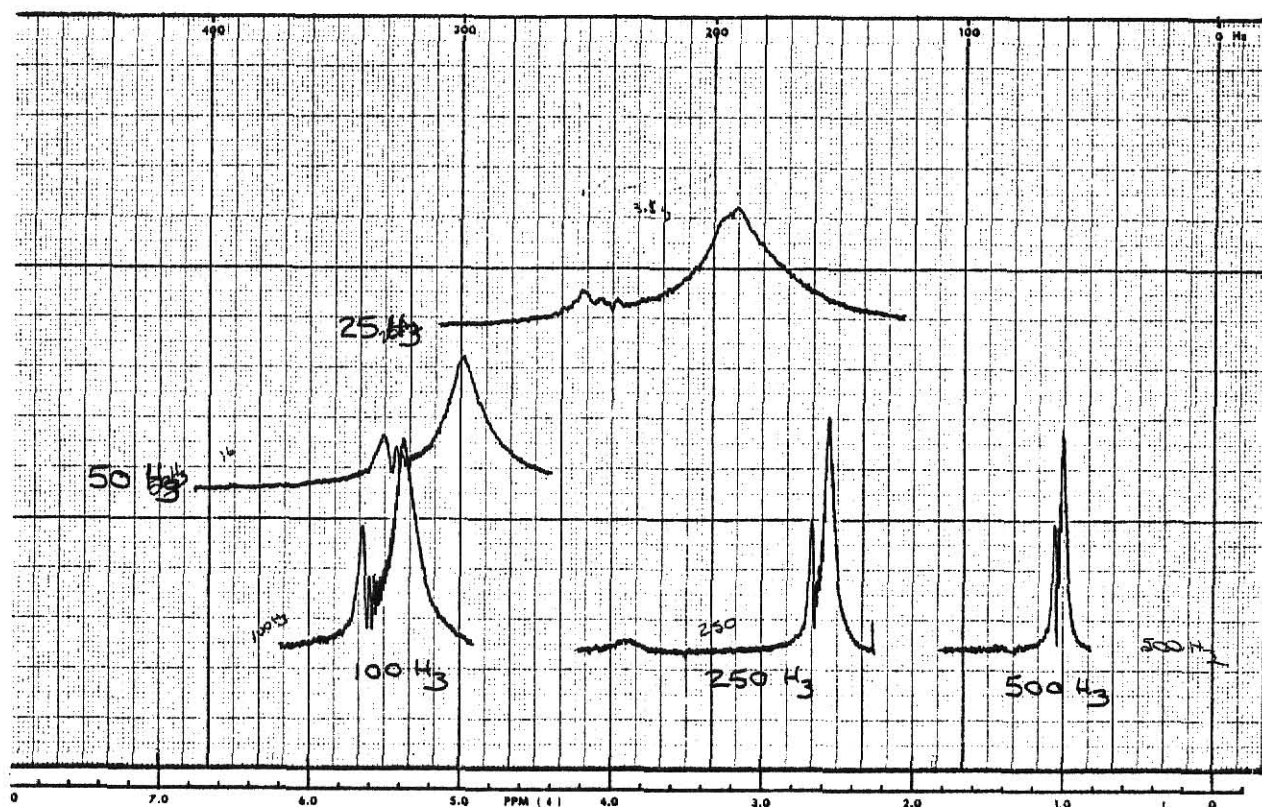
Fig. 5   A typical spectrum using the Evans NMR Method. The smaller
resonance is external TMS and the more intense, broad peak is
TMS shifted by the paramagnetic solute.

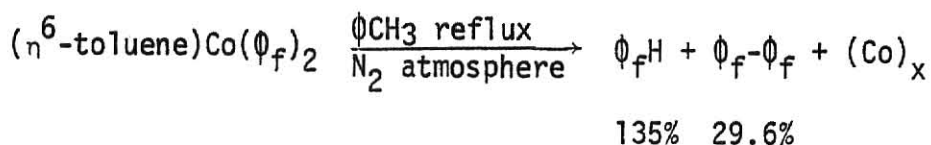## C. Decomposition of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II)

1. Pyrolysis

When crystals of the cobalt arene complex are heated to ca. 150°C decomposition takes place. Reductive elimination of the pentafluorophenyl groups producing decafluorobiphenyl (93% by GLC), release of toluene (100% by GLC) and formation of cobalt particles:

$$(\eta^6\text{-toluene})Co(\phi_f)_2 \xrightarrow[\Delta]{\text{solid state}} \phi_f\text{-}\phi_f + \bigcirc + (Co)_n$$
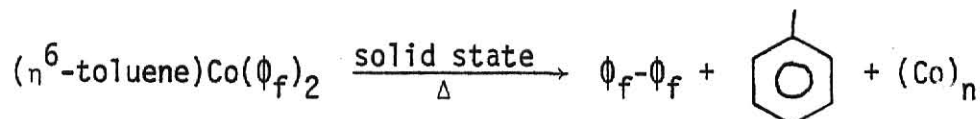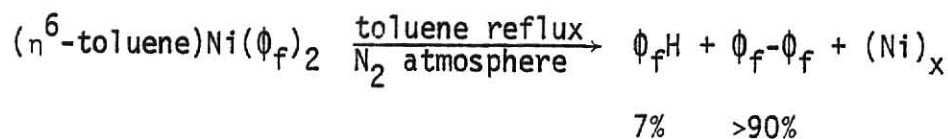
2. In refluxing toluene

A solution of cobalt arene complex was refluxed in toluene under a nitrogen atmosphere for three days. Thermal stability of the complex is excellent. GLC analysis of the reaction medium showed pentafluorobenzene (135%) and decafluorobiphenyl (29.6%).

$$(\eta^6\text{-toluene})Co(\phi_f)_2 \xrightarrow[N_2 \text{ atmosphere}]{\phi CH_3 \text{ reflux}} \phi_f H + \phi_f\text{-}\phi_f + (Co)_x$$
$$135\% \quad 29.6\%$$

Comparison to the nickel analog shows similar reactivity for the pyrolysis experiment (99% decafluorobiphenyl for nickel) but great differences in the solution decomposition study. Only 7% pentafluorobenzene was detected for the nickel complex:[15]

$$(\eta^6\text{-toluene})Ni(\phi_f)_2 \xrightarrow[N_2 \text{ atmosphere}]{\text{toluene reflux}} \phi_f H + \phi_f\text{-}\phi_f + (Ni)_x$$
$$7\% \quad >90\%$$

Apparently the cobalt species undergoes a radical decomposition whereas the nickel complex does not. The cobalt-aryl bond is longer and therefore probably weaker than the nickel-aryl bond[41] and more susceptible to homolytic cleavage.

$$Co-C\sigma \quad 1.931 \ \overset{\circ}{A}$$

$$Ni-C\sigma \quad 1.891 \ \overset{\circ}{A}$$

D. Reaction with Norbornadiene, 1,5-Cyclooctadiene and Propyne

Reactions of Bis(pentafluorophenyl)(η^6-toluene)nickel(II) with NBD and COD produced novel diene complexes.[15] However, no analogous cobalt(II) diene, or for that matter, any cobalt(II) diene complex is known to date. Reasons for this are not available in the literature.

Reaction of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II) with NBD produced a black polymeric solid. Extraction of the solid with toluene, decomposition of the toluene wash (faint red brown color) followed by GLC analysis showed no norbornadiene. Pentafluorobenzene (16%) was present. The polymer contained carbon-fluorine bonds (Infrared).
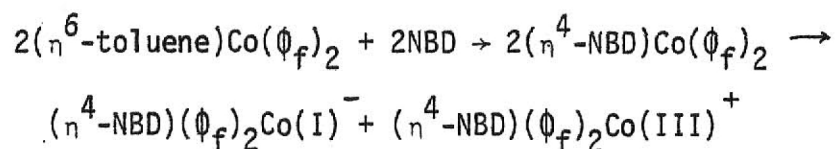
Reaction with 1,5-COD produced decomposition in the form of metallic cobalt and was not analyzed further.

Reaction with propyne resulted in polymer formation, pentafluorobenzene (22%), and small amounts of propyne trimers (1,2,4-trimethyl benzene, 12.8 %; 1,3,5-trimethylbenzene, 4.5%; based on complex). Infrared analysis of the polymer showed the presence of carbon-fluorine bonds.
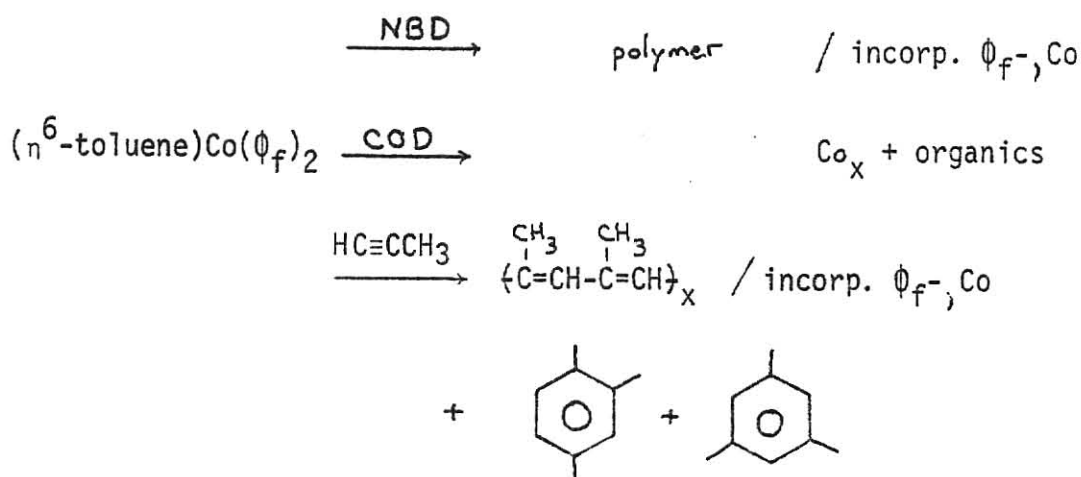
A radical process appears to be operative in the above reactions. The initiation step is unknown. This mode is prevalent for the cobalt complex in solution as observed in solution decomposition studies (vide supra).

Initial displacement of arene by diene followed by disproportionation producing a highly oxidizing cobalt(III) species is not likely because a small amount of unreacted arene complex was extracted from the NBD polymer:

$$2(\eta^6\text{-toluene})Co(\phi_f)_2 + 2NBD \rightarrow 2(\eta^4\text{-NBD})Co(\phi_f)_2 \longrightarrow$$
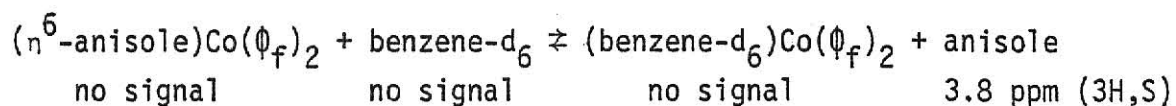$$(\eta^4\text{-NBD})(\phi_f)_2Co(I)^- + (\eta^4\text{-NBD})(\phi_f)_2Co(III)^+$$

If a cobalt(III) species was produced, decomposition would probably be instant.

II. Arene Exchange Reactions

A. Cobalt arenes

Bis(pentafluorophenyl)(η^6-arene)cobalt(II) is a paramagnetic complex. A manifestation of this property is the absence of a detectable ^{1}H NMR signal in the range of -20 to +30 ppm (δ) where TMS = 0 ppm. This was advantageous for studying arene exchange equilibria. The appearance of free arene signals could be monitored after addition of a displacing or reactant arene. The major limitation was the complexed ring had to have a significantly different chemical shift than the displacing arene.

The following equation shows coordinated toluene displacement by benzene-d_6. Cyclohexane or methylene chloride was used as an internal standard to monitor concentrations.

$$(\eta^6\text{-anisole})Co(\phi_f)_2 + \text{benzene-}d_6 \rightleftharpoons (\text{benzene-}d_6)Co(\phi_f)_2 + \text{anisole}$$

  no signal   no signal   no signal   3.8 ppm (3H,S)

The following ^{1}H NMR spectrum (Fig. 6) was recorded after the addition of one equivalent then ten equivalents of benzene-d_6.

Fig. 6
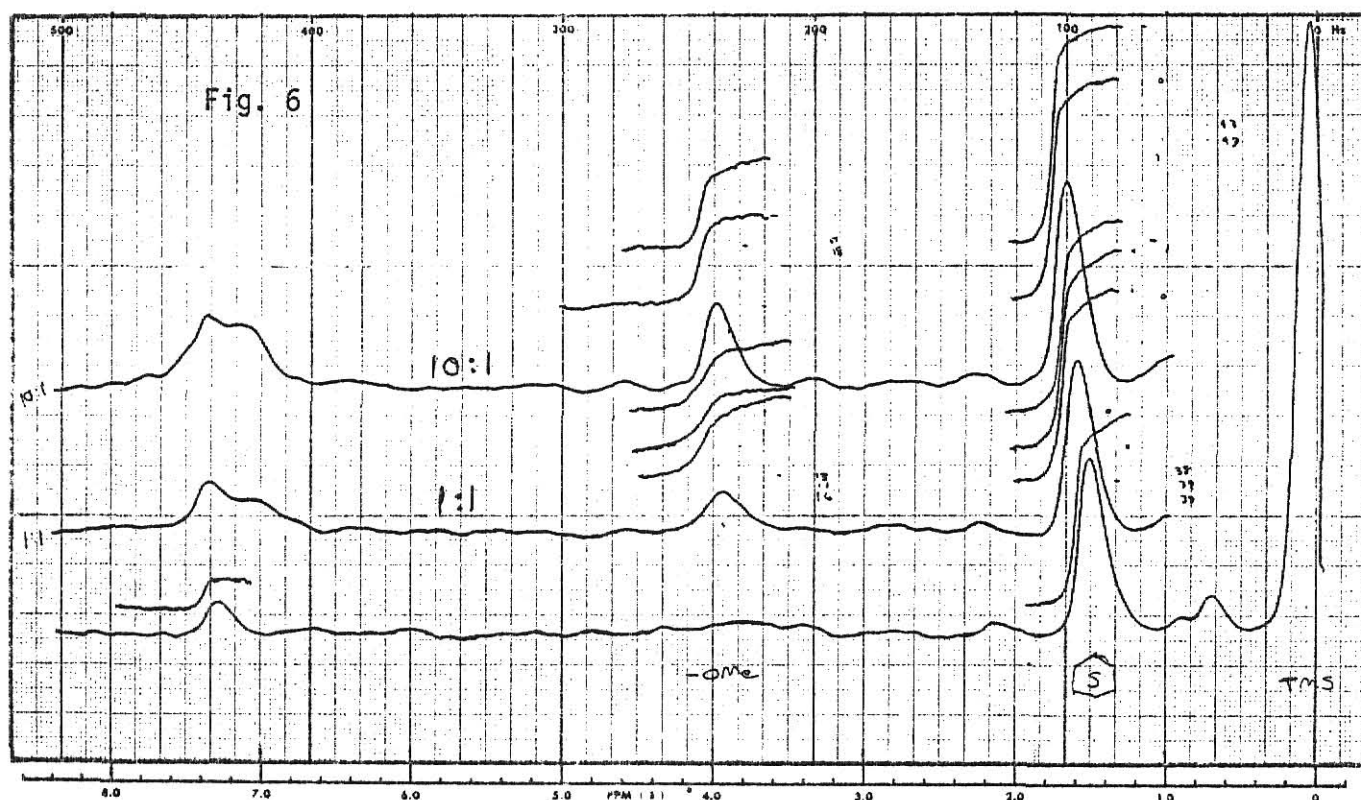
The following data (Table 5) was collected.

Table 5

				% displacement
	+	1 C_6D_6	→	26.1
	+	10 C_6D_6	→	48.1
(η^6-toluene)cobalt(ϕ_f)$_2$	+	10 C_6F_6	→	0
	+	10 C_6H_5F	→	0
	+	10 C_6F_5H	→	0

Data for alkyl substituted reactant arenes was obtained using the anisole complex. Table 6 summarizes the findings:

Table 6

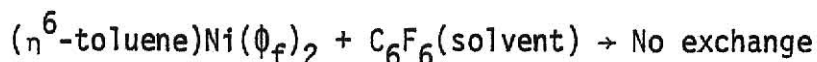|			Reaction #	% exchange
	+	1 C_6D_6	6	68
	+	10 C_6D_6	7	84
	+	1 toluene	8	85
	+	10 toluene	9	100
(η^6-anisole)Co(ϕ_f)$_2$	+	1 mesitylene	10	100
	+	10 C_6F_6	11	0
	+	10 C_6HF_5	12	0
	+	10 1,3,5-trifluoro-benzene	13	0
	+	10 benzotrifluoride	14	0
	+	10 p-ditrifluoromethyl-benzene	15	0

Time between injection of the reactant and recording the spectrum was ca. 15-30 seconds. Equilibrium was attained in this time period and constant thereafter. The results correlate well with data reported by Mahaffy and Pauson.[21] The destabilizing effect of methoxy compared to benzene is clear from reaction 6.

No dissociation of arene complex in $CDCl_3$ was observed for cobalt as was reported for nickel. The above data is in much better agreement with other workers[21] than data reported for the nickel complex.[15] At this point it seemed worthwhile to repeat several exchange reactions with the nickel analog to obtain direct comparisons.

The ^1H NMR spectrum of Bis(pentafluorophenyl)(η^6-toluene)nickel(II) was obtained in $CDCl_3$. No free toluene was detected.

$$(\eta^6\text{-toluene})Ni(\phi_f)_2 + CDCl_3 \;\not\rightleftharpoons\; (CDCl_3)_x Ni(\phi_f)_2 + \text{toluene}$$

The previous report is in error. The earlier study always used recrystallized arene complex which probably had excess toluene trapped within the crystal lattice.[42] In fact a ^1H NMR spectrum was obtained in neat C_6F_6 with no exchange:
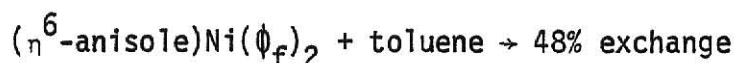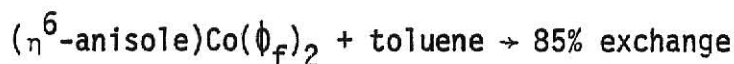
$$(\eta^6\text{-toluene})Ni(\phi_f)_2 + C_6F_6(\text{solvent}) \rightarrow \text{No exchange}$$

Data obtained for the nickel complex is listed in Table 7.

<div align="center">Table 7</div>

Reactant			Reaction #	% Exchange
	+	1 C_6D_6	16	29%
	+	10 C_6D_6	17	50%
	+	20 C_6D_6	18	67%
$(\eta^6\text{-toluene})Ni(\phi_f)_2$	+	30 C_6F_5	19	0
	+	10 1,3,5-trifluorobenzene	20	0
	+	10 C_6F_5H	21	0
	+	20 C_6FH_5	22	0
$(\eta^6\text{-anisole})Ni(\phi_f)_2$	+	1 toluene	23	48%
	+	2 toluene	24	85%

It should be noted that free vs. complexed anisole is not observable in the NMR spectrum (60 - 100 MHz). Free vs. complexed toluene was used for the integration and compared to the total methoxy area. Error was ca. 1%.

All exchange reactions with the nickel complexes were complete in the same time period as for cobalt. The data is much more in line with others.[21] An exception is found with anisole arenes:

$$(\eta^6\text{-anisole})Co(\phi_f)_2 + \text{toluene} \rightarrow 85\% \text{ exchange}$$
$$(\eta^6\text{-anisole})Ni(\phi_f)_2 + \text{toluene} \rightarrow 48\% \text{ exchange}$$

Coordinated anisole in the case of cobalt behaves as expected. Nickel on the other hand appears to be more stable than expected. Invoking a zwitterionic contribution to the resonance hybrid of anisole as was done by Pidcock[9,10] to explain rate data (vide supra) in this case:
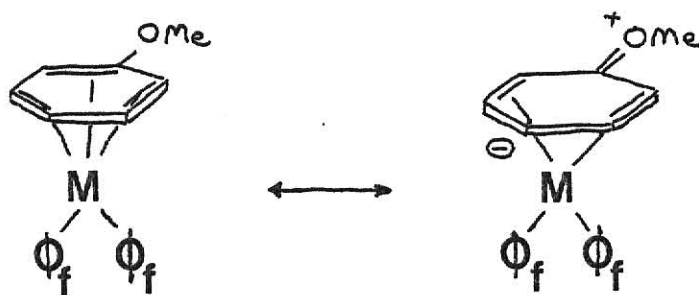
That no cobalt(II) diene complex could be prepared (or is even known) has been shown (see part D). A destabilizing effect of the resonance model is seen. The nickel complex, on the other hand, forms very stable diene complexes and the arene complex reacts irreversibly to form them:[15]

$$(\eta^6\text{-toluene})Ni(\phi_f)_2 + \text{diene} \quad \underset{\longleftarrow}{\overset{\longrightarrow}{\times}} \quad (\eta^4\text{-diene})Ni(\phi_f)_2 + \text{toluene}$$

Clearly the diene character of anisole must stabilize the nickel complex to exchange. This type of arene stabilization has not been noted before and may be unique to the nickel complex.

Reaction with Cyclopentadiene:Preparation of $Cp_3Co_2(\phi_f)_2$

When Bis(pentafluorophenyl)(η^6-toluene)cobalt(II), dissolved in methylene chloride, is treated with a 1:1.5 equivalent excess of cyclopentadiene, a color change from red-brown to yellow or green red occurs. No gas is evolved. GLC analysis of the volatiles shows the presence of one equivalent of both toluene and pentafluorobenzene.

$$2(\eta^6\text{-toluene})Co(\phi_f)_2 + 3\ CpH \rightarrow 2\ \text{toluene} + 2\ \phi_fH + 1$$
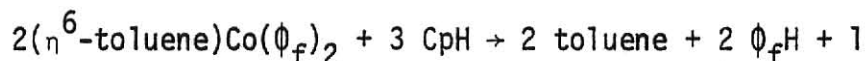
Ca. 30 percent of the residue is initially soluble in toluene. The solute loses stability in 24 hours and precipitates yielding 1.

1 is a red-brown microcrystalline solid. The compound is air stable as a solid and can even be handled as a solution in air for several hours. Thermal stability is excellent with a melting point of 212°C (decomp.).

The infrared spectrum (Fig. 7) shows bands at ca. 1500, 1050, 950, and 800 cm^{-1}. The bands are tabulated in numerical form in Table 8.

Elemental analysis gave an empirical formula of $Cp_3Co_2(\phi_f)_2$. Because the compound could exist as a tetramer or higher oligomer, a molecular weight determination was obtained in 1,2-dichloroethane:

Mol. Wt

found   669

calc   648 for $Cp_3Co_2(\phi_f)_2$

The results are consistent for a dinuclear species. The formula as written is tentative because of inherent error involved with large molecules like this, i.e., one Cp- moiety may be CpH.

Because the results indicate a dimeric complex, a ^{1}H NMR spectrum was obtained. Possibilities exist to form a metal-metal bond which could

produce a diamagnetic complex. The spectrum is shown in Fig. 8.

The spectrum shows only a single broad resonance at 4.63 ppm (δ). A dynamic process could cause signal broadening so a low temperature experiment was carried out (Fig. 9). At ca. -90°C, the peak almost collapses into the base line. Lower temperatures require the use of freon or low molecular weight alkanes as solvents. Unfortunately, the complex is only soluble in methylene chloride, acetonitrile and 1,2-dichoroethane.

Signal broadening could also arise from paramagnetism. A Faraday balance was used to obtain the magnetic susceptibility (μ_{eff}) at various temperatures. The data is listed below in Table 9.

Table 9

T(°C)	μ_{eff}(BM)
-100	1.36
- 34	1.8
25	2.26
60	1.38
89	1.54

Obviously the susceptibility does not follow the Curie Law. The complex appears to possess one unpaired electron at ambient temperatures. This result suggests the two cobalt centers are not in the same oxidation state. Unfortunately without a crystal structure this is not easily (possible to?) proved.

The proposed structure is shown below:
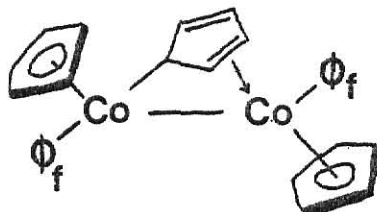
The structure contains cobalt(III) and cobalt(II) centers. The cobalt(III) center is a 17 electron system while the cobalt(II) center is an 18 electron system. Both centers are coordinatively saturated (i.e., 6 sites filled).

1,3-sigmatropic shifts are well known for cyclopentadiene molecules. The shift, anatara facial, is thermally forbidden.

Mixing in of metal orbitals could alter the orbital symmetry of the system to allow the thermal reaction. This is a well known phenomena in homogeneous catalysis. If this is correct, a dynamic process involving the three Cp rings could be operative:
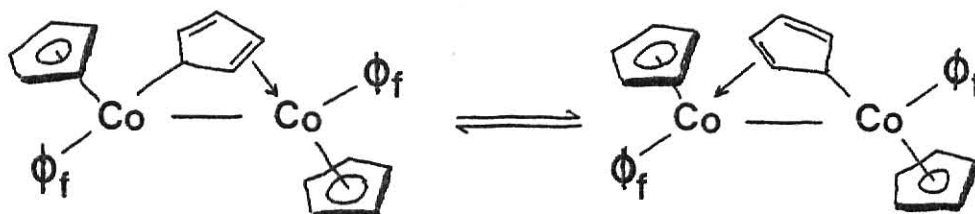
The scheme involves a change of oxidation state (electron transfer?) between the metal centers.
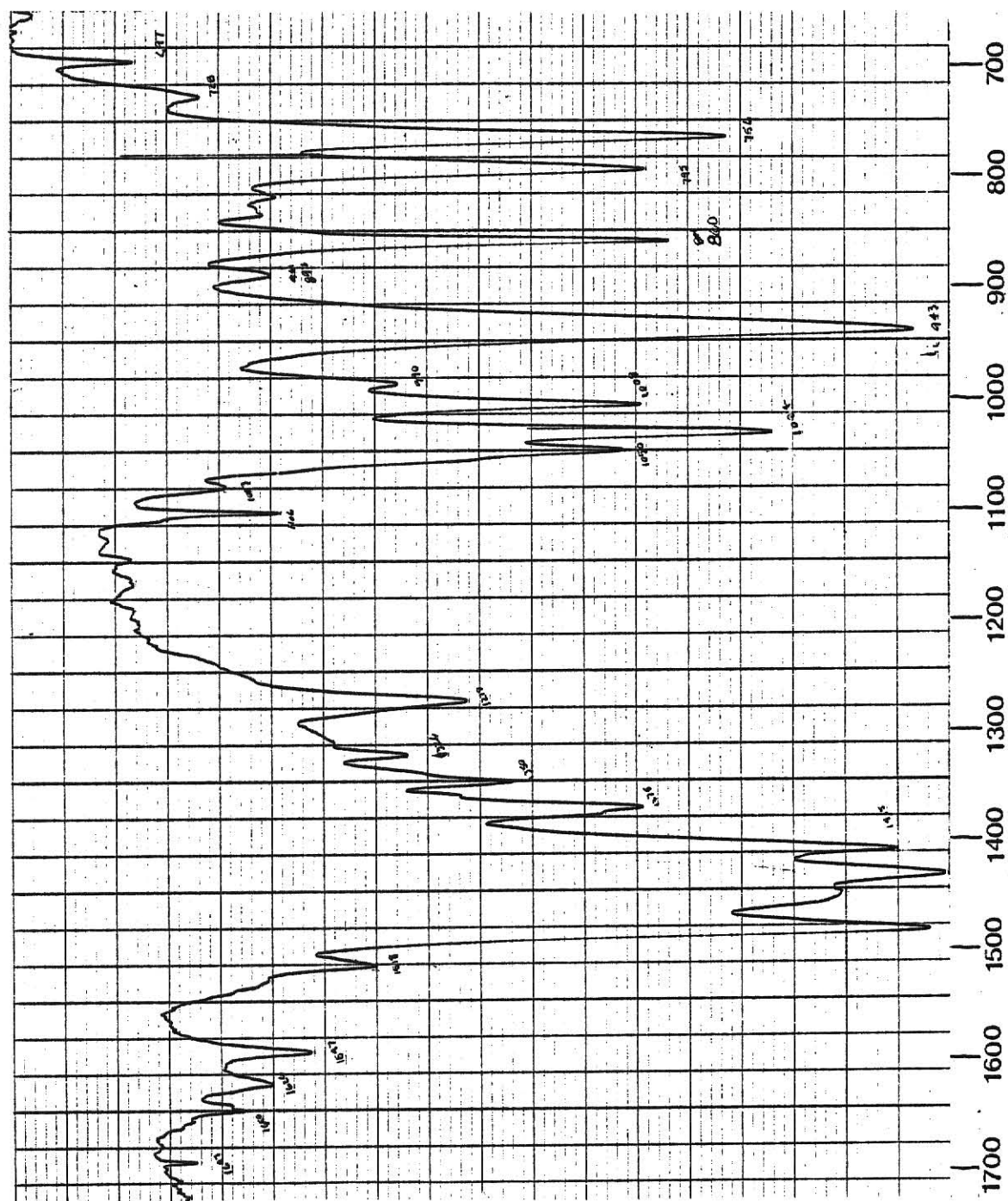
Fig. 7 Infrared Spectrum of $Cp_3Co_2(\phi_f)_2$, (Nujol, Fluorolube)

Table 8 Infrared Spectrum of $Cp_3Co_2(\phi_f)_2$, (Nujol, Fluorolube)

3120 w, 1650 w, 1624 w, 1597 w, 1518 w, 1488 vs, 1450 vs, 1437 vs, 1415 s,

1375 m, 1350 w, 1326 w, 1277 m, 1106 w, 1083 vw, 1050 s, 1034 vs, 1008 s, 990 w,

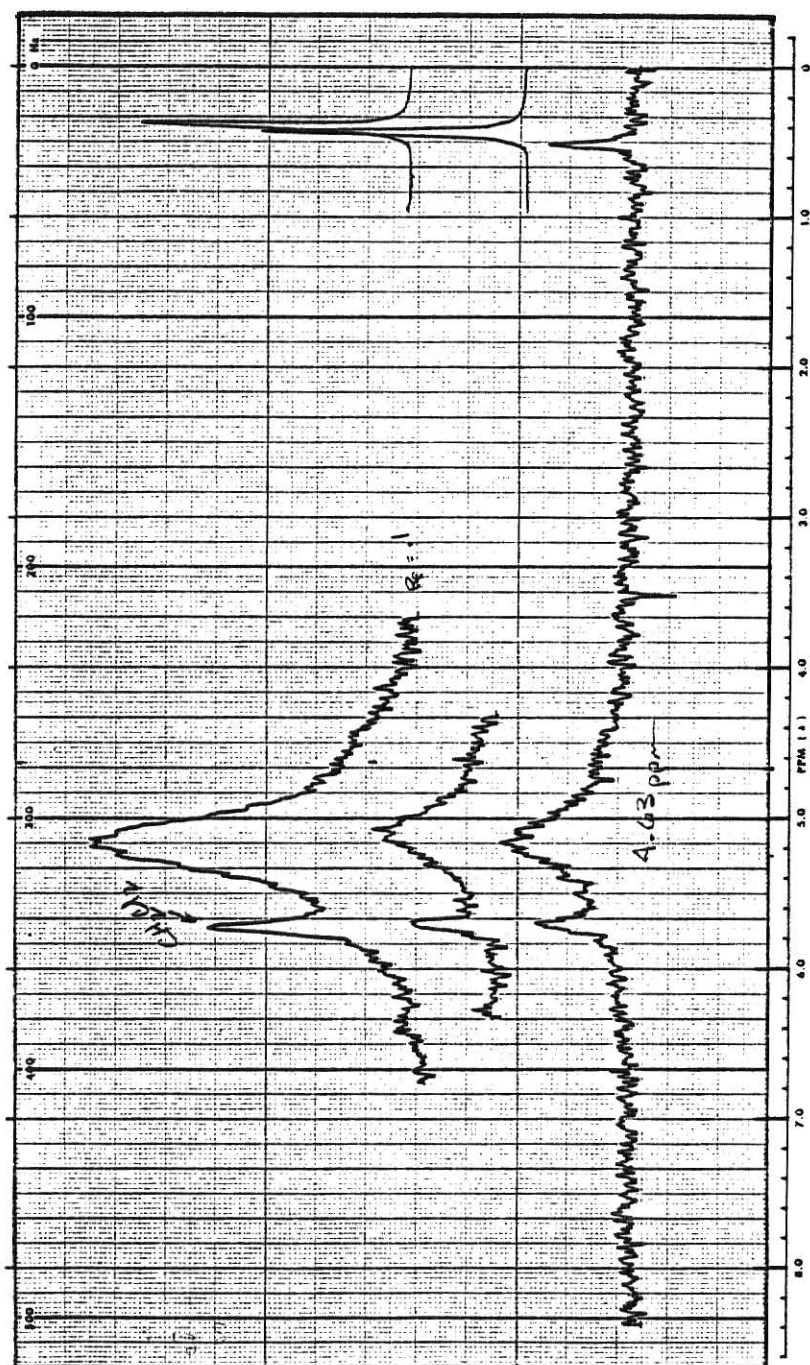943 vs, 892 w, 860 s, 795 s, 754 s, 728 w, 697 w, 585 vw, 524 vw, 497 w, 458 s.

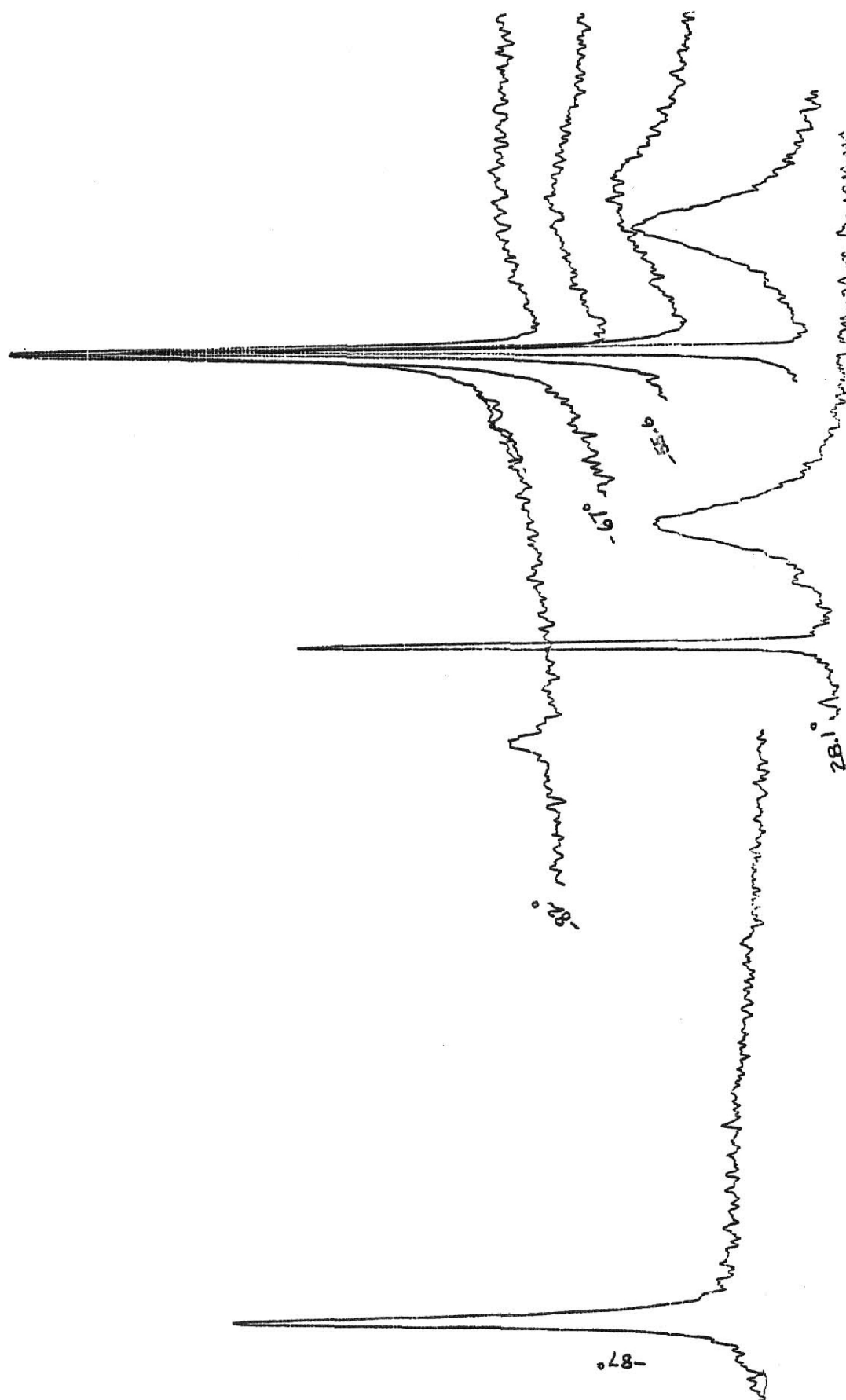Fig. 8 PMR Spectrum of $Cp_3Co_2(\phi_f)_2$ in CD_2Cl_2 at 32°C.

Fig. 9 Variable Temperature PMR of $Cp_3Co_2(\phi_f)_2$ in CD_2Cl_2

Bis(pentafluorophenyl)bis(tetrahydrothiophene)nickel(II)

Preparation and characterization of the bis-THF has been described.[15]
The bis-pyridine[27] and bipyridine[28] derivatives are known but poorly
characterized. The infrared and far infrared spectra are included
earlier in this section.

The title compound has not previously been described. The compound
is a yellow crystalline solid which can be handled in air for ca. 20
minutes without observable decomposition.

The ^{1}H NMR spectrum (Fig. 10) is interesting as it clearly shows
the unsymmetric orientation of the THT ligands bound to nickel.

Fig. 10
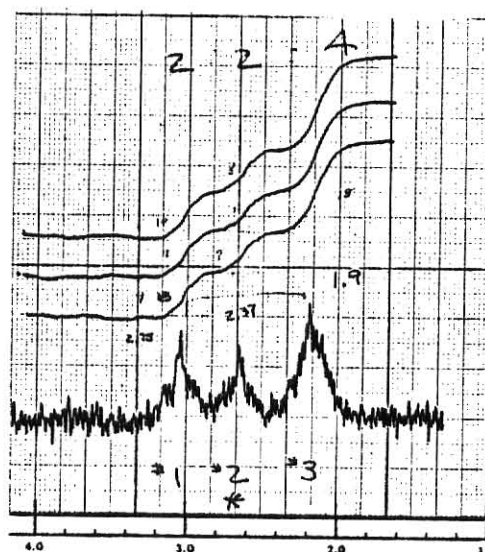
The proposed structure is drawn below with resonance assignments.
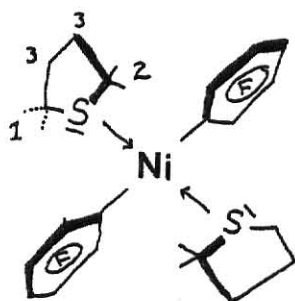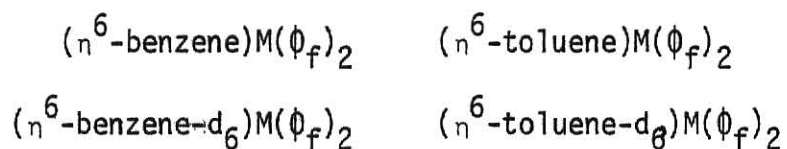

Proton #	resonance(ppm,δ)
1	2.75 (2H)
2	2.37 (2H)
3	1.90 (4H)

The 2 sets of $\underline{\alpha}$-protons on each THT molecule lose their equivalency upon complexation. Free THT has resonances at 2.77 (4H,α) and 1.90 (4H,β). A molecular model clearly shows the #2 protons come very close to the ortho-fluorines of the perfluorophenyl rings during ring-metal bond rotation. The #1 protons do not. The high electron density acts in a sheilding way to produce the observed shift.

Far Infrared Spectra of Selected Cobalt and Nickel Arene Complexes

An attempt was made to identify metal-arene vibrational modes in hopes of better understanding bonding interactions. The following arenes were made by exhaustive exchange:

$$(\eta^6\text{-benzene})M(\phi_f)_2 \qquad (\eta^6\text{-toluene})M(\phi_f)_2$$

$$(\eta^6\text{-benzene-}d_6)M(\phi_f)_2 \qquad (\eta^6\text{-toluene-}d_8)M(\phi_f)_2$$

$$M = Co, Ni$$

The spectra are reproduced in Fig. 11A - H. Note the extreme complexity. No assignments can be made at this time. The spectra are reported for documentation purposes only.
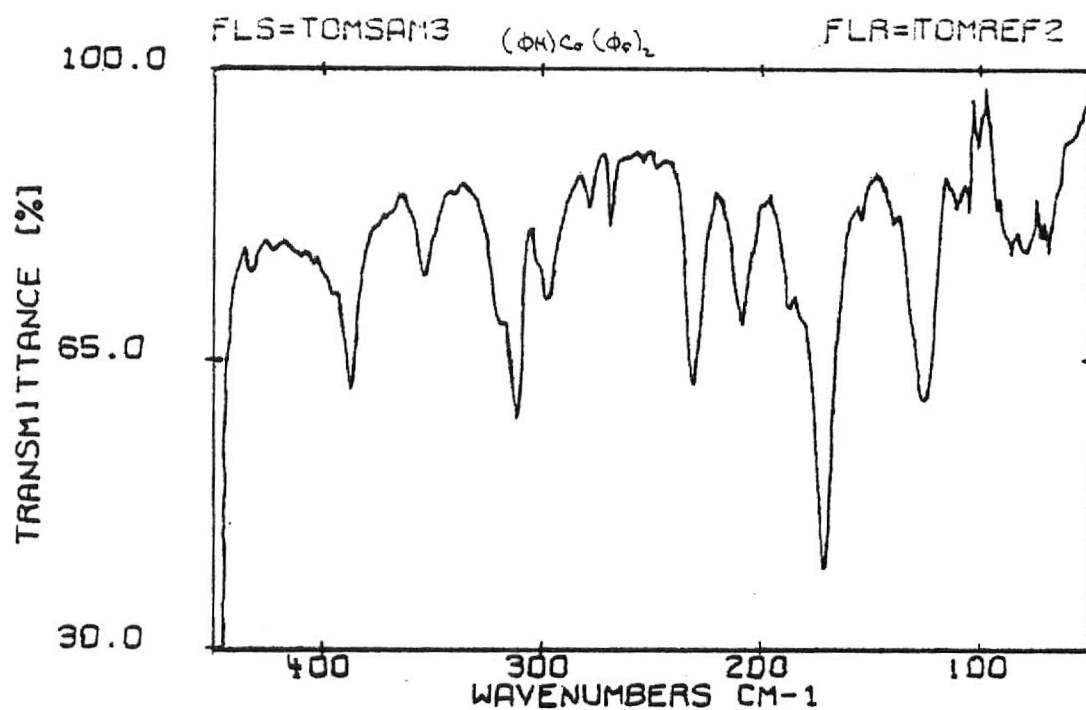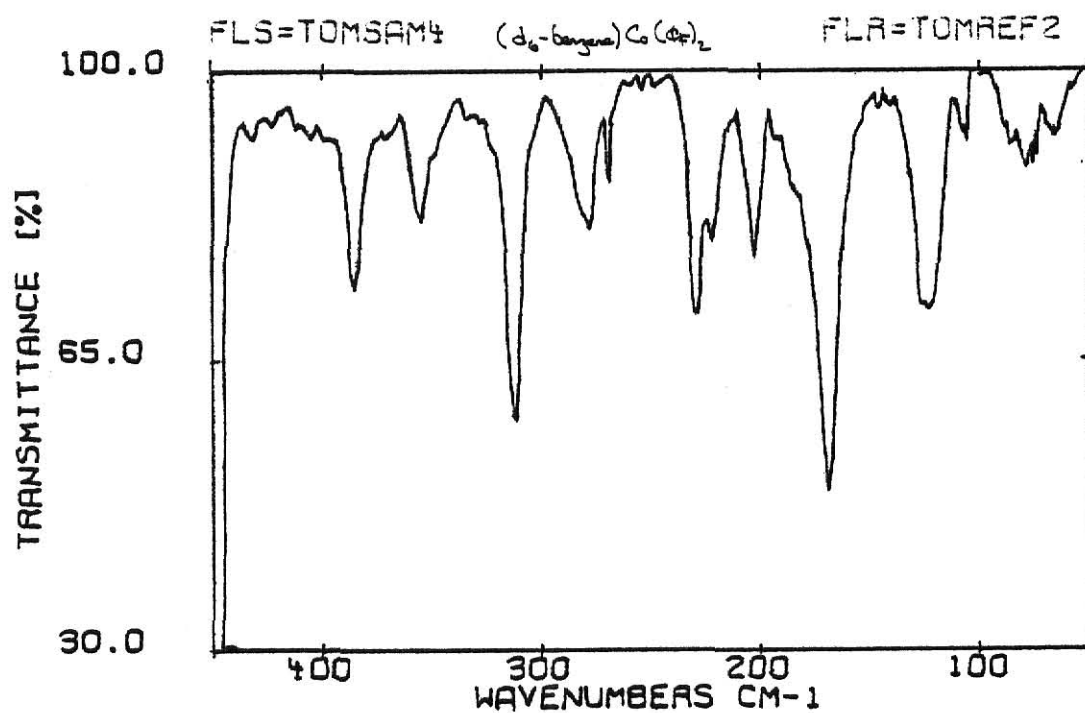
Fig. 11A Far Infrared Spectrum of $(\eta^6$-benzene$)Co(\phi_f)_2$, (Nujol)

FLS=TOMSAM4   (d_6-benzene)Co(Φ_f)_2   FLR=TOMREF2

PEAK TABLE FILE :   KUMAR4

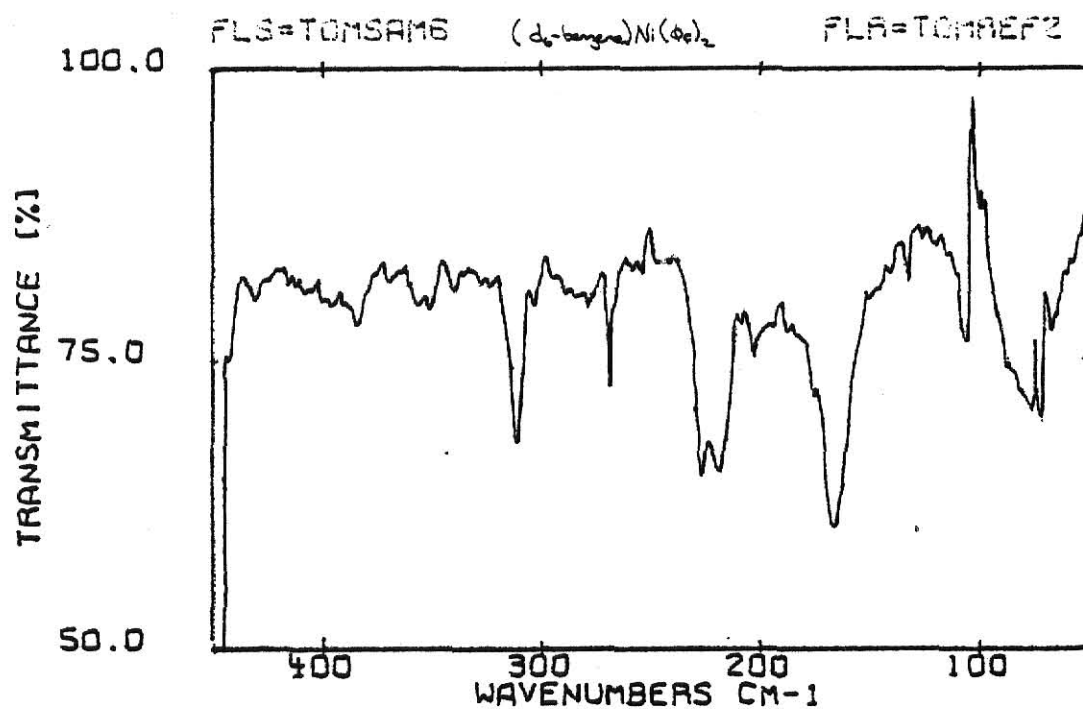| NO.	WAVE-NO.	REL. INTENSITY
1	78.113	78
2	105.115	77
3	122.473	82
4	168.762	87
5	202.515	80
6	229.517	82
7	269.055	79
8	278.699	79
9	311.487	85
10	354.883	79
11	385.742	81
12	447.461	100

$(d^6\text{-benzene})Co(\Phi_f)_2$

Fig. 11B Far Infrared Spectrum of $(\eta^6\text{-benzene-}d_6)Co(\Phi_f)_2$, (Nujol)
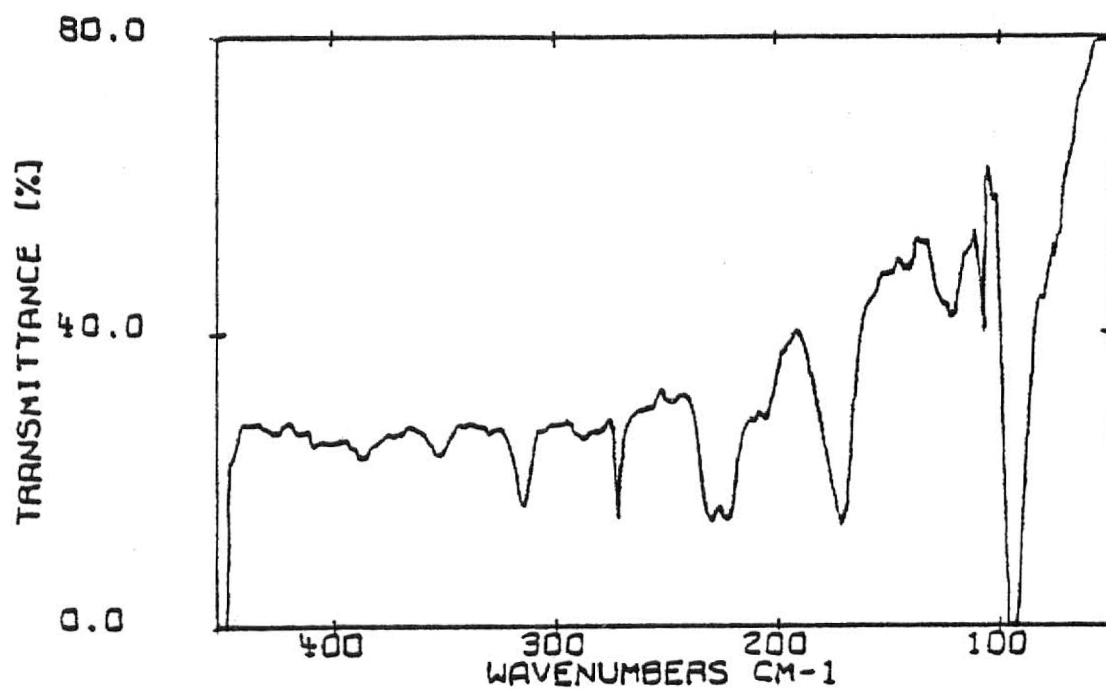
NO.	WAVE-NO.	REL. INTENSITY
1	79.113	86
2	91.614	100
3	105.115	86
4	120.544	95
5	154.297	93
6	169.727	94
7	208.301	89
8	227.598	93
9	269.055	92
10	311.487	91
11	349.097	95
12	381.885	93
13	442.639	78
14	447.461	100

Fig. 11C Far Infrared Spectrum of $(\eta^6$-benzene$)Ni(\phi_f)_2$, (Nujol)

Fig. 11D Far Infrared Spectrum of $(\eta^6\text{-benzene-}d_6)Ni(\phi_f)_2$, (Nujol)

Fig. 11E Far Infrared Spectrum of $(\eta^6\text{-toluene})Co(\emptyset_f)_2$, (Nujol)

Fig. 11F Far Infrared Spectrum of $(\eta^6\text{-toluene-d}_8)\text{Co}(\phi_f)_2$, (Nujol)

Fig. 11G Far Infrared Spectrum of (η^6-toluene)Ni(ϕ_f)$_2$

FLS=TOMSAM11 (d^2-tol)Ni(ϕ_f)$_2$ FLR=TCMREF2
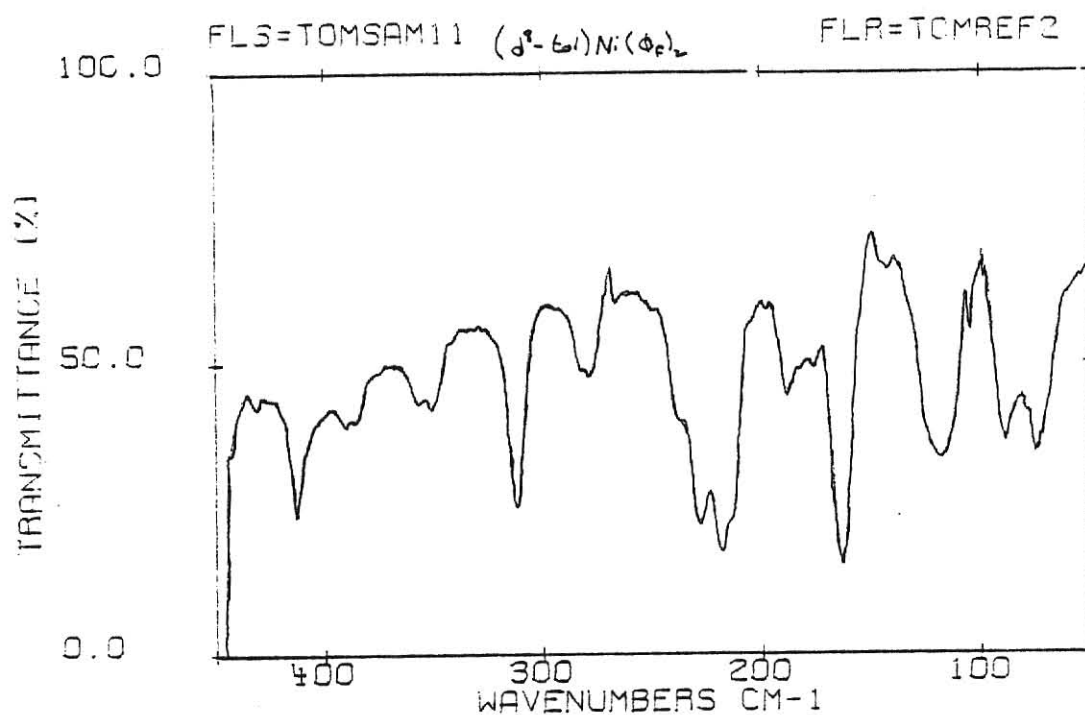
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PEAK TABLE FILE :  KUMAR11
 NO.        WAVE-NO.        REL. INTENSITY
  1          75.220              87
  2          88.721              86
  3         104.150              80
  4         118.616              88
  5         163.940              94
  6         188.049              84
  7         218.909              93
  8         228.552              91
  9         278.699              81
 10         312.451              89
 11         351.025              81
 12         390.564              80
 13         412.744              87
 14         447.461             100
```

Fig. 11H Far Infrared Spectrum of (η^6-toluene-d_8)Ni(ϕ_f)$_2$, (Nujol)

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THE CHEMISTRY OF BIS(PENTAFLUOROPHENYL)(η^6-TOLUENE)COBALT(II):

ARENE DISPLACEMENTS AND EXCHANGE REACTIONS

by

Michael M. Brezinski

AN ABSTRACT OF A MASTERS THESIS

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Abstract

The chemistry of Bis(pentafluorophenyl)(η^6-toluene)cobalt(II) has been explored. The complex possesses a highly reactive metal-arene bond. Treatment with oxygen, sulfur and nitrogen donor molecules results in immediate arene displacement with quantitative formation of bis ligand adducts for monodentate donors and mono ligand adducts for bidentate donors. The new compounds were fully characterized. Treatment of the arene complex with olefins and dienes imitates a free radical decomposition pathway. Reaction with cyclopentadiene causes partial reductive elimination of the pentafluorophenyl groups and produces a novel dimeric compound.

Arene exchange reactions were carried out with several alkyl, alkoxy and fluorine substituted aromatic ring compounds. All exchange reactions equilibrated in seconds. Comparisons to the isostructural nickel (II) analog are made.