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Synthesis and selected reactions of [pi]-(arene) chromium tricarbonyls

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SYNTHESIS AND SELECTED REACTIONS OF

π-(ARENE)CHROMIUM TRICARBONYLS

A THESIS

SUBMITTED TO THE DEPARTMENT OF CHEMISTRY

OF THE GRADUATE SCHOOL OF

THE UNIVERSITY OF RICHMOND

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

BY

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To My Parents and Family

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to:

Dr. Richard A. Mateer for his patience, guidance and friendship.

Dr. W. Allan Powell for his invaluable aid.

Dr. Richard W. Topham for the use of his laboratory.

Ashby French Johnson, Jr. for providing the analyses.

David Powell for his invaluable assistance and friendship.

Pauline Fones for the many hours she spent in typing this thesis.

Melvin Oakley and Christopher Akey for their technical assistance.

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ABSTRACT

The first π-(arene)chromium tricarbonyl compound was synthesized by Fischer and Ofele in 1957. Subsequent experimentation revealed that, in most cases, π-chromium tricarbonyl compounds are synthesized readily and are fairly stable. Since the initial report appeared, a large number of these compounds have been prepared.

This project was concerned with the preparation of two π-(arene)-chromium tricarbonyl compounds that could serve as synthetic intermediates to more complex systems. These intermediates would be particularly well-suited for the preparation of mono-complexed diaryl compounds. The two intermediates selected were π-(acetophenone)chromium tricarbonyl and π-(benzyl bromide)chromium tricarbonyl. After the intermediates had been synthesized, their utility in several selected reactions was to be examined.

Although the π-acetophenone complex apparently was synthesized, the isolation of the compound in pure form was not successful. An extensive investigation of reaction conditions and purification techniques was conducted, but to no avail. The synthesis of the π-benzyl bromide complex was attempted by three alternate routes: direct complexation of benzyl bromide, free radical bromination of π-(toluene)chromium tricarbonyl and conversion of π-(benzyl alcohol)chromium tricarbonyl to the bromide with concentrated hydrobromic acid. The last of these routes was successful. A preliminary examination of the reactions of the π-(benzyl bromide)-chromium tricarbonyl with cyanide and with magnesium was initiated, but the results were inconclusive.

HISTORICAL

π-(Benzene)chromium tricarbonyl was synthesized inadvertently in
1957 by Fischer and Ofele[1] while they were attempting to prepare bis-
benzene chromium. The reaction method employed proved to be generally
applicable for the preparation of a series of π-(arene)chromium tricarbonyls.
The isolation of these compounds generated extensive interest because of
their stability, ease of synthesis and chemical reactivity as compared to
non-complexed arenes. Since the initial synthetic success was reported in
1957, more than a hundred analogous compounds have been produced.

In the initial study, Fischer and Ofele[2] reacted the selected arene
with chromium hexacarbonyl at elevated temperatures in a sealed tube.

$$Cr(CO)_6 \;+\; Arene \;\rightarrow\; (Arene)Cr(CO)_3 \;+\; 3\;CO$$
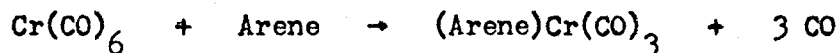
When benzene was used, a twenty-seven percent yield of π-(benzene)-
chromium tricarbonyl was isolated. Alternate synthetic procedures were
developed independently by Natta, Ercoli, and Calderazzo[3] and by Nicholls
and Whiting[4]. In the former case, the reaction was carried out in a closed
system at elevated temperatures, as before, but the system was opened per-
iodically to allow for the release of the carbon monoxide that had been
produced in the reaction. Nicholls and Whiting used an open system to

allow for the continuous release of carbon monoxide. They prevented the loss of the unreacted chromium hexacarbonyl by condensing it on a cooled surface. These procedures necessitated a periodic mechanical return of the sublimed chromium hexacarbonyl to the reaction mixture. In 1961, Strohmeier[5] described an apparatus that would allow for the continuous return of the sublimed chromium hexacarbonyl to the reaction solution, while making possible the escape of evolved carbon monoxide. A circulating organic vapor served as a solvent automatically recycling the sublimed material to the reaction site. The Strohmeier apparatus solved the major technical dilemma of having to return mechanically the sublimed chromium hexacarbonyl, without loss, and simultaneously releasing carbon monoxide. The periodic release or the continuous escape of the carbon monoxide that evolves during the course of the reaction is imperative if the reaction is to be driven further to completion, to give rise to a higher yield of the π-(arene)chromium tricarbonyl complex.

Fischer and Ofele proposed the mechanism for the complexation process illustrated in Figure 1[6]. Three carbonyls from the chromium hexacarbonyl molecule are expelled as the arene molecule approaches.
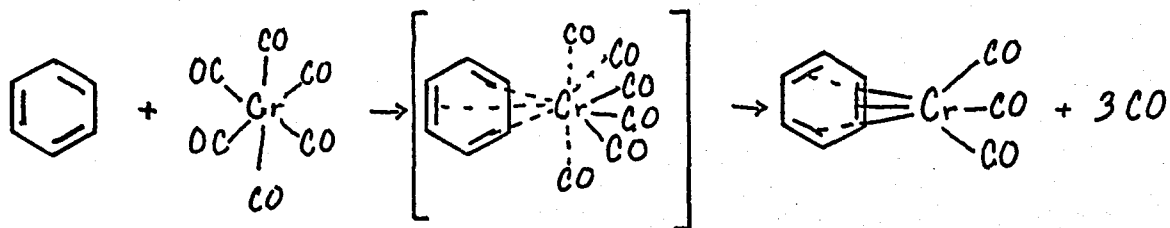

Figure 1.

With the initiation of the characteristic π-bonding, the bonds to the carbon monoxide molecules on the opposite side of the metal gradually

are weakened and finally cleaved.

The ground state electron configuration for the chromium atom in the zerovalent state is $3d^5 4s^1$ (Figure 2a). As complexation occurs, the atom undergoes an electron reorganization and hybridization process. The bonding orbitals that result are of the $d^2 sp^3$ type. This distribution is essential for the formation of chromium hexacarbonyl (Figure 2b) as well as the π-(arene)chromium tricarbonyl complex (Figure 2c).[7]

In the arene complex, six electrons are donated collectively by the three carbon monoxide molecules. These three molecules are held with equal strength to the central metal atom. The aromatic moiety completes the remaining bonding orbitals by donating six π-electrons. The resulting noble gas configuration is an illustration of the Sidgwick Effective Atomic Number Rule.[8]

Because of the electron demands of the chromium tricarbonyl substituent, the complexation of arenes substituted with electron withdrawing groups has met with little success. A competition exists between the original arene substituent and the attacking chromium hexacarbonyl for the available π-electron density. If bond formation to the chromium tricarbonyl substituent does occur, the original electron withdrawing substituent decreases the effect of back-donation from the metal to the carbonyl ligands. The net effect of this competition is a decrease in the stability of the complex.

The complexation of arenes substituted with such electron withdrawing groups as -COOH, -CHO, -CN, and $-NO_2$ has been attempted.[9] Many research groups have circumvented the problem by devising indirect synthetic routes for complexes that contain electron withdrawing groups. Tirouflet and Besançon utilized a second substituent which was electron

Cr^o

$3d^5 4s'$

(a)

$Cr(CO)_6$

$d^2 sp^3$

co   co   co   co   co   co

(b)

$d^2 sp^3$

co   co   co
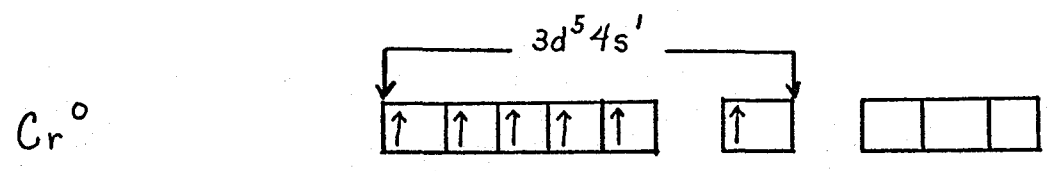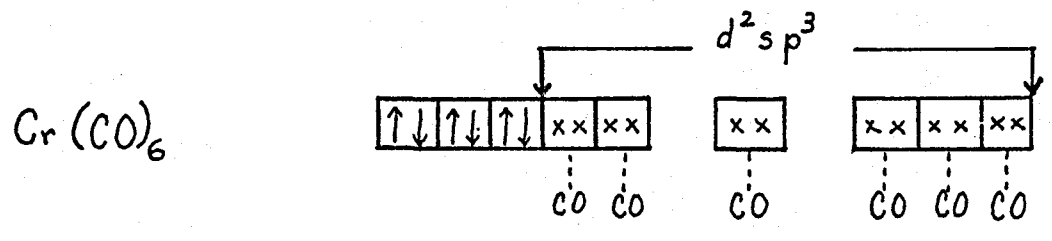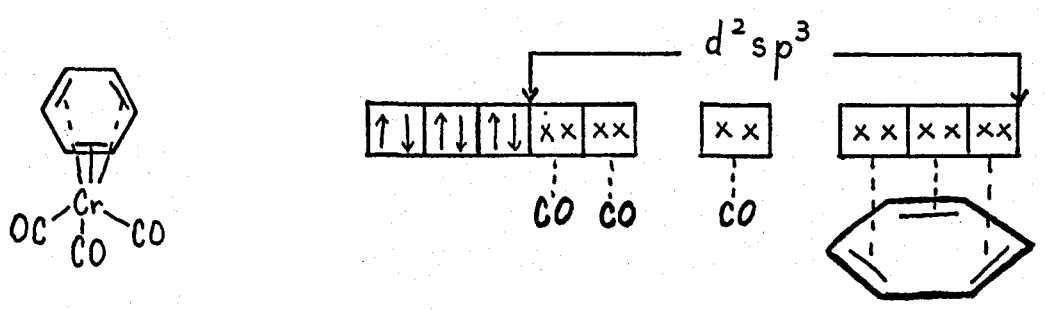
(c)

Figure 2.

releasing to weaken the unfavorable effect of the electron withdrawing substituent.[10] Mostardini, Calderazzo, and Ercoli[11] employed a second method which was also utilized by Dabard and Meyer.[12] Both of these groups de-emphasized the electron withdrawing character of the carbonyl adjacent to the ring by converting it to the less electronegative diethyl acetal. The acetal was reacted directly with chromium hexacarbonyl to form the diethyl acetal of π-(arene)chromium tricarbonyl complex which was then hydrolyzed in an acid environment to give the desired π-(arene)-chromium tricarbonyl. (Figure 4).

Failure to synthesize bis-benzenechromium by heating a mixture of benzene and chromium hexacarbonyl led to the hypothesis that the metal-carbon monoxide bond of the π-(arene)chromium complex is stronger when compared to the metal-arene bond.[13] This view was tested experimentally by altering the reaction conditions of relative and absolute concentrations, solvent, and temperatures. It was also shown that when an equimolar mixture of chromium hexacarbonyl and bis-benzene chromium was heated together, they reacted to give two equivalents of π-(benzene)-chromium tricarbonyl. (Figure 3).[14] Therefore, it has been suggested that the arene caused a strengthening of the bonds to the remaining carbon monoxide ligands.[15]

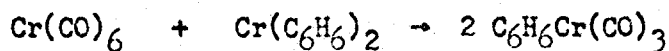$$Cr(CO)_6 \quad + \quad Cr(C_6H_6)_2 \quad \rightarrow \quad 2 \; C_6H_6Cr(CO)_3$$

Figure 3.

Carbon monoxide is bonded to the chromium atom through the donation of an unshared pair of sp-hybridized electrons. A 𝜎-coordinate covalent bond is formed when the occupied sp-orbital overlaps with a vacant hybrid orbital of chromium. A π-bond is created when a low energy p-antibonding
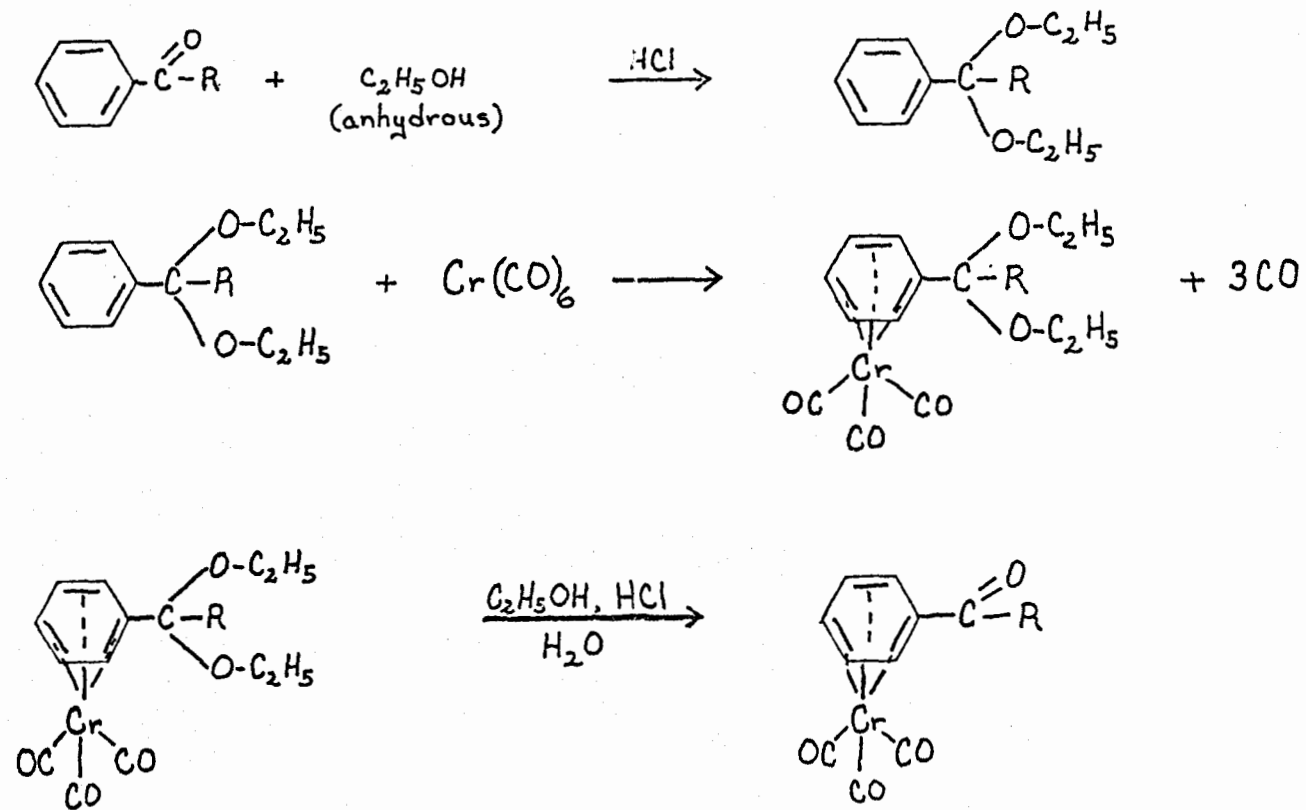
Figure 4.

orbital of the ligand overlaps with a filled nonbonding $\underline{d}$-orbital of the metal.[16] Bonding in the π-arenechromium tricarbonyl complexes arises then by donation of electrons from the ligand to the metal through $\underline{sigma}$-bonding and back-donation of electron density from the filled $\underline{d}$-orbitals of the metal to antibonding orbitals of the ligand.[17] The electron withdrawing or electron releasing properties of an arene substituent not only affect the availability of the π-electrons of the arene to form π-arenechromium tricarbonyl complexes, but they also indirectly influence the amount of back-donation between the metal and the carbon monoxide ligands.

This substituent influence has a significant effect on the total strength of the metal-carbon monoxide bond. Electron releasing groups increase the electron density on the metal and, thereby, enhance the tendency of the metal atom to back-donate electrons to the carbon monoxide ligand. As a result of this situation, the carbon monoxide molecule is not readily displaced by another ligand.

Since the arene cannot readily accomodate the nonbonding $\underline{d}$-electrons offered by the metal atom, the carbonyl groups are much better electron acceptors than the arene. After one weakly accepting arene has replaced three carbon monoxide ligands, the remaining carbon monoxide ligands acquire additional electron density. As the metal-carbon monoxide bond is strengthened, it becomes increasingly difficult to remove the remaining carbonyl ligands. Conversely, electron withdrawing substituents decrease the electron density around the chromium atom making it more positive. A decrease in the degree of back-donation from the metal to the carbon monoxide ligand results and the bond is weakened.[18, 19, 20]

π-Arenechromium tricarbonyl complexes have been extensively

investigated to establish the effect of complexation on the aromatic portion of the molecule. Several comparisons of the relative reactivities of the complexed and non-complexed aromatic systems have been made.[21] In general, π-(arene)chromium complexes have not been found to exhibit a significant degree of aromaticity;[22] the normal reaction characteristics of benzene and its derivatives have been noticeably modified.[23] The observed loss of the aromatic reactivity is considered to be a result of the π-electron donation by the aromatic group to the transition metal.[24]

A limited number of reactions involving the π-(arene)chromium tricarbonyl complexes have been reported. These reactions have involved a functional group located on the ring or sidechain, substitution for ring substituents and ligand exchange for either the arene or a carbonyl. The typical functional group modification reactions that have been carried out include saponification[25], esterification[26], the Claisen condensation[27], reduction[28,29], the Cannizaro[30] and the Wittig reactions[31]. (Table 1).

Saponification of the alkyl benzoate proved advantageous for the formation of complexed benzoic acid in significant yield. The direct complexation of the acid had given rise to unsatisfactory yields. Nicholls and Whiting utilized this method to increase the yield of benzoic acid chromium tricarbonyl from near 0% to 96%. The electron withdrawing characteristic of the chromium tricarbonyl group would facilitate the nucleophilic substitution of the hydroxyl group on the carbonyl. Natta and coworkers had obtained a 72% yield of methylbenzoate by an arene exchange reaction between benzenechromium tricarbonyl and methylbenzoate.

1.

2.

3.

4.

Table 1.

5.

$$\text{(arene)Cr(CO)}_3-C\overset{O}{\underset{H}{\lessgtr}} \quad + \quad H\text{-}C\overset{O}{\underset{H}{\lessgtr}} \quad \longrightarrow \quad \text{(arene)Cr(CO)}_3-CH_2\,OH$$

6.

$$\text{(arene)Cr(CO)}_3-C\overset{O}{\underset{H}{\lessgtr}} \quad + \quad \phi_3\text{-}P^+\text{-}CH_2\,\phi \quad Cl^- \quad \xrightarrow{C_2H_5OLi} \quad \text{(arene)Cr(CO)}_3-C=C-\phi$$

7.

$$\text{(arene)Cr(CO)}_3 \quad + \quad CH_3C\overset{O}{\underset{Cl}{\lessgtr}} \quad \xrightarrow{AlCl_3} \quad \text{(arene)Cr(CO)}_3-C\overset{O}{\underset{CH_3}{\lessgtr}}$$

8.

$$\text{(arene)Cr(CO)}_3-Cl \quad + \quad NaOCH_3 \quad \longrightarrow \quad \text{(arene)Cr(CO)}_3-O\text{-}CH_3$$
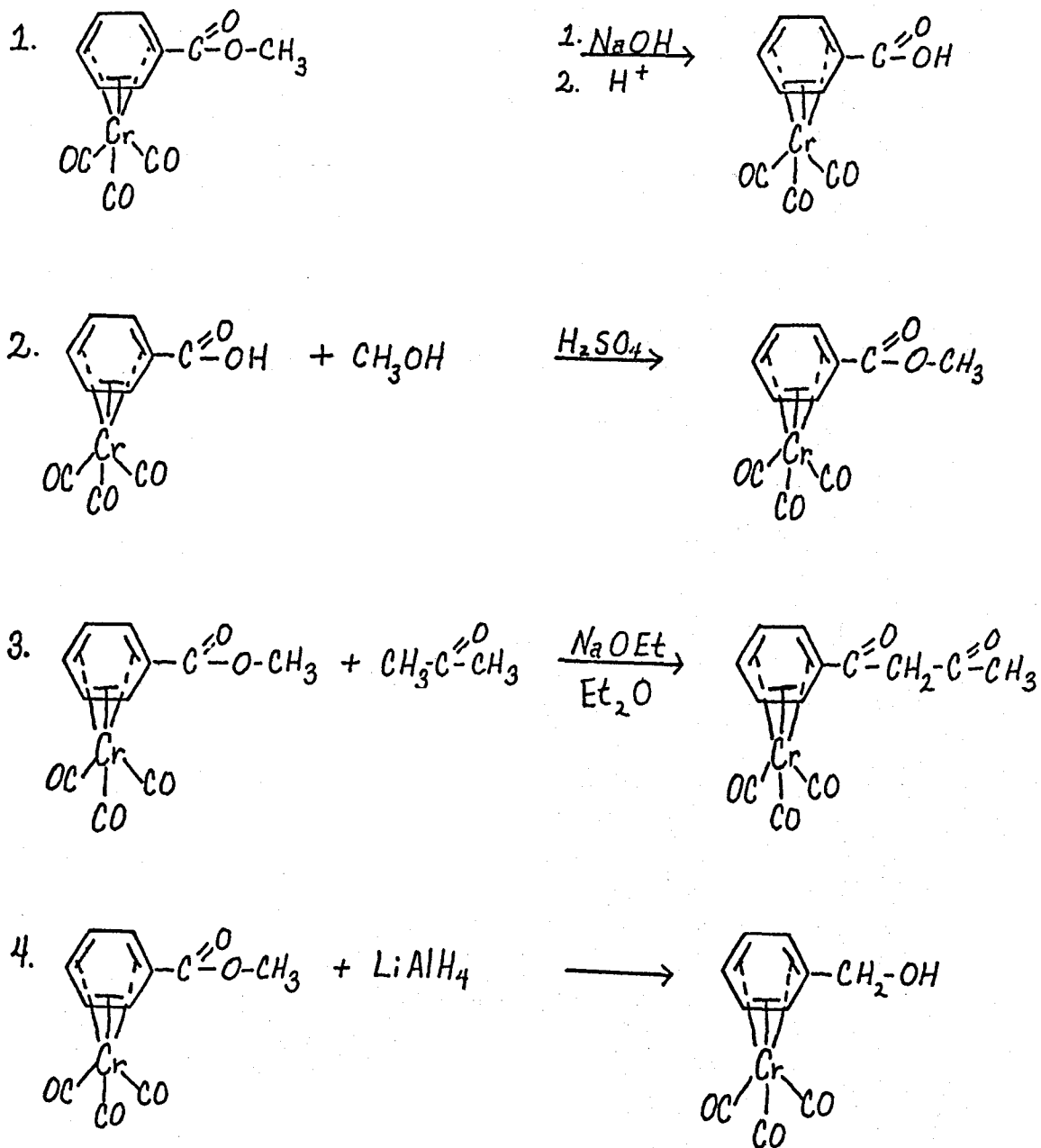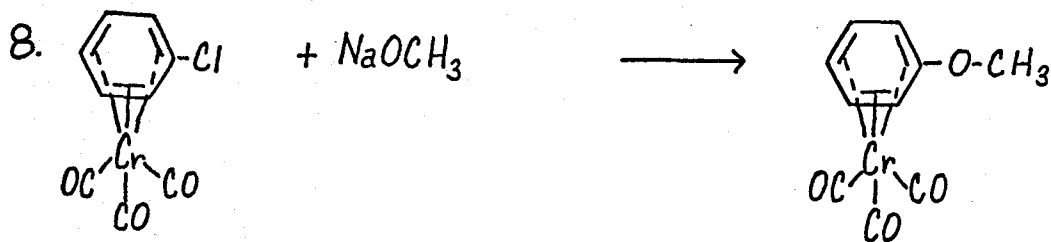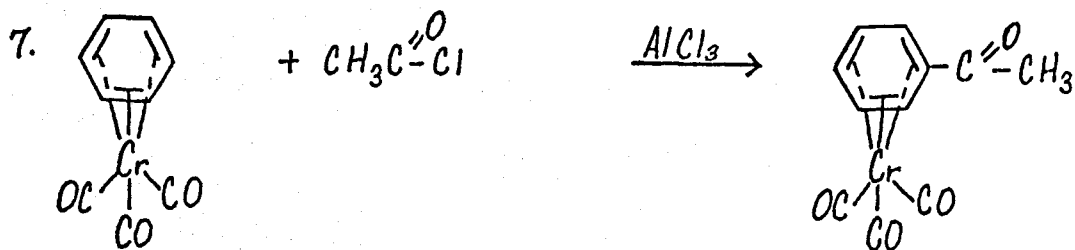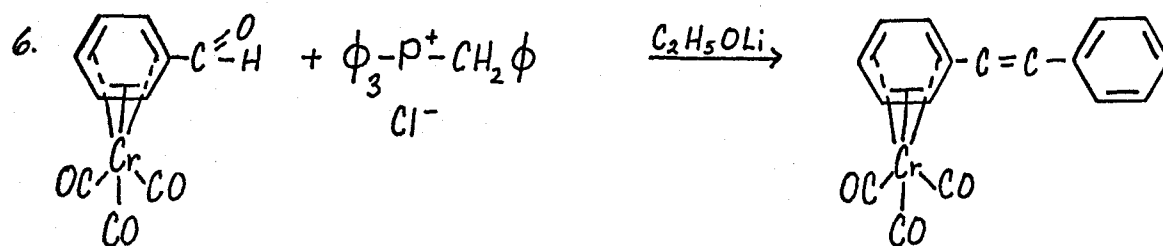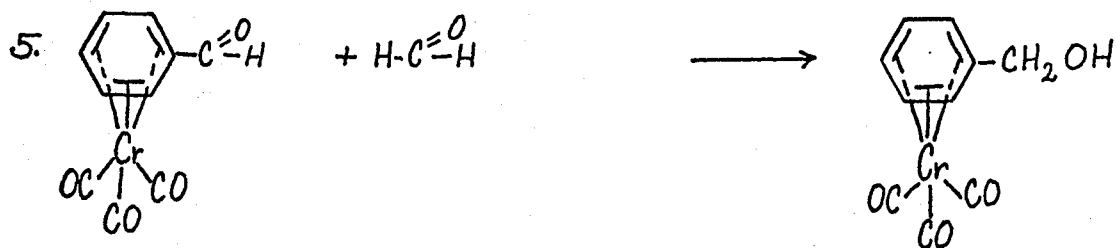
Natta and coworkers also prepared complexed methyl benzoate by the esterification of π-(benzoic)acid chromium tricarbonyl. Since the reactivity of the carbonyl group toward nucleophilic attack is enhanced in an acid solution, Natta chose a concentrated sulfuric acid-methanol solvent system for the reaction. Although the reactants had to be refluxed for several hours, a 50% yield of product was isolated. This result indicated that the complex had significant stability even in a somewhat demanding environment. The Claisen condensation reaction involved acetone and π-(methyl benzoate)chromium tricarbonyl in the presence of ethoxide. The ethoxide ion abstracts a hydrogen from acetone to give the carbanion which attacks the carbonyl functional group of the ester. The methoxide ion is expelled to generate the condensation product, π-(benzoylacetone)chromium tricarbonyl.

Lithium aluminum hydride has been used to reduce both complexed methyl benzoate and complexed benzoic acid to π-(benzyl alcohol)chromium tricarbonyl. Nicholls and Whiting obtained a 96% yield on reduction of the ester while direct complexation of benzyl alcohol gave only a 54% yield. Dabard and Meyer reported that the yields they obtained from these two alternate routes were equivalent. Complexed benzyl alcohol has also been produced via the Cannizaro reaction. Mostardini, Calderazzo and Ercoli utilized this reaction to prove the existence of π-(benzaldehyde)-chromium tricarbonyl. When an alcoholic solution of potassium hydroxide was reacted with the complexed aldehyde, they recovered the complexed alcohol. Drefahl, Hörhold and Kühne made use of the Wittig reaction to synthesize a series of mono-complexed multi-ring systems. They used these systems to illustrate the effect of various arene substituents on the chromium tricarbonyl group. The desired compounds were produced in 40 to

90% yield.

The substitution reactions have included the Friedel-Crafts
acylation and the replacement of ring substituents, such as halogen.
Electrophilic substitution by the Friedel-Crafts acylation of π-(toluene)-
chromium tricarbonyl resulted in a 39:15:46 ratio of ortho-, meta-, and
para- forms of π-(methylacetophenone) chromium tricarbonyl[32]. Under
analogous conditions non-complexed toluene gives a 9:1.5:89.5 ratio[33].
Herberich and Fischer concluded that the chromium tricarbonyl group had
a two-fold effect on the ring, which allowed for the substantial increase
in substitution at the ortho and meta positions. The chromium tricar-
bonyl group created an increase in the bond lengths from 1.36 A to 1.45 A
for the carbon-carbon bonds in the ring. This bond length increase would
negate the steric hinderance of the methyl group to ortho substitution.
The inductive capabilities of the methyl group are also reduced by the
chromium tricarbonyl substituent which results in a greater degree of
substitution at the meta position. Since the electron density in the
ring is not as great in the complexed toluene as in the non-complexed
compound, the complexed compound is less reactive to electrophilic sub-
stitution reactions.

Ercoli[34] employed the Friedel-Crafts reaction for the preparation
of several compounds that did not readily lend themselves to direct
complexation. One such compound was π-(acetophenone)chromium tricar-
bonyl. Acylation of π-(benzene)chromium tricarbonyl gave rise to a 98%
yield of complex, while direct reaction of acetophenone with chromium
hexacarbonyl gave only a 34% yield[35].

The effectiveness of the electron withdrawal of the chromium tri-
carbonyl group is demonstrated by the replacement of ring chlorine by

sodium methoxide. Anisole is not produced when non-complexed chloro-benzene is reacted with sodium methoxide. The electron density around the electronegative chlorine does not facilitate nucleophilic attack at the aromatic carbon by the methoxide ion. p-Nitro-chlorobenzene will slowly react to form p-nitroanisole. Since the electron withdrawing p-nitro group reduces the electron density of the carbon-chlorine bond, the methoxide ion is able to replace the chlorine. Under analogous conditions, π-(chlorobenzene)chromium tricarbonyl readily will yield π-(anisole)chromium tricarbonyl[36]. Nucleophilic substitution is made possible by the donation of π-electrons from the arene to the chromium tricarbonyl group. Electron transfer in this direction creates an electron deficiency on the arene and renders it more susceptible to nucleophilic attack than the non-complexed arene. Nitration and sulfo-nation[37] of the ring have not been successful, apparently because of the low π-electron density in the arene portion of the molecule.

Since electron withdrawing substituents (or ligands) impart elec-trophilic characteristics to the metal atom, it is possible to substitute for a carbonyl a group of equal or greater donating ability, such as pyridine or triphenylphosphine.

$$(Arene)Cr(CO)_3 \ + \ Ligand \ \rightarrow \ (Arene)Cr(CO)_2Ligand \ + \ CO$$

In general, only one nucleophilic molecule may be substituted into the π-(arene)chromium tricarbonyl complex[38]. Because the arene ligand is bonded somewhat weakly to the central metal atom, it can be replaced by other arenes. This situation has served as another indirect method for the preparation of tricarbonyl complexes (Figure 5)[39]. Explanation of this reaction has been restricted to one of two possible mechanisms (Table 2).
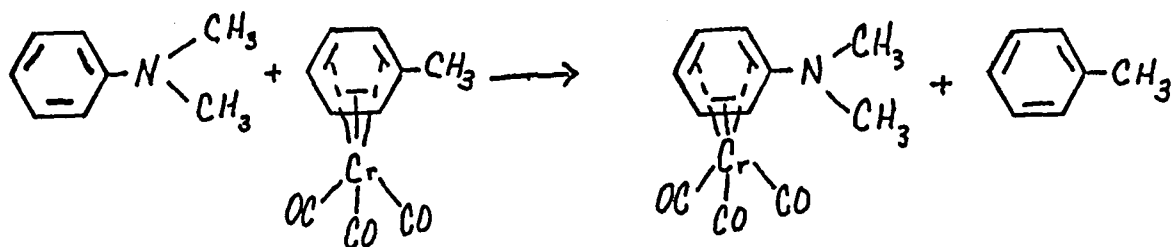
Figure 5.

Of the two plausible mechanisms for the arene exchange reaction, the one accepted as most probable involves nucleophilic attack on the arene bound to the metal (Table 2A).[40]

Another of the electronic effects that the chromium tricarbonyl group exerts on the arene is demonstrated by various pK measurements on complexed and non-complexed arenes. π-(Benzoic acid)chromium tricarbonyl has a pK_a of 4.77 and that of benzoic acid is 5.68. π-(Aniline)chromium tricarbonyl is a much weaker base than aniline; the pK_b values are 13.31 and 11.70 respectively.[41,42,43]

TABLE 2.

PROPOSED MECHANISMS FOR ARENE EXCHANGE REACTIONS

A.
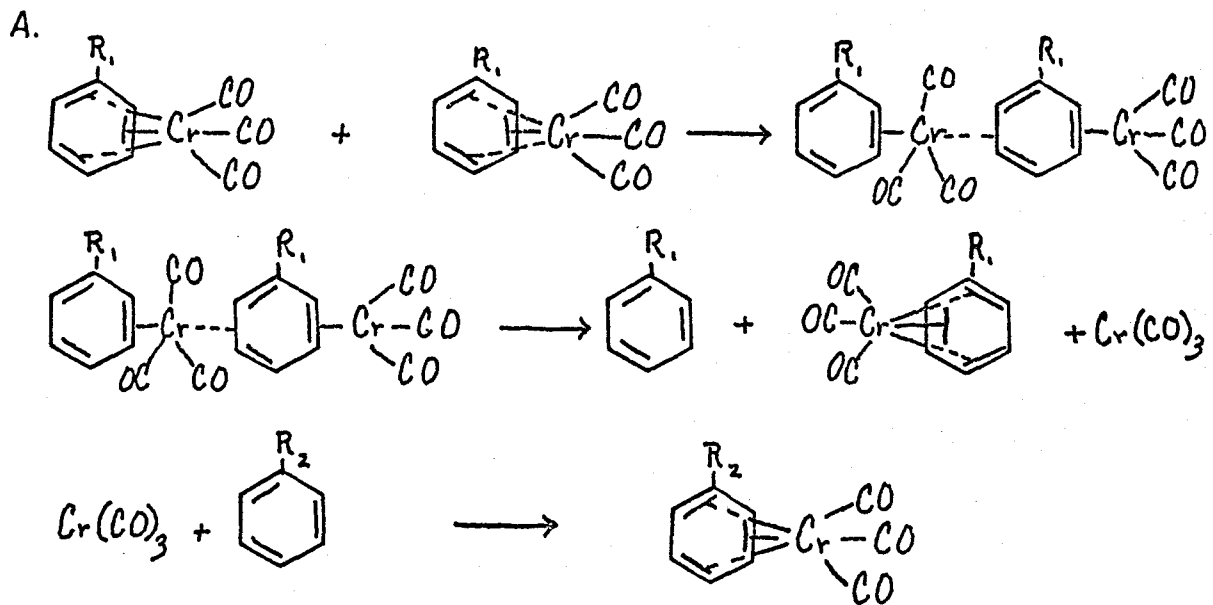
B.
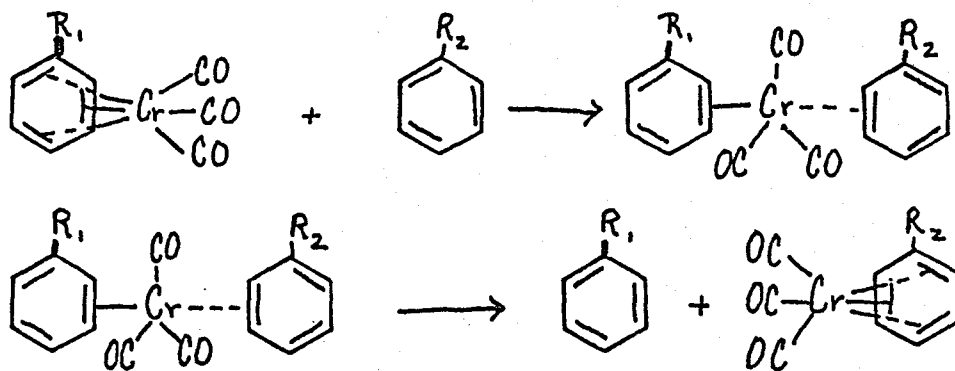
DISCUSSION

While the preparation of many π-arene complexes has been achieved, most of these compounds have been prepared by the direct complexation of a suitable substrate with the complexing agent. Another synthetic route would involve the preparation of a π-arene complex that would serve as a synthetic intermediate to the desired compound. Because of the multi-step nature of the second route, it normally would not be as attractive as direct complexation. On the other hand, the superiority of the direct complexation option would be questionable if the organic substrate had two sites that competed for the complexing agent. This competition problem could be avoided by the alternate route. An intermediate complex that has only one reactive site would be prepared initially, and then the intermediate would be condensed with a second molecule that contains the other site.

The goal of this project was to synthesize π-arene complexes that could serve as intermediates to more complex organometallic compounds. The specific intermediates desired were π-(acetophenone)chromium tricarbonyl and π-(benzyl bromide)chromium tricarbonyl. With the first of these complexes, investigations were to be conducted concerned with the resistance of the chromium tricarbonyl group to reduction and the stability of the compound to condensation reaction conditions. The second compound was to be prepared via two synthetic pathways and then used as a substrate in selected reactions.

Attempted Synthesis of π-(Acetophenone)Chromium Tricarbonyl.

Nicholls and Whiting[44] have reported the most successful preparation of crystalline π-(acetophenone)chromium tricarbonyl. Their procedure

involved the direct complexation of acetophenone with chromium hexa-
carbonyl in an open system. The use of this apparatus requires the
periodic mechanical return of the sublimed material. In the current
investigation, a Strohmeier apparatus was used which allowed for the
continuous return of sublimed chromium hexacarbonyl.

Our attempts to prepare the π-acetophenone complex resulted in the
formation of oils. The infrared spectrum of the oil contained distinct
carbonyl stretching bands at 1900 and 1960 cm^{-1} which are characteristic
of complexed arenes. Recrystallization of the oil from a variety of
solvent systems that had been employed successfully for the purification
of other π-arene complexes did not give rise to crystalline product.
Adsorption column chromatography on several varieties of alumina and on
Florisil did not produce observable separation or purification. Analysis
of the oil by thin layer chromatography suggested that it was composed of
non-complexed acetophenone and complexed acetophenone. The reaction con-
ditions were modified with respect to the relative and absolute concen-
trations of arene and chromium hexacarbonyl, the solvent and the reflux
time, but the results did not vary markedly.

The difficulty in preparing a significant yield of the π-acetophenone
complex probably stems from an unfavorable substituent electronic effect.
To successfully displace the carbon monoxide ligands from the chromium,
the incoming arene ligand must donate effectively its π-electron density.
Since the acetyl group is electron withdrawing, the π-electron density
(as well as ς-electron density) is to some extent shifted to the substitu-
ent. This reorganization renders the acetophenone less attractive as a
possible ligand.

The attempt to prepare π-(benzyl alcohol)chromium tricarbonyl was

successful (vide infra) although the hydroxymethyl substituent is elec-
tron withdrawing.   It should be noted that a crystalline product of
π-(benzyl alcohol)chromium tricarbonyl was obtained only after a 72 hr
reaction period and that a maximum yield required 120 hr. Since the
carbonyl group will more effectively withdraw electron density from the
ring than a hydroxymethyl group, a reaction time of greater than 120 hr
probably would be necessary to ensure a significant yield of π-aceto-
phenone complex.

Preparation of the Diethyl Acetal of π-(Acetophenone)Chromium Tricarbonyl.

Because of the difficulty in obtaining crystalline π-acetophenone
complex by the direct complexation of acetophenone, an alternate approach
was investigated. This procedure initially involved the preparation of
the diethyl acetal of acetophenone which was then reacted with chromium
hexacarbonyl. By utilizing this method, it was hoped that the less elec-
tronegative diethyl acetal substituent would facilitate complexation of
the π-electrons. If the complexed diethyl acetal were formed, it could
then be acidified to yield π-(acetophenone)chromium tricarbonyl.

After refluxing the diethyl acetal of acetophenone for 6 hr at 165°,
0.13 g (4.23%) of crystalline diethyl acetal was obtained. Thus it can
be concluded that the less electronegative diethyl acetal either enhances
the availability of the π-electrons for complexation or enhances the ease
of crystallization of the product.

Because the emphasis of the research was shifted at this time toward
the preparation of another complex intermediate, the diethyl acetal was
not acidified to form the π-acetophenone complex. In subsequent investi-
gations a significant yield of the diethyl acetal should be obtained if

the reaction time were extended. The complexed diethyl acetal could be acidified and the resulting complexed acetophenone could be studied.

Since the attempted preparations of π-(acetophenone)chromium tri-carbonyl did not afford product in a form suitable for use as a chemical intermediate, an evaluation of alternate compounds was begun. As an initial step, the synthesis of π-(toluene)chromium tricarbonyl was inves-tigated. This compound is available commercially although it is quite expensive. In order to gain additional experience in preparing π-complex compounds, as well as for economic considerations, a thorough study of the compound was initiated. Although the methyl side-chain of the complex would be essentially inert, free radical halogenation could introduce reactive functionality into the compound.

Synthesis of π-(Toluene)Chromium Tricarbonyl.

Electron donation from the methyl group to the ring should increase the electron density in the ring. This increased electron density should permit a greater degree of π-electron donation to an electrophile and make toluene more susceptible to complexation than acetophenone or benzyl alcohol. π-(Toluene)chromium tricarbonyl had been prepared successfully by Nicholls and Whiting[45] and by Strohmeier[46].

The preparation of the complex was attempted under a variety of con-ditions in an effort to maximize the yield. The relative and absolute concentrations of toluene and chromium hexacarbonyl were varied, as well as the solvent system and the reaction time. (See Table 4, p. 36). As a result of these modifications, the yield of isolated pure material ranged from 0 to 48%.

The reaction temperature is critical, since it has been shown that the

toluene complex decomposes at 170°. The reflux temperature employed in
the current investigation was varied from 110° to 165°. This temperature
is dictated by the solvent employed and by the design of the apparatus.
The temperature must be sufficient to permit cycling of the solvent to
ensure the return of sublimed chromium hexacarbonyl. Iso-octane was em-
ployed as part of the solvent system because of its volatility.

The choice of reaction solvent did affect the yield of the complex.
The four solvent systems employed were n-butyl ether-iso-octane, diglyme-
iso-octane, iso-pentyl acetate-iso-octane and iso-octane. Because of its
volatility the toluene also could be considered as part of the solvent
system as well as a reactant. For each solvent system the yield of product
increased with reflux period, although the increase was more significant
in the cases of diglyme-iso-octane and iso-pentyl acetate-iso-octane.
Only one experiment was conducted with the system iso-octane-toluene, and
it gave rise to the highest yield. It should be noted that the reflux
time for this experiment was much longer.

With a sufficient quantity of π-(toluene)chromium tricarbonyl avail-
able, a study of the free radical bromination of the complex was started.
N-Bromosuccinimide, which provides a constant, low concentration of bromine,
was employed as the brominating agent. The mechanism for the introduction
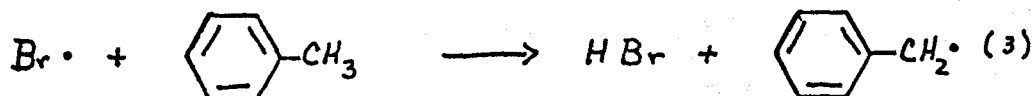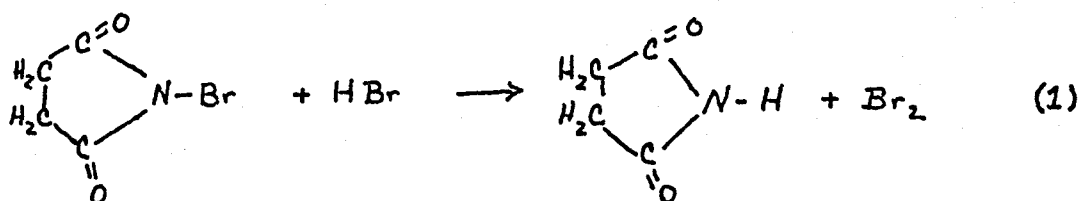of the halogen atom has been shown to involve the following steps:[47]

$$Br_2 \longrightarrow 2\,Br \cdot \qquad (2)$$

$$\langle\!\!\langle \rangle\!\!\rangle\text{-}CH_2\cdot \; + Br_2 \longrightarrow \langle\!\!\langle \rangle\!\!\rangle\text{-}CH_2Br \; + \; Br\cdot \quad (4)$$

Figure 6.

Reaction of π-(Toluene)Chromium Tricarbonyl with N-Bromosuccinimide

The bromination of the π-toluene complex with N-bromosuccinimide was carried out in carbon tetrachloride and in diethyl ether. The relative and absolute concentrations of all reactants and the reflux time were not varied. The reflux temperatures of the two reactions were different as a result of the difference in the boiling point of the two solvents.

When carbon tetrachloride was used as the solvent, there was an apparent reaction based on the decoloration of the reaction solution and the appearance of a green-brown residue in the flask. After a preliminary purification had been effected, the residue was shown to be a chromium oxide, the exact formula of which was not established. This oxide resulted from the decomposition of the π-complex. The oxide also was obtained in each preparation of a π-arene complex. The reaction solution was analyzed by both thin layer and gas chromatographic analysis. The results of these analyses indicated that the π-(toluene)chromium tricarbonyl was no longer present, but that non-complexed toluene and bromine were present.

The results from the ether experiment were somewhat different. A slight decoloration of the reaction solution occurred and a green residue appeared in the flask, but in this case 1.0 g of unreacted starting material was recovered. Thin layer chromatographic analysis of the reaction solution indicated the presence of starting material, while gas chromatographic analysis indicated the existence of non-complexed toluene. The

only advantage in changing the solvent from carbon tetrachloride to diethyl ether was apparently a change in decomposition time. This result is in part determined by the difference in boiling point of the two solvents.

When the significant features of the free radical bromination mechinism are considered, some insight can be obtained with regard to the tendency of the π-complexed toluene to undergo decomposition. Since the bromine radical is somewhat more electronegative than a benzyl carbon, it will hold more than its share of the electron density in the transition state (figure 7) of the rate determining step. Therefore the stability of the transition state depends on the ability of the aromatic system
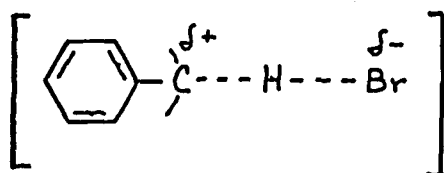
Figure 7.

to accommodate both the odd electron and the partial positive charge. In the benzyl group, the aromatic portion can delocalize the odd electron and stabilizes the transition state. (Figure 8). However, its electron
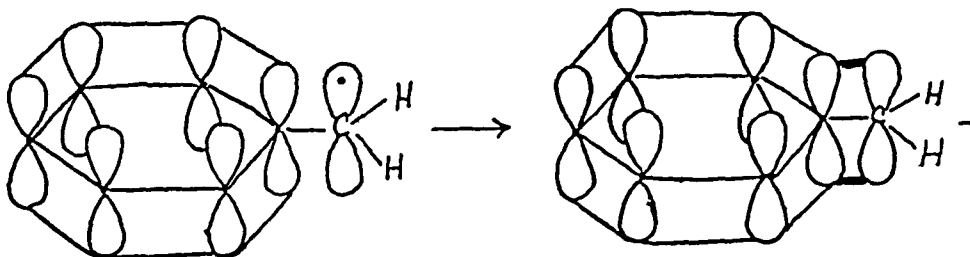

Figure 8.

withdrawing inductive effect intensifies the partial positive charge and thus destabilizes the transition state. In the non-complexed toluene the intensification of the partial positive charge serves to slow down the rate

of the reaction[48]. The complexation of the arene significantly alters

the ability of the arene ring to stabilize the transition state. Since

the π-electrons have been donated partially to the chromium tricarbonyl

group, they are no longer as available to stabilize the electron deficient

carbon of the side-chain. If the electron density were transferred back

to the ring at the expense of back donation to the carbonyl groups, it

would decrease the electron density around the chromium and consequently

weaken the chromium-carbonyl bond. The end result would be decarbonylation[49]

(Figure 9). If decarbonylation occurred, the toluene that resulted could
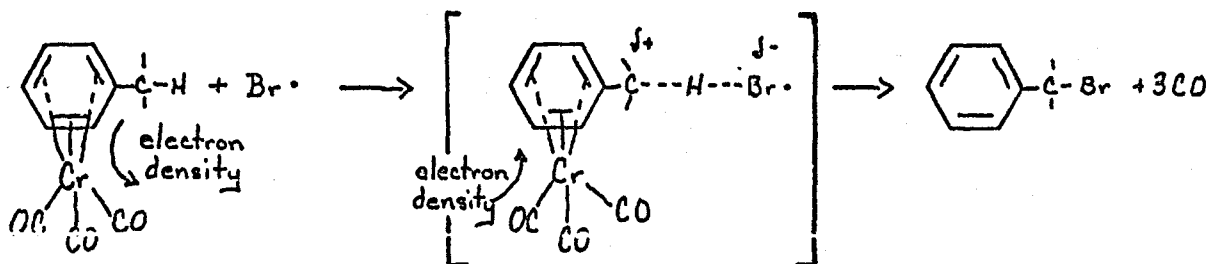
Figure 9.

give rise to non-complexed benzyl bromide. Additionally the electron

withdrawing inductive effect of the ring is accentuated by the chromium

tricarbonyl group.

In the analysis by both thin layer and gas chromatography, there was

no indication that benzyl bromide had been formed. Absence of benzyl

bromide has suggested that the electrophilic bromine radical did not

attack the arene portion of the complex. Since the chromium tricarbonyl

group is strongly electron withdrawing, it has acquired a greater electron

density than the arene. Therefore, the electrophilic bromine radical

would attack the chromium tricarbonyl group instead of the benzyl hydrogen,

resulting in the decomposition of the π-(toluene)chromium tricarbonyl complex.
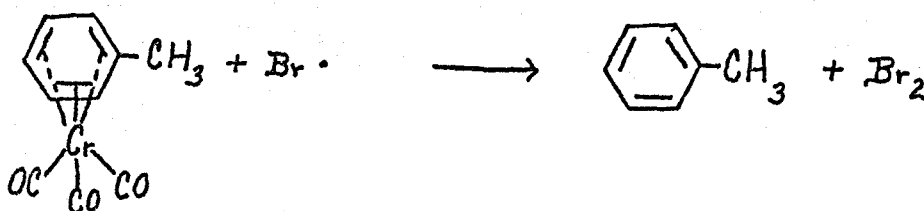
Figure 10.

While the investigation of the free radical halogenation of π-(tol-uene)chromium tricarbonyl was in progress, a study of the direct complex-ation of benzyl bromide was initiated. Since both reactions were expected to yield the same complex, the product from one of the routes could serve as an analytical standard in evaluating the success of the other reaction.

Attempted Preparation of π-(Benzyl Bromide)Chromium Tricarbonyl by Direct Complexation.

All attempts to prepare π-(benzyl bromide)chromium tricarbonyl by the direct complexation of benzyl bromide resulted in the production of 1,2-diphenylethane and bromine as the only isolable products.

The usual reaction conditions of choice of solvent, reflux time and temperature were modified to some degree with no significant effect on the reaction outcome. In one of these experiments, a 65% yield of 1,2-diphenylethane was isolated. To determine if the unexpected results stemmed from the instability of benzyl bromide, it was subjected to the reaction conditions employed. There was no evidence of decomposition of the benzyl bromide or appearance of 1,2-diphenylethane.

An explanation for the observed results is not readily available. Although the bromomethyl group is inductively electron withdrawing, it only should deplete the available ring electron density to a small extent. Additionally other π-complexes with arene substituents more electron

withdrawing than the bromomethyl group have been prepared. Apparently, an additional factor must be operating to make the coupling process energetically favorable.

Since neither the direct complexation route nor the free radical halogenation route to π-(benzyl bromide)chromium tricarbonyl was successful, an investigation of alternate routes was begun. It had been reported in the literature that π-(benzyl alcohol)chromium tricarbonyl could be converted to π-(benzyl chloride)chromium tricarbonyl by reaction with concentrated hydrochloric acid at room temperature.[50] The analogous reaction with hydrobromic acid had not been reported. Since the π-(benzyl alcohol)chromium tricarbonyl was not available commercially, the preparation of a sufficient quantity of the compound for the eventual conversion to the π-complexed bromide was initiated.

Preparation of π-(Benzyl Alcohol)Chromium Tricarbonyl and its Conversion to π-(Benzyl Bromide)Chromium Tricarbonyl.

The preparation of the π-benzyl alcohol had been reported in the literature by Nicholls and Whiting[51]. To ensure that the maximum yield of the π-complex would be obtained, several combinations of reaction conditions were examined. It was soon apparent that the reflux time was a major factor in determining the amount of product. The maximum yield of the complexed alcohol was obtained after a reflux period of 120 hr. In the experiment, 93.5% of the π-complex was isolated after preliminary purification.

The degree of success for this complexation process is somewhat unexpected if only the nature of the arene substituent is considered. Since the hydroxymethyl group is inductively electron withdrawing, the

available π-electron density should be reduced somewhat. This decreased electron density should result in a lower yield of the π-benzyl alcohol complex. Apparently the extended reaction time employed counter-balances this factor.

The π-(benzyl alcohol)chromium tricarbonyl was dissolved in benzene and treated with an excess of 48% hydrobromic acid at room temperature. After the work-up procedure had been effected, a 86% yield of π-(benzyl bromide)chromium tricarbonyl was isolated. This compound had not been reported, heretofore, in the literature.

A determination of the mechanism by which this substitution occurred would be of theoretical interest. The reaction concievably could proceed by either the S_N1 or S_N2 mechanism. (Figure 11).

Since the solvent system is heterogeneous, it is difficult to ascertain whether a mechanism involving the formation of ions, specifically the S_N1 reaction, would be favored or not. The non-polar benzene certainly would not favor ionization, but such a process could proceed to some extent in the more polar concentrated acid solution.

The electron withdrawing nature of the chromium tricarbonyl group should demonstrate a significant influence in the determination of the preferred mechanism. π-Electron delocalization in the direction of the chromium tricarbonyl would not allow for the stabilization of the incipient carbonium ion in the rate determining step. If the π-electron cloud were used significantly to stabilize the arising ion, it would be at the expense of the arene-chromium bonding or the chromium-carbon monoxide bonding. The attempted stabilization of the carbonium ion conceiveably could result in decomplexation or decarbonylation. On the other hand, the

$S_N 1$

A.

$S_N 2$

B.
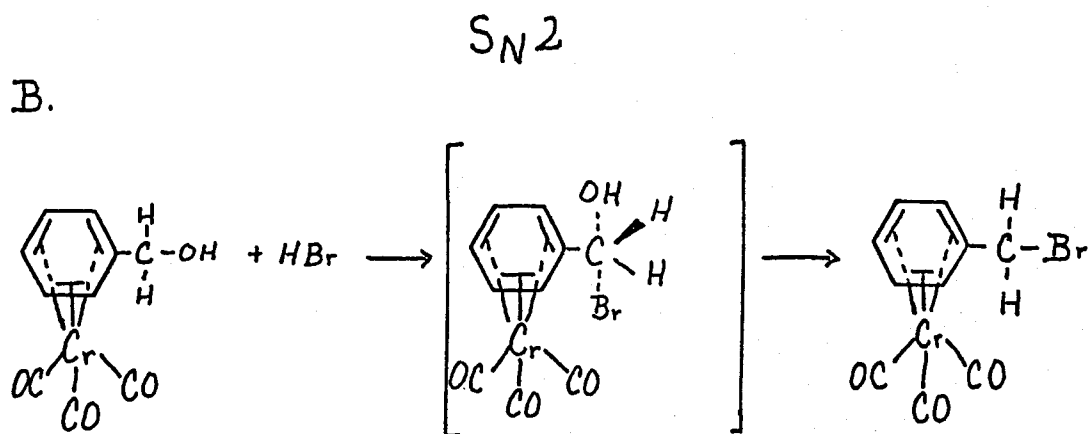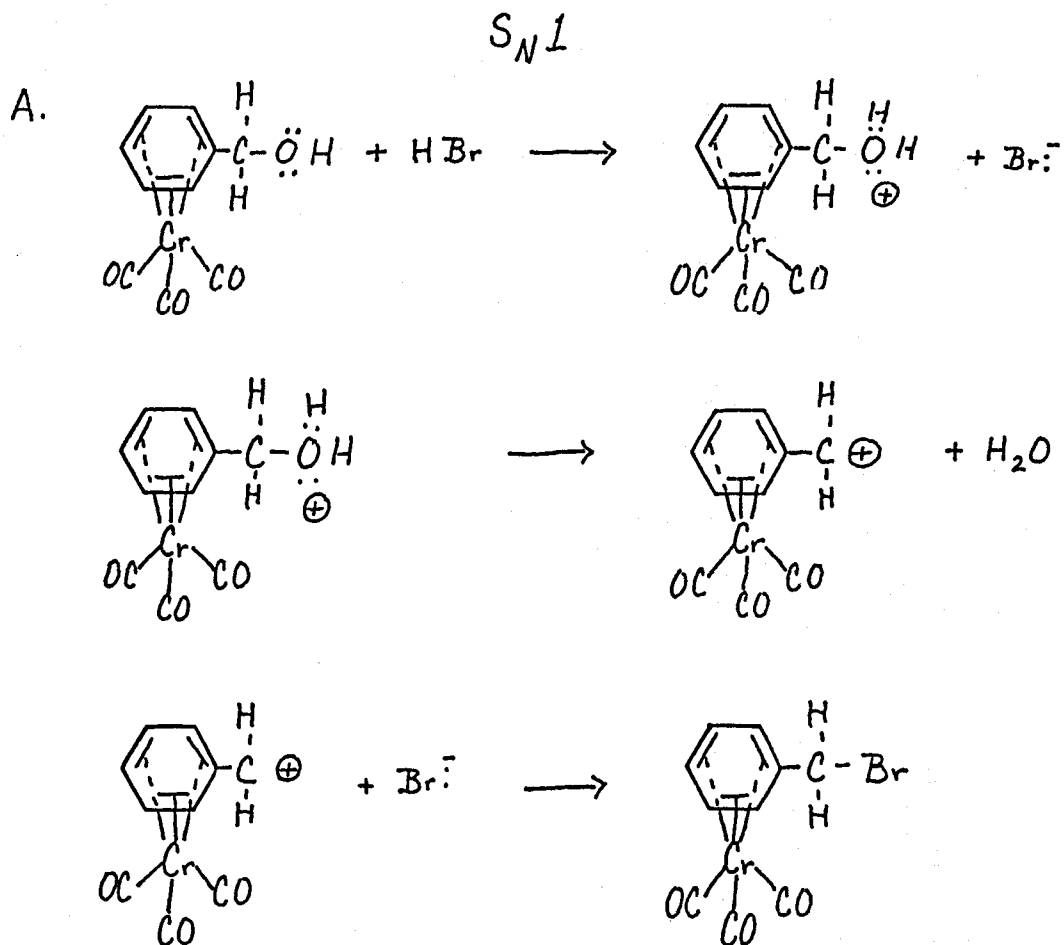
Figure 11.

electron withdrawing chromium tricarbonyl group should enhance the electrophilic character of the ∝-carbon, which would make it more susceptible to nucleophilic attack via an S_N2 mechanism. These predictions are based only on a consideration of the positive inductive effect of the chromium tricarbonyl. It also has been reported in the literature that this group can become more directly involved with a reaction center and thereby affect the reaction mechanism. This possiblity has not been considered in this brief account.

The successful synthesis of π-(benzyl bromide)chromium tricarbonyl satisfied the project goal of the preparation of a π-complexed arene with reactive functionality that could serve as a chemical intermediate for more complex systems. Several reactions then were selected to determine the range of utility of this intermediate. These reactions are illustrated below:

1. Reaction with Sodium Cyanide
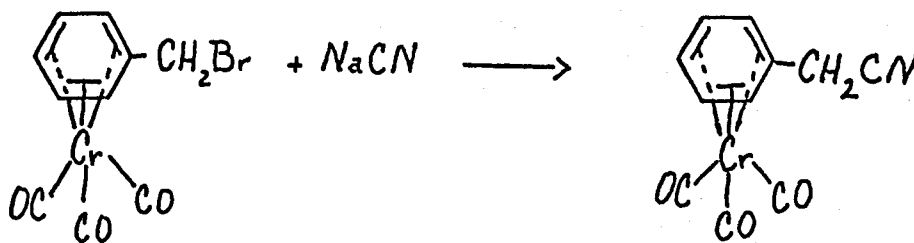
Figure 12.

The product of this reaction could be reduced to the amine, hydrolyzed to the acid, or condensed with a carbonyl containing compound via a carbanion reaction.

2. Conversion to a Grignard Reagent and Subsequent Reaction of the Grignard Reagent.
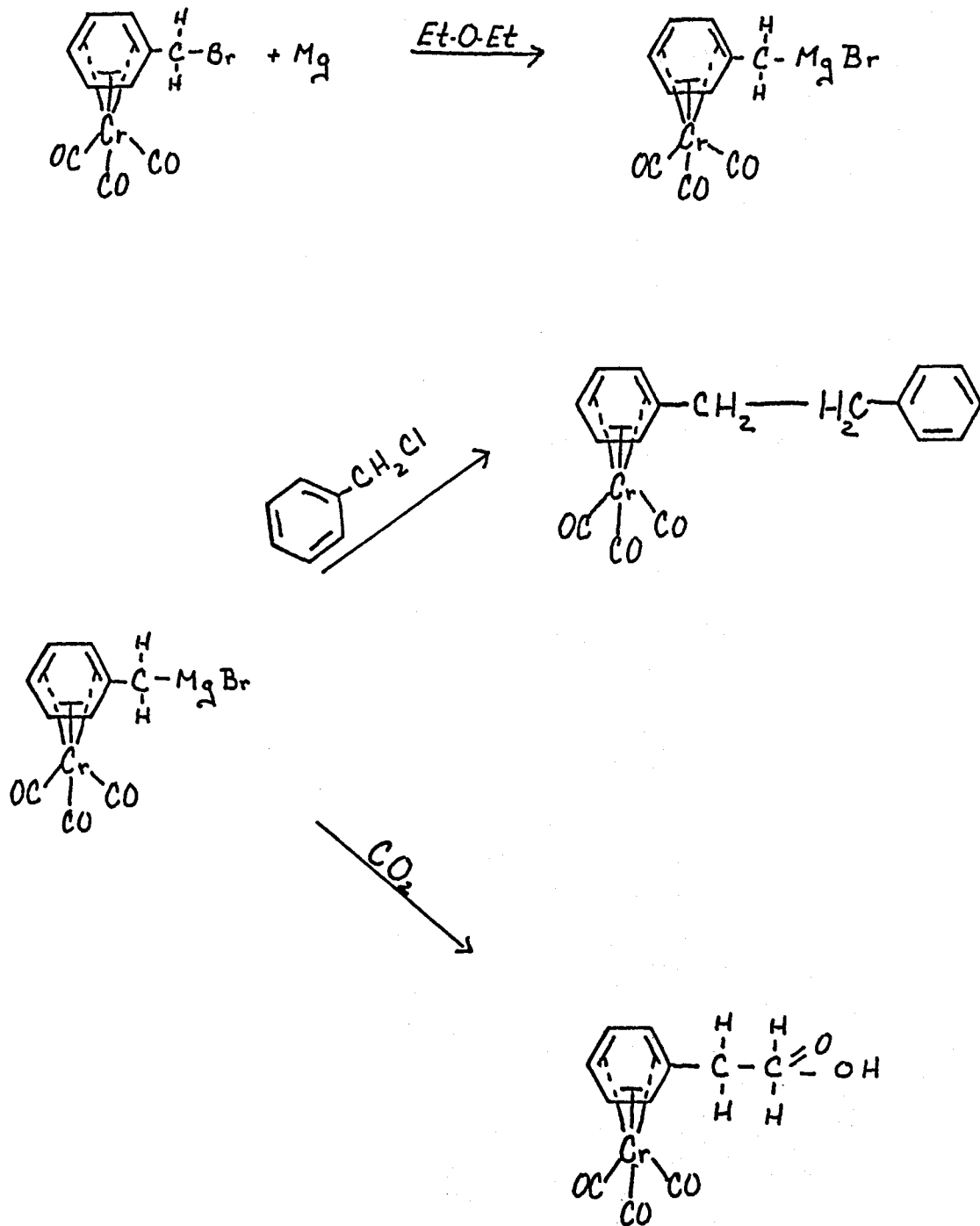
Figure 13.

3. Reaction with Lithium and Subsequent Reaction of the Lithium
Compound.
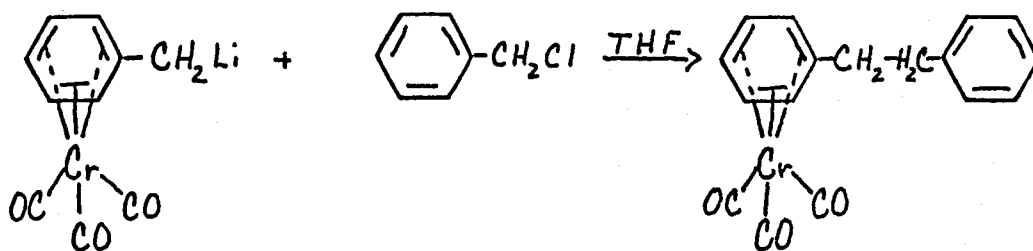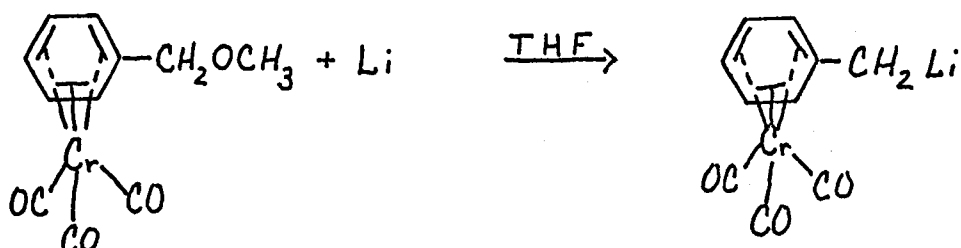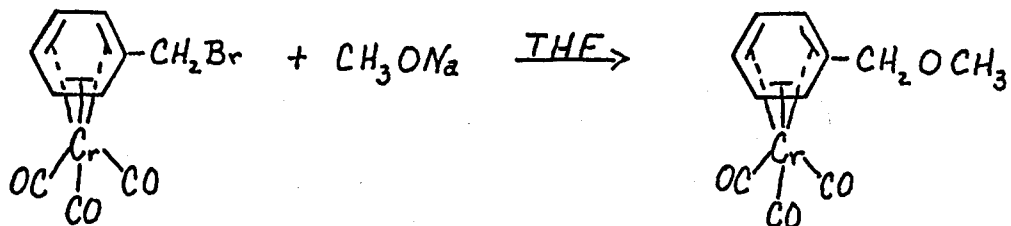
Figure 14.

These proposed reactions have not been fully evaluated at this time
because of the instability of the π-(benzyl bromide)chromium tricarbonyl.
The complex has a tendency to undergo some decomposition while standing
in the air. It was observed that two hours after the complex had been
recrystallized, a significant amount of green color had been imparted to
the initially bright yellow sample. Recrystallization of this impure
sample provided a pure sample again, but this sample likewise proceeded
to decompose. As a result of this instability, the π-benzyl bromide

complex had to be used soon after it was isolated.

Attempted Preparation of π-(Benzyl Cyanide)Chromium Tricarbonyl.

The π-(benzyl bromide)chromium tricarbonyl complex was reacted with sodium cyanide in alcohol employing a procedure adapted from that of Gilman and Blatt[52]. After the prescribed work-up had been effected, a yellow oil was isolated. Analysis by thin layer chromatography indicated that several components were present in the oil. The oil was passed through an alumina column in an effort to separate these components. The fractions were analyzed by thin layer chromatography and similar fractions were combined and concentrated. Thin layer chromatographic analysis indicated only one component now was present. All attempts at recrystallization of the resulting material were unsuccessful. On analysis by infrared, a band at 2230 cm^{-1} characteristic of the cyanide group was observed, but the usually simple carbonyl absorption pattern had been distorted significantly. At this point, no concrete conclusions can be drawn about the structure of the product.

At the present time, preliminary investigations are being conducted on the reactivity of the π-(benzyl bromide)chromium tricarbonyl with magnesium and lithium metals. These studies will provide additional information about the chemical reactivity and the stability of the complex toward metals as well as indicate if these routes are suitable for the preparation of mono-complexed diaryls. More experimental work is currently being conducted on the formation of the π-(benzyl cyanide)chromium tricarbonyl.

EXPERIMENTAL

The procedures used for the preparation of the π-(arene) complexes are cited below. Tables have been used to illustrate such variations in reaction conditions as reaction time, concentrations and solvent. Melting points were taken in capillary tubes using a Thomas-Hoover melting point apparatus and were not corrected. Infrared spectra were recorded on a Perkin-Elmer Model 710 spectrophotometer. Elemental analyses were performed by the A. H. Robins Pharmaceutical Co., Inc., of Richmond, Va. Thin layer chromatography (TLC) analyses were conducted on 25 X 75 mm microscope slides with Mallinckrodt SilicAR TLC-7GF as the stationary phase. The chromium hexacarbonyl was obtained from the Pressure Chemical Company (Pittsburgh, Pa.) and all other chemicals from the Aldrich Chemical Co. or J. T. Baker Co. Complexation reactions were run in the Strohmeier apparatus,[53] unless otherwise noted.

Attempted Preparation of π-(Acetophenone)Chromium Tricarbonyl.--This procedure was adapted from that described by Nicholls and Whiting.[54]

To a flame dried 100-ml flask containing 16 ml of freshly distilled n-butyl ether and 4 ml of sodium dried iso-octane were added 4.22 g (0.035 mole) of freshly distilled acetophenone and 2.06 g (0.009 mole) of chromium hexacarbonyl. The mixture was refluxed 4.5 hr at 170°C. The reddish-brown solution was cooled by an ice-water bath and then filtered by suction. The flask was washed with three 25 ml portions of hot n-hexane and the washings passed through the filter. The solution was concentrated to approximately 5 ml on the rotary evaporator. The residue was transferred to a 1-inch diameter chromatography column packed with 9 inches of neutral alumina (Activity 1) and eluted with benzene; each fraction consisted of

10 ml. The fractions were evaporated to dryness and 20 ml of n-hexane-ether solution were added. The resulting solution was concentrated and allowed to cool. No crystals were formed in the concentrated solution. A reddish-orange oil was all that remained. The oil was analyzed by Infrared Spectroscopy and Thin Layer Chromatography. The infrared spectrum of the oil was compared to that of the non-complexed material. There were distinct carbonyl stretching bands at 1900 and 1960 cm^{-1}, which is characteristic of complexed arenes. The TLC results indicated two spots. A standard of non-complexed acetophenone was utilized to identify one of the spots. The remaining spot was believed to be that of the complexed material.

Preparation of the Diethyl Acetal of π-(Acetophenone)Chromium Tricarbonyl. --The procedure utilized for the formation of the acetal was similar to that of Pfeifer and Adkins.[55] The method for the complexation of the acetal was adapted from that reported by Mostardini, Calderazzo and Ercoli[56]

To a flame dried 100-ml flask equipped with a condenser and calcium chloride drying tube were added 15.45 g (0.129 mole) of freshly distilled triethyl orthoformate, 15.0 ml (0.214 mole) of absolute ethanol and two drops of concentrated hydrochloric acid. The mixture was magnetically stirred for 24 hr and was then neutralized with anhydrous potassium carbonate and filtered by suction. The filtrate was distilled under reduced pressure to give 3.08 g (86.0%) of the ketal, bp 58°C (2mm).

To a flame dried 100-ml flask were added 3.42 g (0.02 mole) of acetophenone diethyl acetal, 2.19 g (0.01 mole) of chromium hexacarbonyl, 10 ml of freshly distilled n-butyl ether, and 10 ml of sodium dried iso-octane. The reaction mixture was heated at 165°C for 6 hr. The reaction

Attempted Acetophenone Complexation Reactions

Arene/Cr(CO)$_6$ (g/g)	Solvent (ml)	Time (hr)	Temperature (^{o}C)	% Yield
4.17/7.42	10 ml butyl ether/10 ml iso-octane	4.5	180	Oil
2.41/2.20	8 ml butyl ether/8 ml iso-octane	24	165	Oil
2.42/2.21	8 ml butyl ether/8ml iso-octane	6	165	Oil
10.3/1.57	10 ml diglyme/10 ml iso-octane	24	165	Oil
15.5/5.00	20 ml butyl ether/15 ml iso-octane	120	170	Oil

Table 3.

solution was cooled by an ice-water bath, filtered by suction and the residue washed with three 25 ml portions of hot n-hexane. The filtrate was concentrated and allowed to cool. The yellow crystalline product was isolated by suction filtration and washed with cold n-hexane to give 0.13 g (4.23%) of product, mp 49-51°, (Lit., mp 52-54°C).

Preparation of π-(Toluene)Chromium Tricarbonyl.—This method was adapted from that described by Nicholls and Whiting[57].

To a flame dried 200-ml flask were added 3.03 g (0.033 mole) of freshly distilled toluene, 3.60 g (0.016 mole) of chromium hexacarbonyl, 50 ml of freshly distilled n-butyl ether, and 50 ml of iso-octane. The reaction mixture was refluxed 4.5 hr at 145°C. The reaction mixture was cooled by an ice-water bath and filtered using a water aspirator and the residue washed with ether. The filtrate was concentrated and n-hexane added to the residue. The solid product was isolated by suction filtration and washed with cold n-hexane to give 0.08 g (2.3%) of yellow crystals, mp 78-80°, (Lit., mp 82-83°C).

Attempted Preparation of π-(Benzyl Bromide)Chromium Tricarbonyl by Direct Complexation.

To a flame dried 100-ml flask were added 18.72 g (0.110 mole) of benzyl bromide, 3.00 g (0.014 mole) of chromium hexacarbonyl, 20 ml of sodium dried iso-octane and 20 ml of freshly distilled bis-(2-methoxyethyl)ether (diglyme). The reaction mixture was refluxed for 6 hr at 165°C and then cooled by an ice-water bath. The reaction mixture was filtered using a water aspirator and the residue washed with three 10 ml portions of ether. The filtrate was evaporated to dryness using a rotary evaporator and vacuum pump. The resulting residue was dissolved in 5 ml

Toluene Complexation Reactions

Arene/Cr(CO)$_6$ (g/g)	Solvent (ml)	Time(hr)	Temperature (°C)	% Yield
3.00/7.45	21 ml butyl ether/19 ml iso-octane	6	165	Decomp.
3.13/3.8	5 ml butyl ether/5 ml iso-octane	4.5	165	1.53
1.83/2.20	4 ml butyl ether/4 ml iso-octane	3	165	Decomp.
1.83/2.19	4 ml butyl ether/4 ml iso-octane	24	165	10.5
1.82/2.21	4 ml butyl ether/4 ml iso-octane	12	165	5.7
1.84/2.20	8 ml butyl ether/8 ml iso-octane	3	165	Decomp.
1.82/2.21	4 ml butyl ether/8 ml iso-octane	36	165	8.77
1.82/2.21	4 ml iso-pentyl acetate/4 ml iso-octane	6	165	14.03
1.83/2.20	8 ml iso-pentyl acetate/8 ml iso-octane	12	165	17.54
1.83/2.20	4 ml butyl ether/4 ml iso-octane	6	165	5.26
1.83/2.21	8 ml iso-pentyl acetate/4 ml iso-octane	10	165	10.53
1.83/2.34	4 ml iso-pentyl acetate/4 ml iso-octane	36	165	20.18
1.87/2.29	7 ml diglyme/4 ml iso-octane	4.5	165	3.8

Table 4.

Toluene Complexation Reactions (Continued)

Arene/Cr(CO)$_6$ (g/g)	Solvent (ml)	Time (hr)	Temperature (^{o}C)	% Yield
1.82/2.20	7 ml diglyme/4 ml iso-octane	4.5	165	1.53
1.82/2.20	7 ml diglyme/4 ml iso-octane	4.5	145	4.3
1.82/2.20	7 ml diglyme/4 ml iso-octane	4.5	110	0.0
1.83/2.20	7 ml diglyme/4 ml iso-octane	4.5	120	0.75
1.89/2.21	7 ml diglyme/4 ml iso-octane	4.5	130	1.53
3.64/2.21	7 ml diglyme/7 ml iso-octane	4.5	140	4.2
3.64/2.21	7 ml diglyme/7 ml iso-octane	12	165	17.6
3.64/2.21	7 ml iso-pentylacetate/7 ml iso-octane	6	165	9.2
20.0/3.00	Excess toluene/13 ml iso-octane	68	165	48
11.3/3.00	20 ml diglyme/20 ml iso-octane	12	165	16.5

Table 4.

of ether and filtered by suction. The filtrate was transferred to a

beaker and a quantity of hexane was added to induce crystallization. A

white solid was isolated by suction filtration to give 2.66 g (65.07%)

of material melting at 48-50°C. Infrared and elemental analyses indi-

cated that the product was 1,2-diphenylethane.

Preparation of π-(Benzyl Alcohol)Chromium Tricarbonyl.--This pro-

cedure was adapted from that of Nicholls and Whiting[58].

To a flame dried 100-ml flask were added 7.28 g (0.068 mole) of

freshly distilled benzyl alcohol, 1.5 g (0.0068 mole) of chromium hexa-

carbonyl, 10 ml of freshly distilled diglyme and 10 ml of sodium dried

iso-octane. The reaction mixture was refluxed for 24 hr and then cooled

by an ice-water bath. The reaction mixture was diluted with 15 ml of

ether and the resulting solution was filtered using suction. The

residue in the filter was washed with several small portions of ether.

The filtrate was concentrated on the rotary evaporator and the remain-

ing liquid removed by distillation. The residue was dissolved in ether

and filtered utilizing suction. The remaining residue in the filter was

washed with several small portions of ether. The product was recrystal-

lized from the filtrate by addition of hexane to give 0.46 g (27.7%) of

yellow crystals, mp 91-93°C).

Preparation of π-(Benzyl Bromide)Chromium Tricarbonyl.--This pro-

cedure was adapted from that of Holmes, Jones and Petit[59].

Into a separatory funnel were placed 0.504 g (0.0016 mole) of

π-(benzyl alcohol)chromium tricarbonyl and 12 ml of benzene. To the re-

sulting solution was added 7 ml of 48% hydrobromic acid. The solution was

shaken for 10 min and allowed to separate into layers. The benzene layer

Attempted Complexation of Benzyl Bromide

Arene/Cr(CO)$_6$ (ml/g)	Solvent (ml)	Time (hr)	Temperature (°C)	Identified Product
13/3.04	20 ml diglyme/20 ml iso-octane	12	165	1,2-diphenyl ethane
13/3.02	20 ml diglyme/20 ml iso-octane	24	165	1,2-diphenyl ethane
13/3.00	Excess benzyl bromide/40 ml iso-octane	6	165	1,2-diphenyl ethane
6.5/3.00	20 ml butyl ether/20 ml iso-octane	6	165	1,2-diphenyl ethane
5/3.00	20 ml diglyme/20 ml iso-octane	6	130	1,2-diphenyl ethane
13/3.06	Excess benzyl bromide/60 ml iso-octane	6	130	1,2-diphenyl ethane
5/3.06	60 ml iso-octane	6	130	1,2-diphenyl ethane

Table 5.

Preparation of π-(Benzyl Alcohol)Chromium Tricarbonyl

Arene/Cr(CO)$_6$ (ml/g)	Solvent (ml)	Time (hr)	Temperature (°C)	% Yield
7/1.5	20 ml diglyme/20 ml iso-octane	6	165	Oil
10/1.5	Excess benzyl alcohol/20 ml iso-octane	6	165	Oil
20/3.00	20 ml diglyme/20 ml iso-octane	12	165	Oil
20/3.00	20 ml diglyme/20 ml iso-octane	72	170	70.51
20/3.00	20 ml butyl ether/20 ml iso-octane	6	170	Oil
20/3.00	20 ml butyl ether/20 ml iso-octane	72	170	81.41
20/3.00	20 ml butyl ether/20 ml iso-octane	120	170	93.47
20/3.00	20 ml butyl ether/20 ml iso-octane	72	145	74.68

Table 6.

was washed with two 12 ml portions of water and then dried over anhydrous
sodium sulfate. The liquid was then decanted from the anhydrous sodium
sulfate which was washed, in turn, with several small portions of benzene.
The benzene was removed, and the residue dissolved in ethyl ether. Hexane
was added to induce crystallization. The crystals were collected on a
Hirsch funnel and washed with a small amount of cold n-hexane to give
0.435 g (86.32%) of bright yellow product, mp 69-71°C. [Calc: C, 39.11%;
H, 2.30%. Found: C, 39.25%; H, 2.44%.].

Reaction of π-(Toluene)Chromium Tricarbonyl with N-Bromosuccinimide in Carbon Tetrachloride.

To a flame dried 25-ml flask, equipped with a condenser and calcium
chloride drying tube, were added 1.61 g (0.007 mole) of the π-(toluene)-
chromium tricarbonyl complex, 1.24 g (0.007 mole) of N-bromosuccinimide,
0.0011 g of benzoyl peroxide, and 10 ml of freshly distilled carbon tetra-
chloride. The reaction mixture was refluxed for 2 hr at 77-80°C. The
reaction mixture was cooled by an ice-water bath and filtered by suction.
The green-brown residue in the funnel was washed with several portions
of ether. The red-brown filtrate was concentrated and analyzed by both
thin layer and gas chromatography. The standard compounds used for thin
layer chromatographic analysis were complexed and non-complexed benzyl bro-
mide and complexed toluene. The standard compounds used for gas chromato-
graphic analysis were non-complexed toluene, carbon tetrachloride and a
5% solution of bromine in carbon tetrachloride. The results of the anal-
yses indicated that the π-(toluene)chromium tricarbonyl was no longer
present, but that non-complexed toluene and bromine were present.

Reaction of π-(Toluene)Chromium Tricarbonyl with N-Bromosuccinimide
in Anhydrous Ethyl Ether.

To a flame dried 25-ml flask, equipped with a condenser and calcium
chloride drying tube, were added 1.63 g (0.007 mole) of the π-(toluene)-
chromium tricarbonyl complex, 1.24 g (0.007 mole) of N-bromosuccinimide,
0.0012 g of benzoyl peroxide, and 10 ml of anhydrous ethyl ether. The
reaction mixture was refluxed for 2 hr at 35-40°C. The reaction flask
was cooled by an ice-water bath and the reaction mixture filtered by
suction. The green residue in the filter was washed with several por-
tions of ether. The yellow filtrate was analyzed by thin layer chroma-
tography. The standard compounds used for the thin layer chromatographic
analyses were complexed and non-complexed benzyl bromide and complexed
toluene. The filtrate was concentrated and n-hexane was added dropwise
until crystals were formed. The crystals were isolated by suction filtra-
tion and then washed with cold n-hexane (mp 70-74°C). The infrared spec-
trum showed absorption at 1175 cm^{-1}, characteristic of the -CH$_2$Br wag in
the complexed π-(benzyl bromide)chromium tricarbonyl. A carbonyl absorp-
tion was present at 1710 cm^{-1}, which was not evident in the infrared spec-
tra of either π-(toluene)chromium tricarbonyl or π-(benzyl bromide)chromium
tricarbonyl.

From the 1.00 g of recrystallized material, 0.1 g was removed and
placed in a 25-ml separatory funnel. The sample was then dissolved with
5 ml of ethyl ether and concentrated nitric acid was added dropwise until
the complex had decomposed and the ether layer was no longer colored. The
ether layer was separated and analyzed by gas chromatography. By a com-
parison with the retention times of known compounds, ether, acetone,

hexane and non-complexed toluene were identified. The infrared spectra of acetone and hexane were run and compared to the spectrum of the recovered material. The absorption at 1710 cm^{-1} was assigned to the carbonyl of acetone. The pattern at 1175 cm^{-1} was caused by n-hexane. The remaining portions of the spectrum were identical to complexed toluene.

Attempted Preparation of π-(Benzyl Cyanide)Chromium Tricarbonyl.—This procedure was adapted from that described by Gilman and Blatt[60]

To a three-neck 50-ml flask, equipped with a dropping funnel and condenser was added 0.961 g (0.02 mole) of sodium cyanide dissolved in 10 ml of 95% ethanol. The solution was refluxed at 75-80°C for 0.5 hr, at which time all the sodium cyanide had dissolved. To the dropping funnel was added a solution of 2.01 g (0.007 mole) of π-(benzyl bromide)-chromium tricarbonyl dissolved in 10 ml of 95% ethanol. The π-(benzyl bromide)chromium tricarbonyl solution was added dropwise over a 0.5 hr period. The mixture was allowed to reflux for 4 hr. The reaction mixture was cooled by an ice-water bath and filtered into a single-neck 50-ml flask. The white crystalline residue was washed with several portions of ethyl ether. The filtrate was concentrated on the rotary evaporator and the remaining liquid removed by distillation at reduced pressure (0.25 mm). The yellow residue was dissolved in a minimum amount of ethyl ether and filtered utilizing suction. The residue was washed with several small portions of ethyl ether. A yellow oil formed when n-hexane was added dropwise to the filtrate. The oil and filtrate were adsorbed on 2.0 g of neutral alumina (Activity 1), by evaporating the solvent with the rotary evaporator. The alumina was transferred to the top of a neutral alumina (Activity 1) column (1 X 9 in). The column was eluted with

n-hexane and 20 ml fractions collected. The fractions were analyzed by thin layer chromatography and similar fractions were combined and evaporated to dryness. The resulting oil was then dissolved in a minimum amount of ethyl ether and n-hexane was added dropwise to give an oil. Analysis by thin layer chromatography indicated only one component was present. The characteristic cyanide band was present in the infrared spectrum, although the simple carbonyl absorption pattern had been perturbed markedly.

Attempted Synthesis of Complexed Benzyl Cyanide

Arene[*]/Cyanide[**] (g/g)	Solvent	Time (hr)	Temperature (°C)	% Yield
2.01/1.37	95% ethanol	4	75-80	Oil
2.52/1.27	95% ethanol	4	75-80	Oil
0.437/0.092	95% ethanol	4	75-80	Oil
0.444/0.098	95% ethanol	6	75-80	Oil

Table V.

[*] π-(Benzyl bromide)chromium tricarbonyl

[**] Potassium cyanide

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