

THE REACTION OF TRANSITION METAL ATOMS WITH ARENES: LOW TEMPERATURE π -COMPLEX FORMATION *

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(Received September 8th, 1977)

Summary

Benzene, benzene- d_6 , and fluorobenzene were found to react with chromium, iron, cobalt, and nickel atoms upon co-deposition without diluents at 77 K or diluted in argon matrices at 10 K. Infrared studies of the co-condensation products indicate that the initial reaction of these transition metal atoms with an aromatic system is π -complex formation. Studies of concentration effects show that the chromium atom reaction is approximately second-order with respect to benzene, as expected, while the iron, cobalt, and nickel atom reactions appear to be first-order with respect to benzene concentration. The stoichiometry of these complexes was determined by co-deposition of the metal vapors with benzene/benzene- d_6 or benzene/fluorobenzene mixtures. Also, the relative strengths of the metal–arene bonds were determined to be $\text{Cr} > \text{Fe} > \text{Co} > \text{Ni}$. Manganese atoms were found not to react with benzene under these conditions.

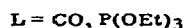
Introduction

The co-condensation of transition metal vapors with arenes at 77 K has permitted the direct synthesis of a large number of bis-arene complexes of chromium [1], vanadium [1f], titanium [2,3], molybdenum [4], and tungsten [4], many of which are unobtainable by classical [5] methods owing to side reactions that occur with arenes bearing halogenated substituents or functional groups, such as amino or methoxy groups, which possess lone pair electrons. Previous work has demonstrated that the co-condensation of iron vapor [1a] or nickel vapor [6] with arenes at 77 K leads to the formation of highly reactive and thermally unstable organometallic complexes. The *F*-benzenenickel complex [6a] has

* Presented in part at the 11th Middle Atlantic Regional Meeting, Newark, DE, April 1977. Abstr., IN-14.

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been identified as a 1/1 metal-arene complex from the results of a series of low temperature reactions of this complex with carbon monoxide or triethyl phosphite which yielded equimolar quantities of *F*-benzene and Ni^0L_4 species.



Some aspects of the chemistry of the metal-arene complexes of manganese and iron have also been previously reported [1e,7]. Co-condensation of manganese vapor with benzene and cyclopentadiene [1e,7a] produced η^6 -benzene(η^5 -cyclopentadienyl)manganese(I) in low yield; analogous products were also formed from the reaction of manganese atoms with toluene [1e,7a] or mesitylene [1e] and cyclopentadiene. In the case of iron atoms, mesitylene reacted to form η^6 -mesitylene(η^4 -1,3,5-trimethylcyclohexa-1,3-diene)iron [1e]. Mixtures of arenes and trifluorophosphine have been reported to react with iron vapors forming (η^6 -arene)(PF_3)₂Fe complexes, along with a number of trifluorophosphineiron complexes [1c,e,7b,c]. Iron atoms have also been reported to form η^6 -benzene(η^4 -1,4-cyclohexadiene)iron(0), an 18-electron complex, from a co-deposition reaction with benzene [7c], while the isomeric 1,3-diene complex has been isolated from 1,3-cyclohexadieneiron reaction mixtures [7b]. The uncharacterized adduct formed in the reaction of toluene with iron vapor was found to react with 1,3-butadiene to give η^4 -1,3-butadiene(η^6 -toluene)iron(0) in moderate yields [7b].

Recently, the structure of η^6 -toluene bis(*F*-phenyl)cobalt(II) was reported [8]. This was the first example of an organometallic complex containing a π -bonded arene and two σ -bonded aryl groups.

Prior to this work, the reaction of benzene with chromium atoms, generated by argon discharge sputtering, was reported to produce dibenzenechromium on co-condensation at 14 K as well as from annealing of the argon matrix [9]. In our study, thermally generated ground state chromium atoms were also found to yield dibenzenechromium on co-condensation with pure benzene at 77 K as well as with dilute argon/benzene mixtures at 10 K. However, as described later, an extension of these studies to other metal systems, in an investigation of some of the basic mechanisms of metal atom reactions, was found to produce 1/1 metal-arene adducts rather than the expected bis-arene compounds.

Experimental

Benzene (B&A, reagent), benzene-*d*₆ (Merck, 99.8% D) and fluorobenzene (PCR) were subjected to several freeze-thaw degassing cycles prior to use. Iron (Fischer, reagent), cobalt (Fischer, CP), and nickel (Baker, reagent) were evaporated from aluminum oxide tubes (Norton, 9.6 mm OD, 6.5 mm ID × 50 mm) wrapped with a tungsten filament heater (Sylvania Emissive Products, No. Fil-3002 4 × 0.030). Chromium (Fischer, 99%+) was sublimed from an identical source which was fitted with a 0.5 mil tantalum liner to minimize the reaction of chromium with the alumina refractory. The evaporation sources were coated on the outside with high temperature alundum cement for better

heat transfer. Average power inputs were 5.25–6.25 V at 60–75 A. Average rates of metal deposition onto the window were measured at 600–700 $\mu\text{g}/\text{h}$ and were found to be in satisfactory agreement with those rates calculated from vapor pressure data [10].

Reactions at liquid nitrogen temperature [11] were performed by depositing the respective metals into neat matrices of benzene, benzene- d_6 , or fluorobenzene. In several runs, a 50/50 mixture of benzene/benzene- d_6 or benzene/fluorobenzene was co-deposited with the metal atoms. Deposition rates for the arenes were approximately 1.2 mmol/h which gave a final benzene-to-metal ratio of 100. IR spectra of the 77 K reactions were recorded on a Perkin–Elmer 457 infrared spectrometer; band frequencies are accurate to $\pm 4 \text{ cm}^{-1}$.

Several experiments were performed by co-depositing metal atoms with argon (Linde, prepurified)/benzene (25/1–200/1) gas mixtures onto a 10 K CsI window. The apparatus used in these experiments has been described previously [12] with slight modification to accommodate the metal atom source. Argon matrix samples were usually deposited at the rate of 3–4 mmol/h. These conditions yielded an argon-to-metal atomic ratio of about 500 which has been shown to be effective in isolating atomic nickel in pure argon [13]. With a high concentration (i.e., 1%) of reactant such as benzene to “scavenge” the metal, aggregation of metal atoms is expected to be negligible [14]. Argon matrix IR spectra were recorded on a Beckman IR-12 spectrophotometer and band positions are accurate to within $\pm 0.5 \text{ cm}^{-1}$.

Results and discussion

In this study, we have gained further insight into the basic reactions of metal vapors on co-condensation with arenes and the nature of the highly reactive iron and nickel complexes previously discussed.

Manganese atoms did not react with benzene upon co-deposition at 77 K. A black matrix was obtained and an infrared spectrum matching that of benzene deposited under the same conditions was observed, a result also independently observed by Skell [15].

Chromium

Thermally generated chromium vapor was found to react with benzene at either 77 K or at 10 K to form dibenzenechromium. The IR spectrum of the product at 77 K was in complete agreement with the reported spectrum for dibenzenechromium [16] and remained unchanged on warming to remove excess benzene. The argon matrix dibenzenechromium spectrum agreed with that reported by Boyd et al. [9]. Increasing the argon/ C_6H_6 ratios from 50 to 200, while maintaining the amount of chromium approximately constant, did not produce any new bands or any significant changes in the relative intensities of the observed bands. However, there was a 12- to 13-fold decrease in the overall intensity of the product bands upon fourfold dilution with argon. This is close to the expected 16-fold decrease in intensity (i.e. $[(\text{C}_6\text{H}_6)_2\text{Cr}] \propto [\text{C}_6\text{H}_6]^2$) [1] characteristic of an apparent termolecular process yielding dibenzenechromium. The only result of warmup of the argon matrix samples to 30–35 K was an increase in the product absorptions.

Changing the argon/C₆H₆ ratio from 50 to 200 should have increased the (C₆H₆)Cr/(C₆H₆)₂Cr ratio by a factor of four if monobenzenechromium were formed in the reaction. Since no new bands were observed either on dilution or on chromium atom diffusion, it is reasonable to conclude from the spectroscopic evidence, that monobenzenechromium is not formed in the reaction of chromium atoms with benzene.

Iron, cobalt, and nickel

When iron, cobalt, or nickel vapors were co-condensed with benzene, either at 77 K or in argon at 10 K, a red-brown matrix, typical of metal atom-arene reactions, was observed. Similar IR spectra were recorded at both temperatures with some slight variations in frequencies due to temperature and matrix effects (cf. Table 1). The most striking feature of these spectra is the absence of the two intense IR bands in the 300–500 cm⁻¹ region, which are characteristic of diarene sandwich complexes [17] as well as di-η⁵-cyclopentadienylmetal complexes [17b]. A comparison of the dibenzenechromium spectrum in Fig. 2 with the benzene-iron, -cobalt, and -nickel complex spectra in Fig. 1 and 2 illustrates this striking difference. Instead of the very strong asymmetric metal-ring stretching and tilting absorptions in the 300–500 cm⁻¹ region [16,17], very weak absorptions were observed in the 350–380 cm⁻¹ and 440–480 cm⁻¹ regions, while “perturbed” benzene vibrations were observed with increased relative intensities in the latter experiments. These far-IR bands decrease in frequency through the iron, cobalt, and nickel series (cf. Table 1). In the 600–1500 cm⁻¹ region, the IR spectra of the iron, cobalt, and nickel com-

TABLE 1
INFRARED SPECTRA OF METAL-BENZENE COMPLEXES ^a

Iron		Cobalt		Nickel	
10 K Ar/C ₆ H ₆ = 25	77 K	10 K Ar/C ₆ H ₆ = 25	77 K	10 K Ar/C ₆ H ₆ = 25	77 K
366 ^b	370	366(12)	370	346(2)	350
—	485	454(8)	460	—	445
716 ^c		745 ^c		736 ^c	
762(37)	785	758(34)	765	748(40)	755
812(3)	810(sh)	805(24)	810	793(1)	808
848 ^c	855 ^c	852 ^c	860 ^c	818(35)	825
953(1)		918 ^c		844 ^c	860 ^c
968 ^c	968	971(22)		927 ^c	915 ^c
983(6)		991(4)		966 ^c	930
993(2)		1001 ^c		974 ^c	
1010 ^c		1006 ^c		989(7)	
1179(5)	1175	1012 ^c		1010(3)	
1246(1)		1121(5)	1120	1178(3.5)	1178
1392(4)		1198(9)	1175	1391(2)	
1430(1)		1313(3)	1335	1431 ^c	1440 ^c
1443(5)	1435	1341(5)		1452(2.5)	1445
		1394(4)			
		1425(2)			
		1444(22)	1440		

^a Wavenumber in cm⁻¹ (relative OD). ^b Ar/C₆H₆ = 75. ^c Aggregate band.

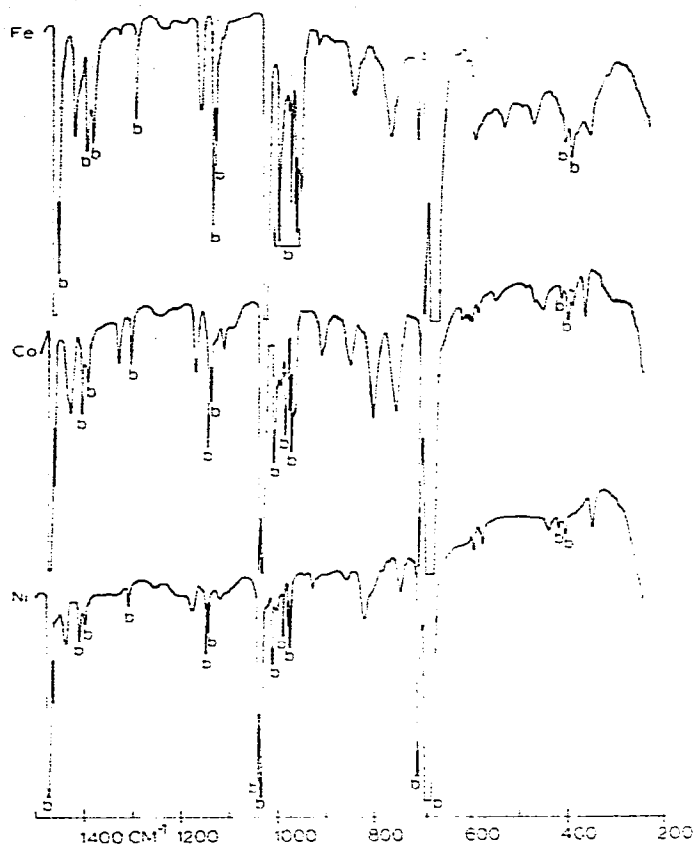


Fig. 1. Infrared spectra of iron, cobalt, and nickel atoms co-condensed with benzene at 77 K (b = benzene absorptions).

plexes were qualitatively similar to that of dibenzenechromium with some shifts in the metal-perturbed benzene vibrations. There were definite trends, however, in the shifts of the C=C stretching and out-of-plane (o.p.) ring bending modes.

In the 10 K matrix spectra, the relative intensities of several IR absorptions were observed to vary from one experiment to another or on dilution or diffusion of the argon/benzene matrices. In the less concentrated matrices ($\text{Ar}/\text{C}_6\text{H}_6 = 25 \rightarrow 75 \rightarrow 150$), these bands were greatly reduced in intensity relative to the other product absorptions, but their intensities increased substantially in the course of matrix warmup to 30–35 K. On the basis of this behavior, we can assign these bands (identified by "a" in Fig. 2) to some type of a benzene-metal aggregate which, in all probability, contains two or more metal atoms. Aggregate formation was also observed in the 77 K benzene matrices, especially in those experiments involving iron atoms.

Controlled warmup of the argon matrices effected several intensity changes in the metal-arene absorptions. With iron atoms, the aggregate band (716 cm^{-1}) grew, while the OD of the predominant reaction product band (767 cm^{-1}) either remained constant or decreased slightly. Both of these features are attributable

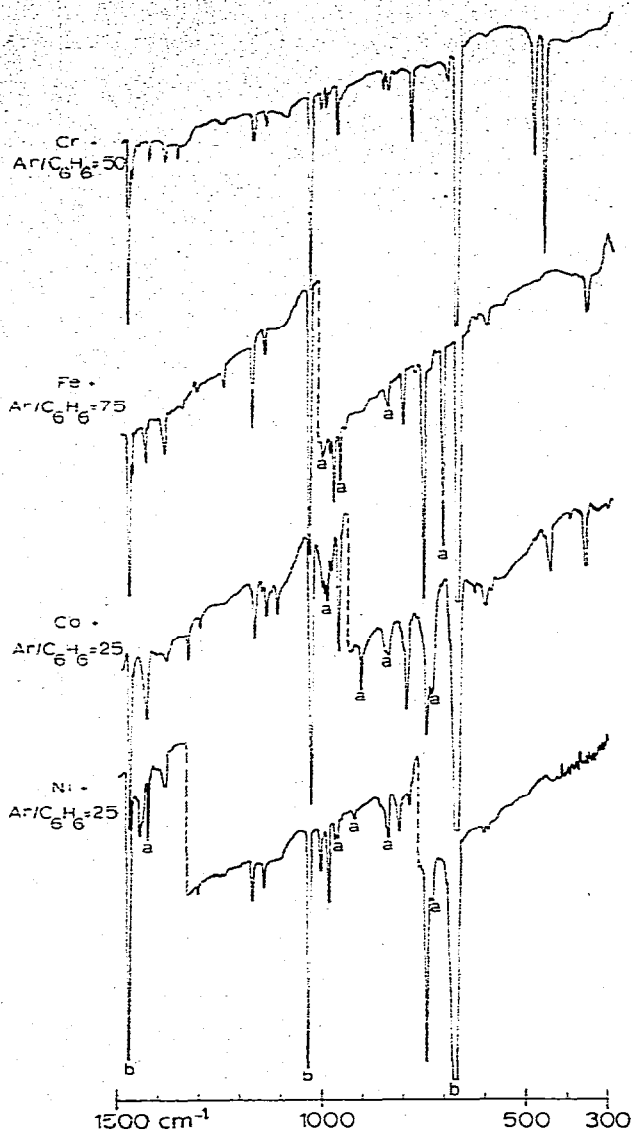


Fig. 2. Infrared spectra of metal atoms co-deposited with benzene in argon at 10 K (b = benzene absorptions, a = aggregate absorptions).

to the o.p. bending vibrations of a perturbed benzene molecule (C—H deformation (1) [18]). With cobalt, there were slight increases in the intensities of both primary product and aggregate bands upon warming to 30–35 K. On the other hand, the nickel-containing matrices exhibited a sizable increase in the product absorptions upon warmup to equivalent temperatures. This was in contrast to the aggregate features which experienced only slight increases in intensity.

The relative strengths of the metal—arene bonds were obtained from the shifts in the C=C stretching and C—H o.p. bending frequencies of the benzene ligand.

Previously, the magnitude of shift to higher wavenumbers of the C—H o.p. bend has been used as an indirect method for obtaining relative metal—ring bond strengths in both arene and cyclopentadienyl complexes [17a]. On proceeding from chromium to nickel, the C=C stretching frequencies were observed to undergo progressively smaller shifts to lower wavenumbers, while the o.p. bending mode exhibited decreasing shifts to higher wavenumbers (cf. Tables 1 and 3).

These results indicate successively decreasing perturbations of the benzene ligand in the iron, cobalt, and nickel complexes. The far-IR bands of these complexes also shift to lower wavenumbers in the same series of metals. This trend in the strengths of the metal—arene bonds (*viz.* Cr > Fe > Co > Ni) is in agreement with the ability of these metals to serve as acceptors of π -electron density as well as their thermal stabilities [6a]. Similar results were also obtained in the benzene- d_6 experiments (cf. Table 2).

Stoichiometry

In an effort to determine the stoichiometry of the metal—arene complexes, several mixed arene experiments were conducted. In one experiment, chromium atoms were co-condensed at 10 K with a mixture of Ar/C₆H₆/C₆D₆ = 50/0.7/1. The resultant IR spectrum contained two 1/2/1 triplets in the vicinity of 500 cm⁻¹ (cf. Fig. 3). The highest frequency components of each triplet (492 and 466 cm⁻¹) are assigned to dibenzenechromium (the 492 cm⁻¹ band appearing as a shoulder on the C₆D₆ band), while the lowest frequency bands of each triplets (481 and 427 cm⁻¹) are assigned to dibenzene- d_6 -chromium. The central absorptions (487 and 445 cm⁻¹), which are approximately twice the intensity of the flanking bands, are assigned to the mixed complex: benzene(benzene- d_6)-chromium. Also, in the chromium atom-mixed benzene/benzene- d_6 experiment, the absorptions at 487 and 445 cm⁻¹, assigned to skeletal vibrations of (C₆H₆)-(C₆D₆)Cr⁰, were the only new bands observed in the IR spectrum. Previously, other workers, [1c,e,19] have employed a similar mixed ligand reaction for the preparative scale synthesis of benzene(fluorobenzene)chromium(0).

The results of the co-deposition of iron or cobalt atoms with benzene/benzene-

TABLE 2
INFRARED SPECTRA OF METAL—BENZENE- d_6 COMPLEXES ^a

Iron	Cobalt	Nickel
349	335	330 ^b
468 ^b	422	410 ^b
534 ^c	566	565
585	578	634
632	633	793
787	757	870
797 ^c	778	925
869	797	
924	898	
970	931	

^a Wavenumbers in cm⁻¹ as measured in 10 K argon matrices. ^b Benzene- d_6 matrix at 77 K. ^c Aggregate band.

TABLE 3

FAR-INFRARED BANDS AND SHIFTS OF THE C=C STRETCHING AND C-H o.p. BENDING VIBRATIONS OF BENZENE UPON COMPLEXATION^a

Complex	$\Delta\nu(\text{C}=\text{C})$ stretch ^b (cm^{-1})	$\Delta\nu(\text{C}-\text{H})$ o.p. bend ^b (cm^{-1})	Far-infrared (cm^{-1})
$(\text{C}_6\text{H}_6)_2\text{Cr}$	-49	+122	492, 466
$(\text{C}_6\text{H}_6)\text{Fe}$	-40	+89	485 ^c , 366
$(\text{C}_6\text{H}_6)\text{Co}$	-39	+85	454, 366
$(\text{C}_6\text{H}_6)\text{Ni}$	-31	+75	445 ^c , 346

^a Argon matrices at 10 K unless otherwise noted. ^b + and - indicate shifts to higher and lower wave-numbers, respectively. ^c Benzene matrix at 77 K.

d_6 and a mixture of the two arenes in argon matrices are illustrated in Fig. 3. With iron atoms, only the 366 cm^{-1} benzene and the 349 cm^{-1} benzene- d_6 product absorptions, which were recorded in the individual benzene/benzene- d_6 runs,

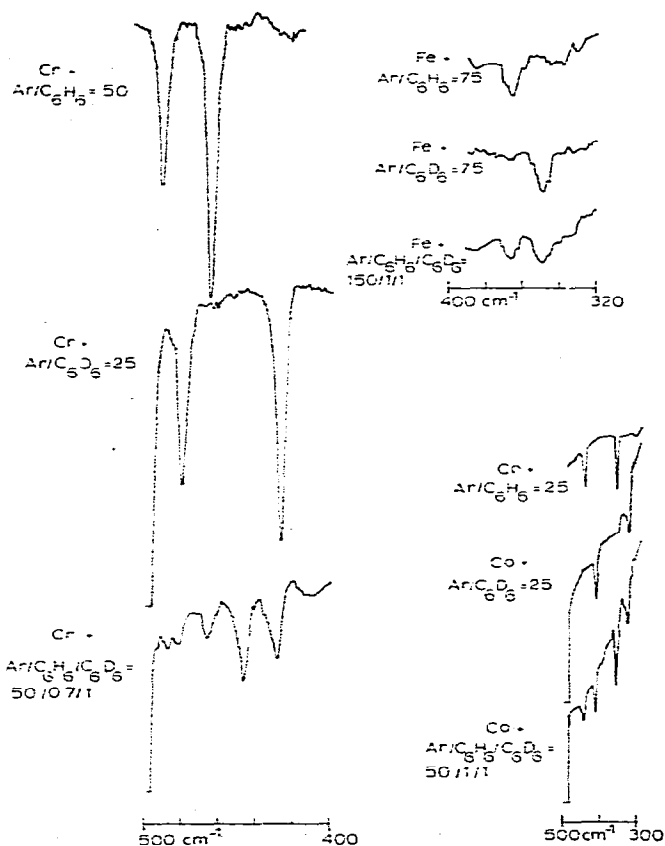


Fig. 3. Far-infrared spectra of chromium, iron and cobalt reactions with benzene, benzene- d_6 , and benzene/benzene- d_6 mixtures in argon matrices at 10 K.

were observed in the mixed arene experiment *. Cobalt atoms, under identical conditions, produced a pair of doublet absorptions whose frequencies agreed with those of the individual benzene- and benzene- d_6 -cobalt adducts. Similar findings were observed in those experiments where iron or cobalt vapors were deposited with neat benzene/benzene- d_6 mixtures at 77 K. The definitive aspect of these experiments, along with the subsequent nickel atom results, is that no new features were observed which were attributable to the formation of mixed-ligand complexes. Hence, the spectroscopic evidence indicated that only one arene was bound to the metal.

The far IR bands from the argon matrix reaction of nickel atoms with benzene and/or benzene- d_6 were too weak for reliable resolution. The same reactions, conducted neat at 77 K with benzene, benzene- d_6 , fluorobenzene, benzene/benzene- d_6 , and benzene/fluorobenzene are shown in Fig. 4. Both series of experiments gave the same net results; namely, only individual $\text{Ni}(\text{C}_6\text{H}_6)$, $\text{Ni}(\text{C}_6\text{D}_6)$, and $\text{Ni}(\text{C}_6\text{H}_5\text{F})$ complexes are formed under mixed ligand deposition conditions. The nickel-benzene absorptions were located at 350 and 445 cm^{-1} , while the nickel-fluorobenzene complex bands were observed at 310 and 390 (sh) cm^{-1} . The nickel-benzene- d_6 product bands were observed at 410 and 330 cm^{-1} . The shoulder on the 410 cm^{-1} nickel-benzene- d_6 band is due to solid benzene in the mixed arene experiment.

In the 500–1500 cm^{-1} region, the IR spectra of the mixed experiments with iron, cobalt, or nickel atoms and benzene/benzene- d_6 mixtures showed absorptions indicative of the individual metal-arene complexes **.

Since only those absorptions corresponding to the individual metal-arene complexes were detected and no mixed isotope effects were evident in either of the far IR absorptions, which are presumably skeletal vibrations of the complex, or the "perturbed" benzene vibrations, we are forced to conclude that the adducts are 1/1 metal-arene complexes. This result is in contrast to the diarene structure suggested for the product formed from the reaction of iron atoms with benzene [1a,20,21]. If indeed the products were diarenemetal sandwich complexes, new bands at approximately twice the intensity of the individual complex bands would have been observed in the far IR. This was precisely the case for chromium where the observation of a 1/2/1 triplet in the mixed ligand experiment indicated the presence of two equivalent arenes bound to the same metal atom [21]. Similar arguments can be made to eliminate other 2/1-type structures involving a tightly bound arene and a weakly bound arene or nonequivalent

* The same experiment at 77 K gave bands at 475, 445, 365, and 340 cm^{-1} corresponding to the individual iron-arene complexes. In this case, the matrix was diluted with butane 50/1/1 to eliminate interferences from solid phase arene bands. In pure arene matrices, the bands are at 487 and 370 cm^{-1} for $\text{Fe}(\text{C}_6\text{H}_6)$ and 468 and 350 cm^{-1} for $\text{Fe}(\text{C}_6\text{D}_6)$.

** Weak bands at 724 and 540 cm^{-1} were observed near the 716 and 534 cm^{-1} aggregate bands for the iron and benzene/benzene- d_6 mixed experiment. These bands were always observed as weak but well-resolved shoulders on the stronger bands identified as aggregates and are therefore assigned to a mixed aggregate species such as $(\text{C}_6\text{H}_6)(\text{M})_n(\text{C}_6\text{D}_6)$. The deuterium shift reveals these bands to be perturbed benzene C-H out-of-plane deformations. The most likely origin of these two bands is a symmetric out-of-plane vibration which is inactive for the symmetric (i.e., $(\text{C}_6\text{H}_6)(\text{M})_n(\text{C}_6\text{H}_6)$ or $(\text{C}_6\text{D}_6)(\text{M})_n(\text{C}_6\text{D}_6)$) species, but is observed due to symmetry-relaxed selection rules in the mixed aggregate species.

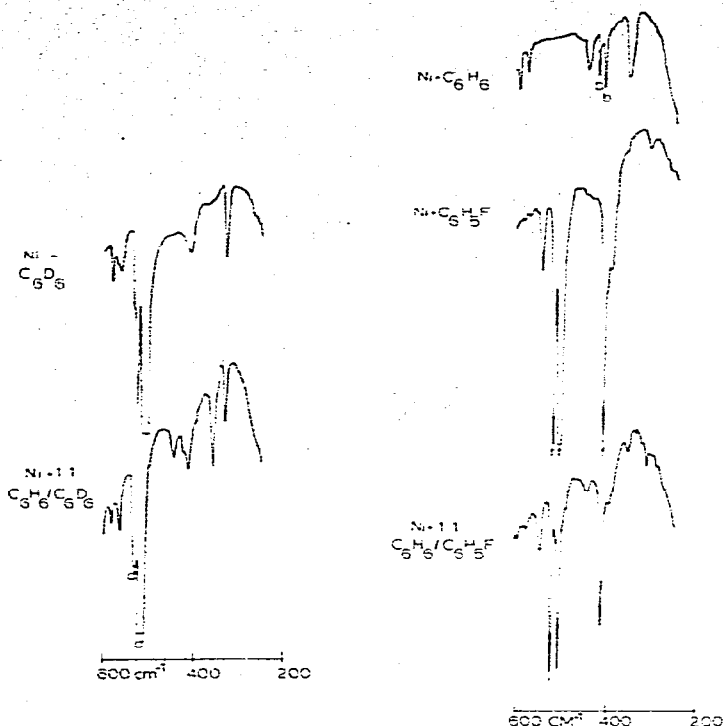


Fig. 4. Far-infrared spectra of nickel vapor-mixed arene experiments at 77 K (b = benzene absorptions, d = benzene- d_6 absorptions and f = fluorobenzene absorptions).

arenes both tightly bound to the same metal *. The formulation of the iron, cobalt, and nickel complexes as 1/1 adducts is further supported by concentration studies, where a first-order dependence on benzene concentration in the argon matrix was observed, as contrasted to chromium where second-order benzene concentration effects were observed, i.e.: $[C_6H_6-M] \propto [C_6H_6]$ vs. $[(C_6H_6)_2Cr] \propto [C_6H_6]^2$ ($M = Fe, Co, Ni$).

Indirect support is gained from the results of the mesityleneiron vapor experiments previously discussed where the isolated product was the 18-electron η^6 -arene(η^4 -cyclohexa-1,3-diene)iron complex [1e] rather than the 20-electron diarene complex. In fact, it is exceedingly rare to find sandwich complexes containing more than 18 electrons as products of metal atom reactions [20]. It is well documented that the presence of methyl groups tends to stabilize metal-arene π -bonds [22]; hence it is more likely to isolate a diareneiron complex formed with mesitylene, rather than benzene, but this is not the case.

* The former structure could possibly account for the observed isotopic data since the complex could behave as a 1/1 complex "slightly perturbed" by the weakly bound arene. Such a structure should manifest itself in the "perturbed ring vibrations": namely, there should be three sets of benzene ring vibrations observed, i.e., an "unperturbed" benzene, a "slightly perturbed" benzene, and a "strongly perturbed" benzene, corresponding to unbound, weakly bound, and tightly bound benzene. Since no "slightly perturbed" benzene is observed, it indicates that the hypothetical arene nearest neighbor to the metal-arene complex is indistinguishable from the free arene itself. Tightly bound 2/1 complexes with non-equivalent arenes would show a quartet of skeletal bands under mixed isotope conditions (cf. ref. 21).

Conclusions

Our results indicate that π -complex formation is the primary reaction of most first row transition metal atoms with aromatic systems upon co-condensation at either 77 or 10 K. This complexation prevents metal-metal recombination and stabilizes the metal atom in the matrix, thereby making it available for subsequent reactions such as oxidative insertion into carbon-halogen bonds [23]. Evidence for these reactions is provided by new infrared bands corresponding to a "perturbed-benzene spectrum" consisting of several benzene-like vibrations, along with skeletal vibrations of the metal-benzene complex between 300 and 500 cm^{-1} . By varying the benzene concentration in argon matrix experiments, a second-order benzene dependence was determined for the chromium reaction, in accord with the stoichiometry of the known product, dibenzenechromium. On the other hand, the other metals, iron, cobalt, and nickel, showed a first-order dependence with benzene concentration. This result, coupled with the fact that no new infrared absorptions were observed in mixed benzene/benzene- d_6 or fluorobenzene reactions with iron, cobalt, or nickel atoms, leads us to conclude that these adducts are one-to-one metal-benzene complexes. From the shifts in characteristic arene vibrations upon complex formation, the relative metal-arene bond strength was determined to be $\text{Cr} > \text{Fe} > \text{Co} > \text{Ni}$.

Currently, other matrix investigations are in progress on the reactions of metal atoms with halogenated and fluorinated substrates.

Acknowledgements

Two of the authors (HFE and DET) wish to express their appreciation to the National Research Council and the Naval Research Laboratory who made this work possible through the NRC/NRL Resident Research Associateship program.

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