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The reaction of arenetricarbonylchromium complexes with alkyllithium compounds

Roger John Card
Iowa State University

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The reaction of arenetricarbonylchromium

complexes with alkyllithium compounds

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Roger John Card

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Ames, Iowa

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I. LITERATURE REVIEW

Interest and activity in organometallic chemistry has increased rapidly throughout the last decade. A large portion of this interest presently concerns the chemistry of organic species bonded to transition metals. The large volume of this literature makes it impossible for a complete review to be presented. Fortunately, a guide to the literature of organometallic chemistry is available (1). This review will discuss the reactions of transition metal complexed organic π systems with nucleophiles and bases.

A. Proton Abstraction Processes

Since its discovery in 1951, ferrocene and its derivatives have become one of the most thoroughly studied systems in organometallic chemistry (2). The metalation of ferrocene, its derivatives and other metallocenes by alkyllithium and alkylsodium reagents has been reviewed (3). First reports of the metalation of ferrocene appeared from two independent groups in 1954 (4). Both mono- and dimetalation are observed.
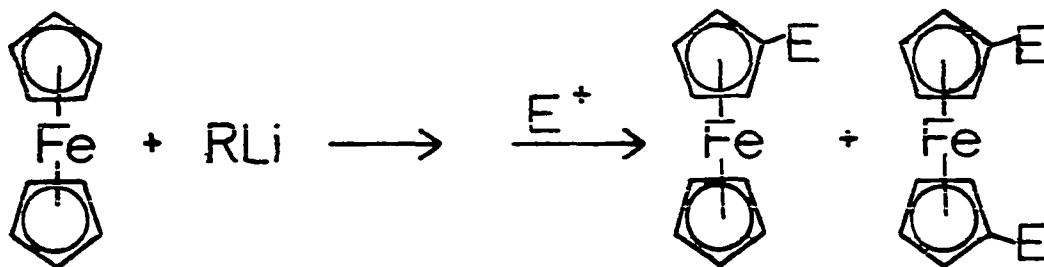
A large number of quenching reagents can be used (3). Ruthenocene and osmocene react in a similar manner (5).

Bisbenzenechromium has been dimetalated with n-amylsodium (6) and with n-butyllithium (7). Benzenetricarbonylchromium has been converted to (benzoic acid)tricarbonylchromium in low yield (8).
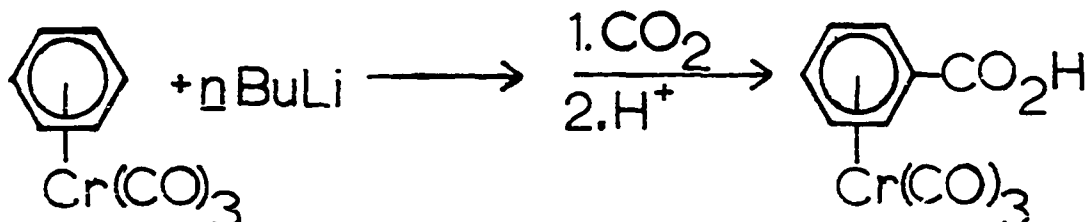
Gloth and Rausch have reported the synthesis of (phenyllithium)tricarbonylchromium from the reaction of bis(benzenetricarbonylchromium)mercury and excess n-butyllithium (9). Conversion to (benzoic acid)tricarbonylchromium was reported
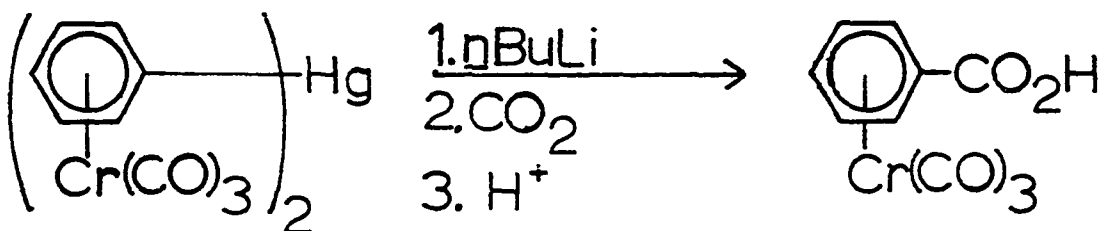
in ca. 19% yield, similar to the results of Nesmeyanov et al. (9a, 8).

Quenching the (phenyllithium)tricarbonylchromium generated in this manner with an excess of acetyl chloride led to a mixture of products including (acetophenone)tricarbonylchromium in ca. 18% yield (9a). Quenching with trimethylsilyl chloride led to only very small amounts of (trimethylsilylbenzene)tricarbonylchromium, while quenching with diphenylchlorophosphine led to a 54% yield of (diphenylphosphinobenzene)tricarbonylchromium (9a).

The cyclobutadiene substituent of (cyclobutadiene)-
(cyclopentadienyl)cobalt is preferentially metalated by n-
butyllithium (10). The cycloheptatrienyl ligand is metalated
on interaction of (cycloheptatrienyl)(cyclopentadienyl)-
titanium with n-butyllithium (11). Metalation of an analogous
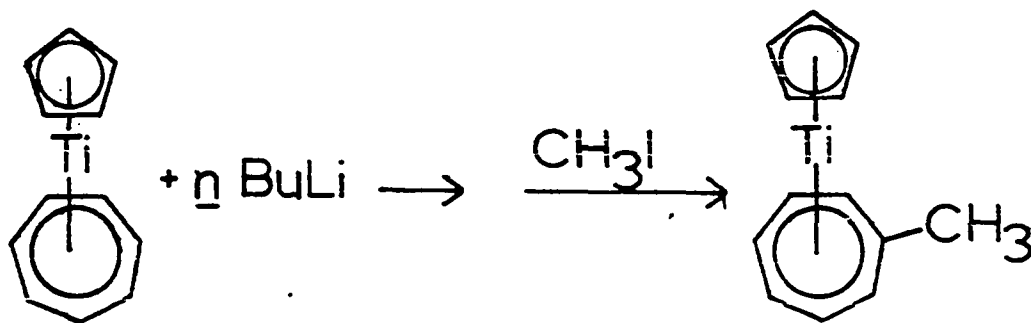
chromium complex, (cycloheptatrienyl)(cyclopentadienyl)-
chromium, requires more severe conditions, and occurs
preferentially on the cyclopentadienyl ring (11).

Monoalkylferrocenes are metalated in the 1' or 3 position
by n-amylsodium (12). Similarly, interaction of bis(arene)-
chromium complexes with n-butyllithium results almost
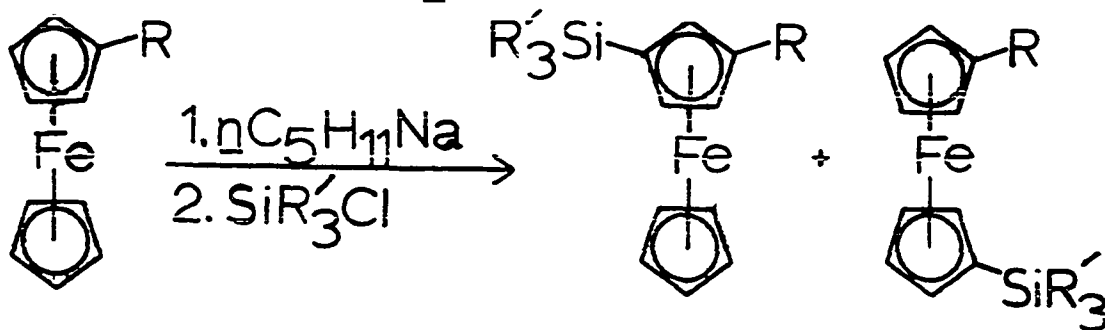
exclusively in ring metalation (13). Metalation is reported
to occur principally in the meta and para positions relative
to the alkyl substituent (13b).

Metalation of substituted ferrocenes is directed to the 2-position by chloro (14), methoxy (3,15), alkoxymethyl (3) and dialkylaminomethyl (3,16) substituents.

Catalytic isotopic hydrogen exchange has been observed for substituted benzenetricarbonylchromium (17), bis(arene)-chromium (18), bis(cyclopentadienyl)nickel (19) and a variety of (cyclopentadienyl)iron (20) complexes. Ring hydrogen
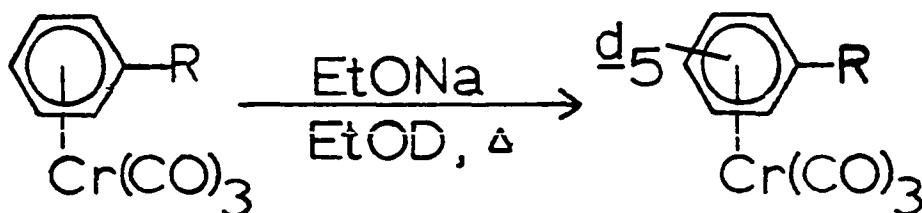
exchange is observed even when the substituent is a methyl group (17,18). In an unusual example, proton abstraction from a cationic complex by n-butyllithium has been observed
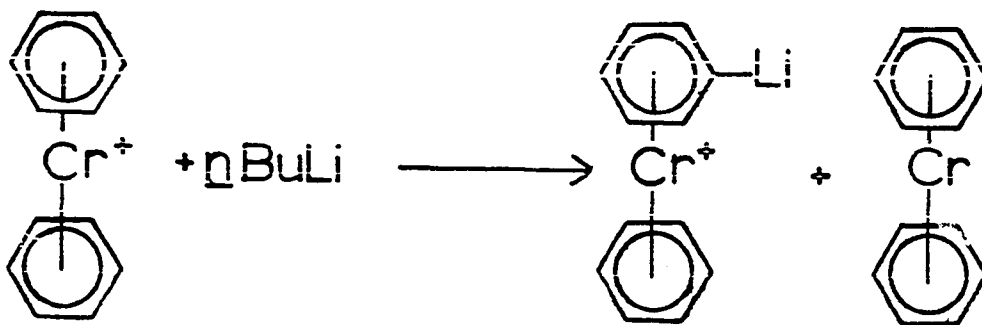
(21). This occurs in low yield, with reduction of the cationic complex being the major process.

Interestingly, only a few examples of abstraction of protons α to a complexed π system have been observed. In all but two reports, an anion stabilizing α substituent is present.

Three iron systems have been studied. The first is illustrated below (22).
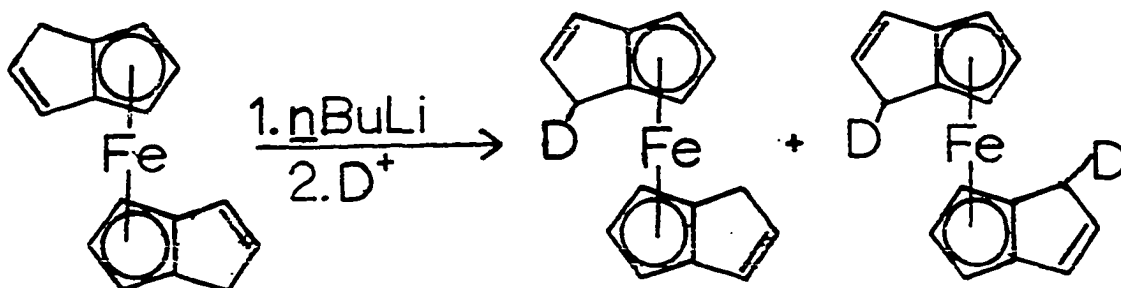
($\underline{h}^4$-Cycloheptatriene)tricarbonyliron exchanges one methylene hydrogen for deuterium under mildly basic conditions (23). The anion is generated in ca. quantitative
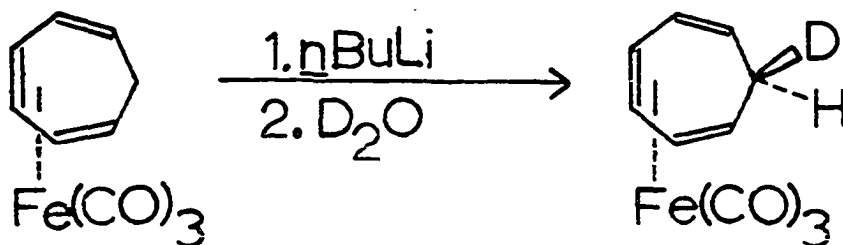
yield upon treatment of the cycloheptatriene complex with n-butyllithium at low temperature. The anionic intermediate appears as a singlet by ^{1}H nuclear magnetic resonance spectroscopy (23).

(Cyanomethyl)ferrocene yields both methylene hydrogens to n-butyllithium (24). This is especially interesting in light of the total lack of α proton abstraction by
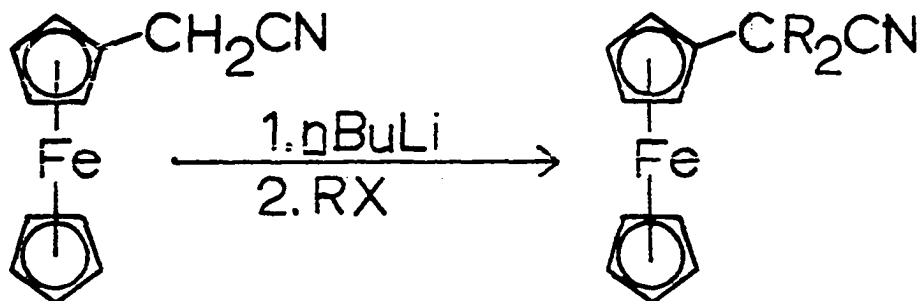
n-butyllithium from methylferrocenes (3,12). The consistent absence of α proton abstraction from alkylferrocenes led one author to conclude: unlike benzylic carbanions, little stabilization appears to accrue to α-ferrocenyl carbanions by virtue of conjugation with the aromatic ring (25).

Thus, it appears that some extra anion stabilizing substituent at the α carbon is necessary before α proton abstraction can compete with ring proton abstraction in the ferrocenyl system.

Abstraction of α protons has been observed in one
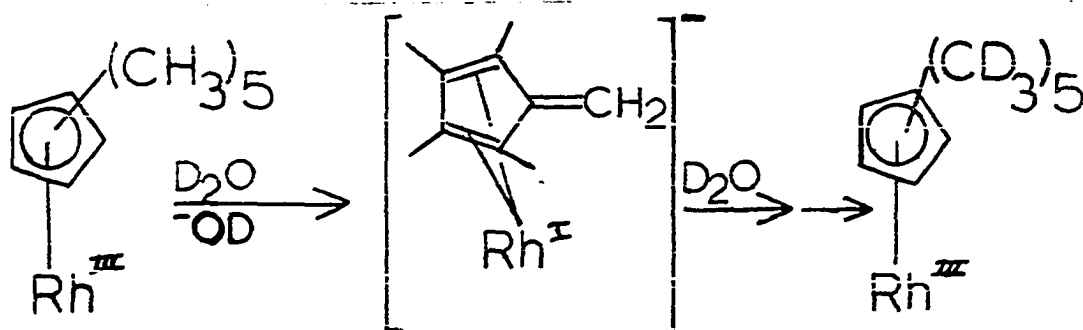
rhodium system in which there are no ring protons (26).

Protons α to a tricarbonylchromium complexed benzene ring may be abstracted by base (27). In work from our

laboratory, it has been demonstrated that α proton abstraction
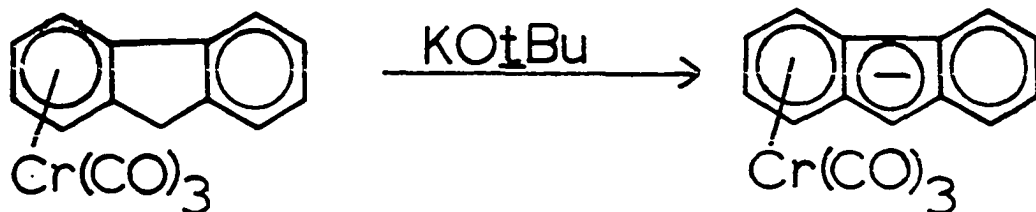
occurs in the absence of stabilizing α substituents (28). The
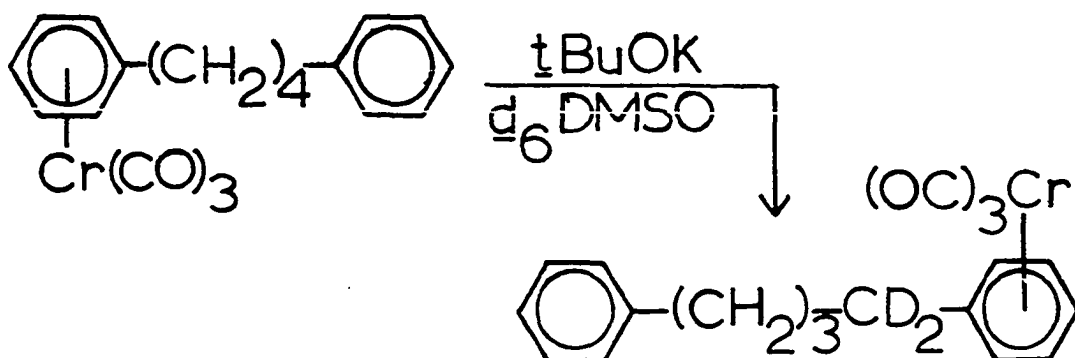
proton abstraction process is stereoselective in rigid

systems (28).
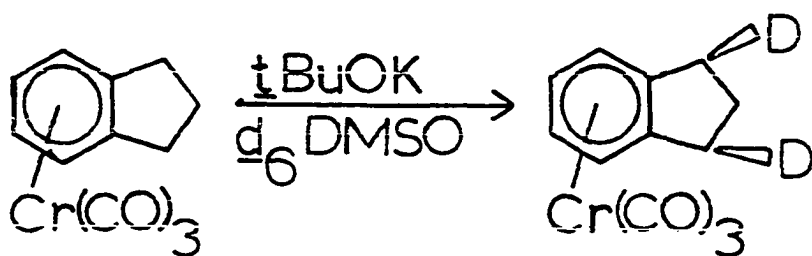
B. Nucleophilic Addition to π-Complexed Ligands

Nucleophilic addition of anions to the complexed organic π system of cationic organotransition metal complexes is a very commonly observed process. A review of the study of this reaction through 1967 is available (29). Cationic alkenyl (30), cyclobutadiene (31), cyclopentadienyl (32), cyclohexadienyl (33), cycloheptadienyl (34) and cycloheptatrienyl (35) complexes, among others, have been observed to undergo this type of reaction.

This review will consider only nucleophilic attack on benzene complexes. This is closest to the research to be presented and illustrates the wide range of nucleophiles and metals which can be used.

The generality of this process is nicely illustrated by some of the pioneering work in this area (36). Bisbenzene-rhenium triiodide is converted to (benzene)(cyclohexadienyl)-rhenium in low yield by interaction with lithium aluminum hydride (36).

Bisbenzeneruthenium diperchlorate reacts with sodium borohydride to yield the neutral (benzene)(cyclohexadiene)-ruthenium complex (36). Benzeneruthenium dichloride is
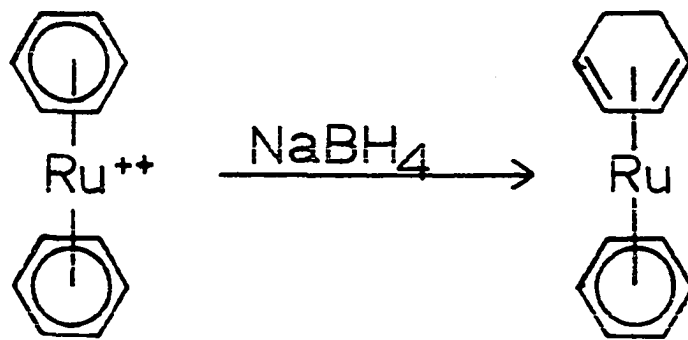
converted to (cyclohexadiene)ruthenium in a similar manner
(37). The products obtained in this complex reaction are
dependent on the relative concentrations of the two reagents
(37). Monocationic complexes such as (benzene)tricarbonyl-
manganese(I) are converted to neutral cyclohexadienyl complexes
by interaction with sodium borohydride (36,38).

When (benzene)(cycloheptatrienyl)molybdenum hexafluoro-
phosphate is allowed to react with sodium borohydride, it is

$$\text{Mo}^+ \xrightarrow{\text{NaBH}_4} \text{Mo}$$
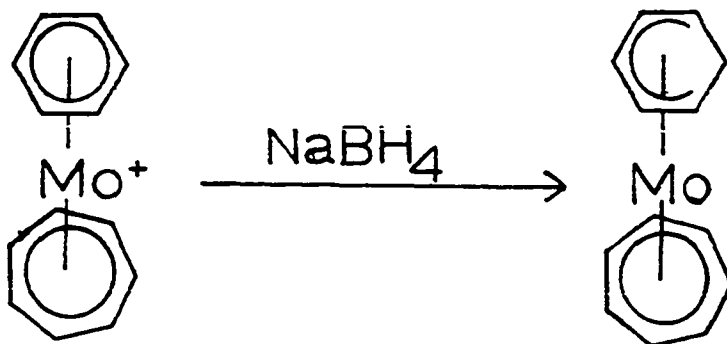
the benzene ligand which is attacked (39). Butyllithium adds
to (benzene)(tetraphenylcyclobutadiene)cobalt bromide to
yield (n-butylcyclohexadienyl)(tetraphenylcyclobutadiene)-
cobalt (40). Ethyllithium adds to (benzene)(cyclopentadienyl)-
iron tetrafluoroborate to yield (cyclopentadienyl)(ethylcyclo-
hexadienyl)iron in a complex process whose mechanism is not
understood (41).

In light of the reaction of bisbenzeneruthenium di-
perchlorate with sodium borohydride (36), it is interesting
that interaction of this complex with phenyllithium yields
bis(phenylcyclohexadienyl)ruthenium (36). Addition of
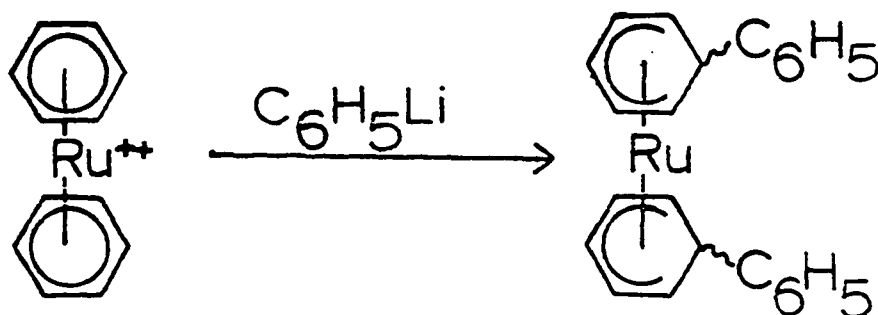
phenyllithium to the complexed benzene ring of (benzene)-
(cyclopentadienyl)iron tetrafluoroborate and benzenetri-
carbonylmanganese perchlorate has also been reported (36).
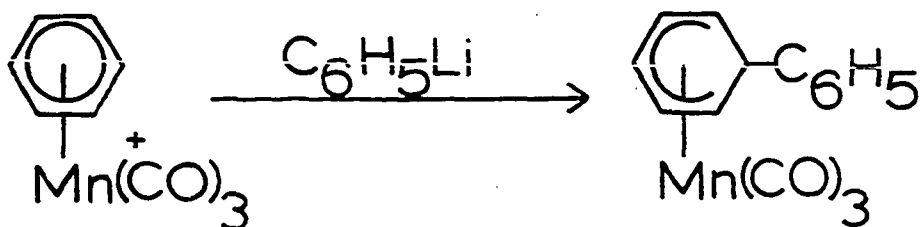
In general, nucleophilic attack on cationic alkylbenzene
complexes occurs preferentially at the unsubstituted carbons
of the benzene ring (42-45). (1,2,4,5-Tetramethylbenzene)-
(dicarbonyl)(nitrosyl)chromium hexafluorophosphate is
methylated at one of the unsubstituted ring carbon atoms by
methyllithium (42). A similar reaction with sodium borohydride
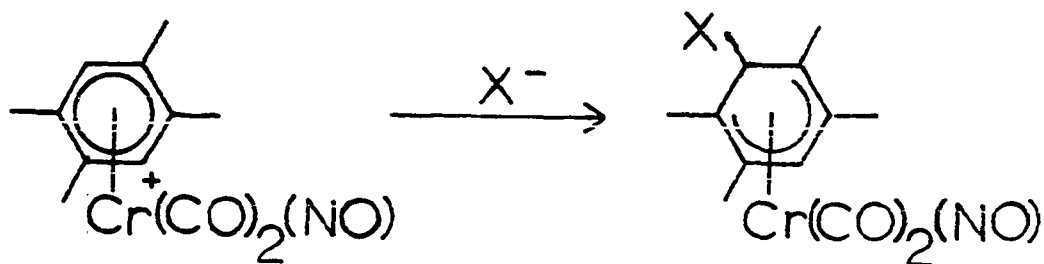
was also observed (42). Interaction of (mesitylene)(tri-
carbonyl)manganese iodide with sodium cyanide at 0° occurs

with addition of cyanide to one of the hydrogen bearing carbons
of the ring (43). Similar alkylation of cationic complexes by
phenyl-, vinyl- and t-butyllithium has been observed (44,45).

Cationic fluorobenzene and chlorobenzene complexes undergo
substitution of the halogen by a wide variety of nucleophiles
(41).
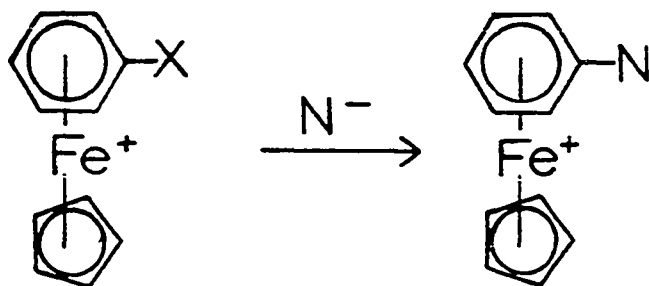
In contrast to the wide variety of nucleophilic attack
on cationic benzene complexes which has been observed, little
has been published concerning the reaction of neutral benzene
complexes with nucleophiles. Net nucleophilic displacement
of fluoro or chloro substituents from (fluorobenzene)tri-
carbonylchromium (46,47), (chlorobenzene)tricarbonylchromium
(46,47) and bis(fluorobenzene)chromium (48) has been observed.
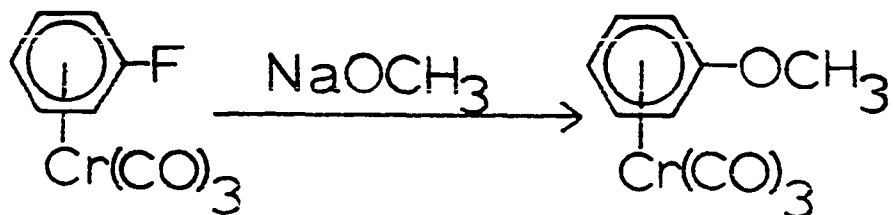
The work with (fluorobenzene)tricarbonylchromium again demonstrates the strong electron withdrawing power of the tricarbonylchromium moiety. This electron withdrawing effect is similar in magnitude to that of a para-nitro substituent (49,46).

The displacement of chloride from (chlorobenzene)tricarbonylchromium by 2-lithio-2-cyanopropane has been studied in some detail (47b). The mechanism for this process is very complex. Part of the reaction appears to involve reversible addition of the carbanion to the complexed aromatic ring.
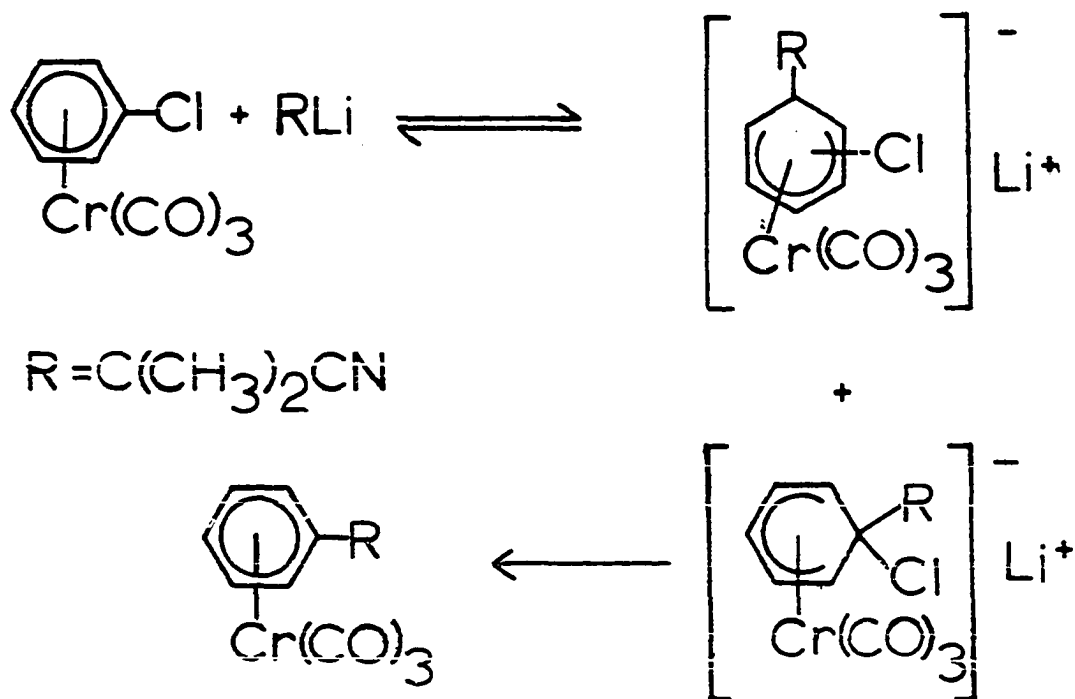
This is followed by irreversible loss of chloride from one of the intermediates, the anionic (6-(1-cyano-1-methylethyl)-6-chlorocyclohexadienyl)tricarbonylchromium complex (47b). The

reaction was followed by nuclear magnetic resonance spectroscopy.

By an unknown mechanism, bis(aniline)chromium results
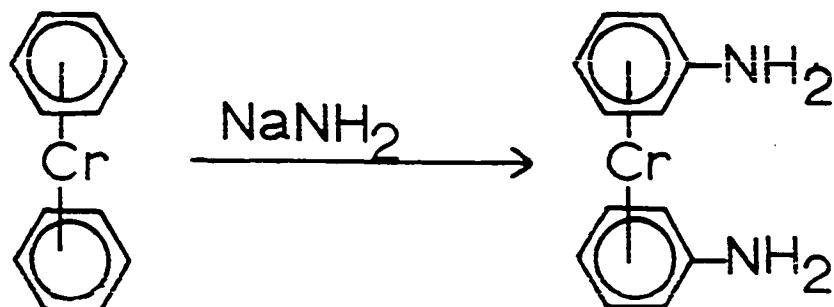
from the interaction of bisbenzenechromium with sodium amide (13a).

C. Other Reactions of (Arene)(carbonyl)metal Complexes

The carbonyl ligands of (arene)(carbonyl)metal complexes are also reactive towards nucleophiles. Benzenetricarbonylchromium reacts with phenyllithium to yield a carbene complex (50). The yield is low. The carbonyl ligands of benzenetri-

carbonylchromium are much less reactive towards phenyllithium than are the carbonyl ligands of hexacarbonylchromium (50). Other (arene)tricarbonylchromium complexes react with phenyllithium in a manner similar to that of benzenetricarbonylchromium (51).
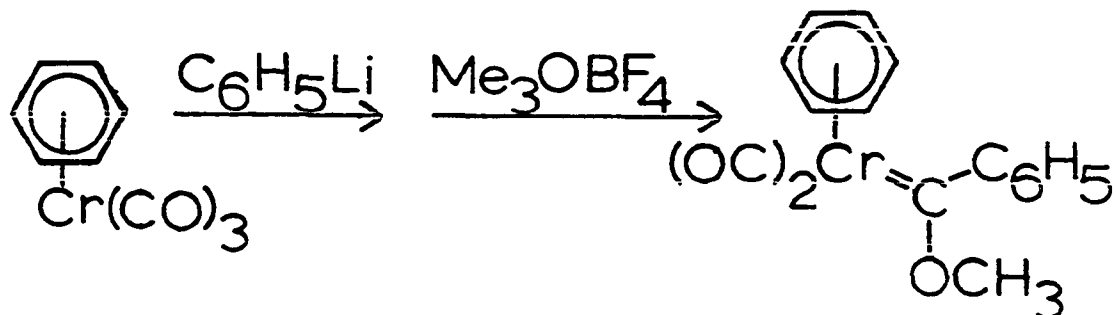
Cationic (arene)tricarbonylmanganese complexes react with
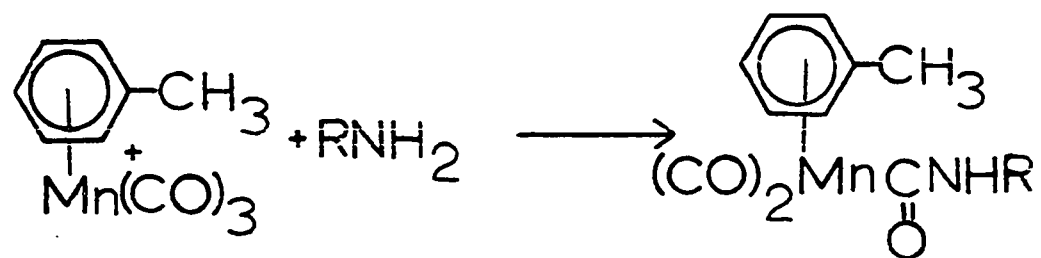
amines to yield carbamoyl complexes (52).

The electrochemical reduction of benzenetricarbonyl-chromium has received some attention. At the dropping mercury electrode an irreversible two electron reduction is observed with a half wave potential of -3.0 volts relative to the standard calomel electrode (53). No electron spin resonance (esr) spectrum was observed during or after the reduction.

The tricarbonylchromium moiety has been shown to exert a stabilizing effect on benzylic cations (54,55) and has shown the amazing ability to vary the extent of electron donation to an electron deficient center (56).

II. INTRODUCTION

The reaction of arenetricarbonylchromium complexes with alkyllithium could proceed _via_ a variety of pathways to yield any of several possible products. To investigate this problem, the reaction of benzenetricarbonylchromium with n-butyllithium has been examined in some detail.

Results will be presented and discussed which indicate that proton abstraction from the arene ligand and nucleophilic attack on the metal are both important processes. The effect of substituents on each of these processes will be presented and discussed.

III. RESULTS

A. Benzenetricarbonylchromium

The addition of methyl iodide to the cold, stirred solution resulting from the reaction of benzenetricarbonylchromium with n-butyllithium resulted in the formation of (toluene)tricarbonylchromium in a 50% isolated yield. In this
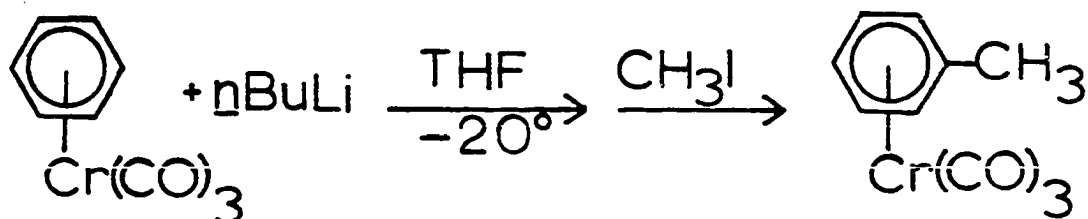
reaction, 2 ml of 1.6 M n-butyllithium in hexane was added to a stirred solution of 2^0 mg benzenetricarbonylchromium in 10 ml tetrahydrofuran (THF) at -20° under an argon atmosphere. The resulting solution was stirred at -20° for 30 min and then 2 ml methyl iodide was added. After an aqueous work up and purification by sublimation, 109 mg (toluene)tricarbonylchromium was obtained.

In similar reactions, toluene was obtained by oxidation of the (toluene)tricarbonylchromium complex after the aqueous work up. The yield of toluene was determined by gas phase chromatography (glpc) by the use of an internal standard. The yields from two runs were 71 and 71%, respectively. When yields are mentioned throughout this section, the average yield from several runs is presented followed by the standard deviation.

When no standard deviation is given, only one run was performed.

In a manner similar to that above, (iodobenzene)tricarbonylchromium was obtained in an isolated yield of $26\pm2\%$.

$$\text{benzenetricarbonylchromium} + \underline{n}\text{BuLi} \xrightarrow[\substack{< -20°}]{\text{THF}} \xrightarrow{I_2} \text{(iodobenzene)tricarbonylchromium}$$
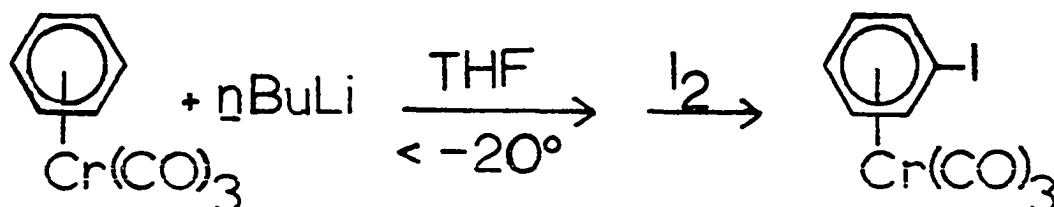
An intermediate formed from the interaction of benzenetricarbonylchromium with $\underline{n}$-butyllithium has been observed by ^{1}H nuclear magnetic resonance (nmr) spectroscopy. A series of three spectra is presented in Figure 1. The top spectrum is of benzenetricarbonylchromium in tetrahydrofuran at $\underline{ca}$. $-20°$. The middle spectrum resulted from the addition of $\underline{n}$-butyllithium to the solution from which the top spectrum was obtained. The singlet of benzenetricarbonylchromium has been transformed into two multiplets, both upfield from the original position of the benzenetricarbonylchromium absorption. It is not known how much of this shift is due to the solvent change by the addition of the hexane solution of $\underline{n}$-butyllithium. The bottom spectrum is of phenyllithium under conditions very similar to those of the middle spectrum. The phenyllithium was generated by the addition of $\underline{n}$-butyllithium to a THF solution of diphenylmercury. The similarities of the middle

Figure 1.   Nuclear magnetic resonance spectra of benzene-
            tricarbonylchromium (top), (phenyllithium)tri-
            carbonylchromium (middle) and phenyllithium
            (bottom) in tetrahydrofuran at -20°
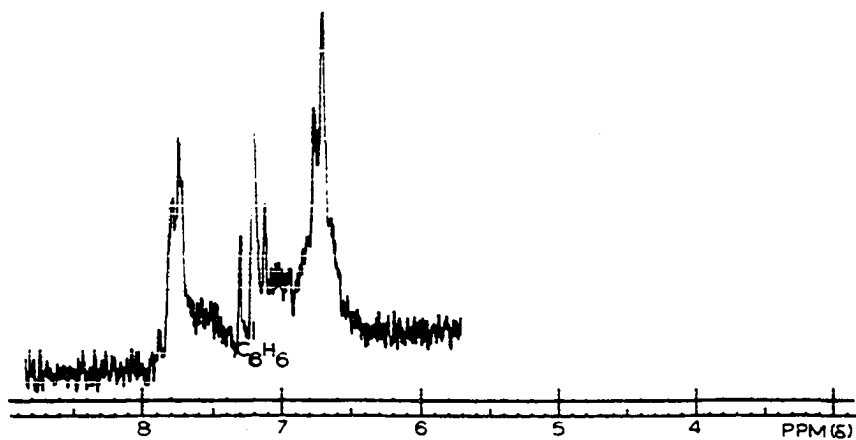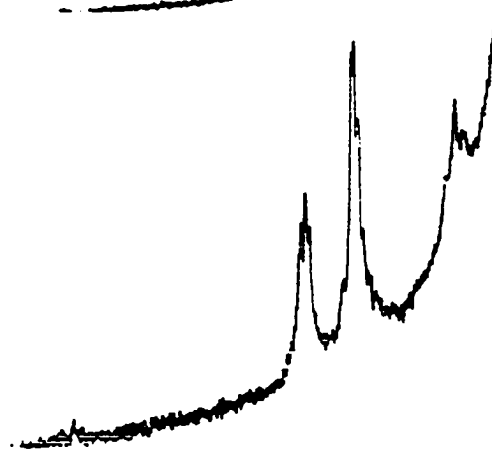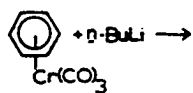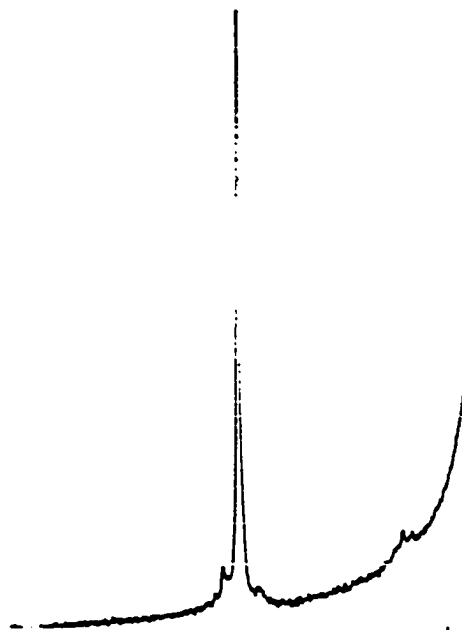
and bottom spectra provide strong evidence that the inter-
mediate is (phenyllithium)tricarbonylchromium.

When the intermediate generated at -20° was allowed to
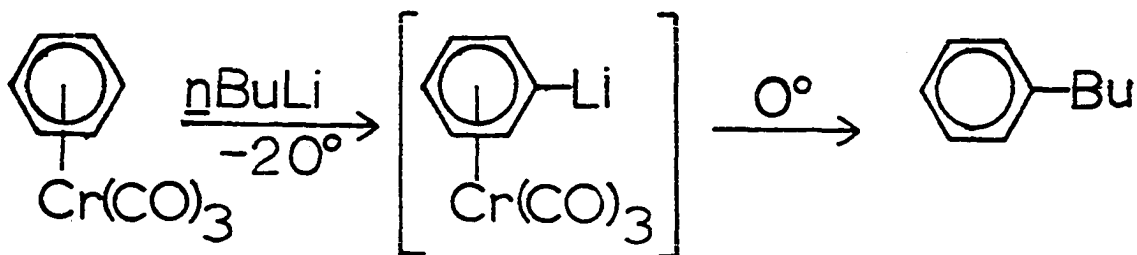
warm to 0° and then stirred at 0° for ca. 30 min, an 80±1%
yield of n-butylbenzene was obtained. A similar yield of
butylbenzene was obtained when n-butyllithium was added to a
THF solution of benzenetricarbonylchromium at 0°. Butyl-
benzene was obtained directly from the aqueous work up: no
oxidation step was required. The butylbenzene was collected
by glpc and identified on the basis of its nmr spectrum. The
spectrum and glpc retention times were identical to commercial
butylbenzene.

When d_6-benzenetricarbonylchromium was allowed to react
with n-butyllithium under these conditions d_5-butylbenzene
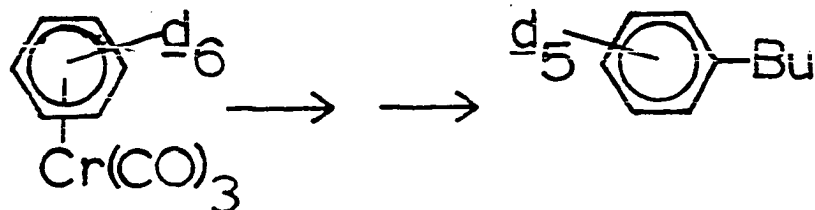
was obtained. The product was collected by glpc and analyzed
by mass spectroscopy. Less than 2% d_4, and no d_3 or d_2

species were observed. The mass spectral data are presented in the Experimental section (Table 10).

This reaction is extremely sensitive to the reaction conditions. The effect of temperature is especially dramatic. The results from the experimental runs are presented in Table 9 in the Experimental section. These data are presented graphically in Figure 2. As the temperature was changed from -20° to 0°, the yield of butylbenzene increased from 16±0% to 78±3%.

When tetramethylethylenediamine was added to the reaction solution at -25° and the resulting solution was then allowed to stand at 0° for 30 min, a 16±8% yield of butylbenzene was obtained.

The reaction of benzenetricarbonylchromium with t-butyl-lithium is much less sensitive to temperature changes than the analogous n-butyllithium reaction. Thus, when benzene-tricarbonylchromium was allowed to react with t-butyllithium at 25°, 0° or -30° a ca. 30% yield of t-butylbenzene was obtained (Table 11). The addition of 2 equivalents of N-chlorosuccinimide to the reaction at -30° significantly increased the yield. After benzenetricarbonylchromium was allowed to react with t-butyllithium at -30° for 30 min, two equivalents of N-chlorosuccinimide (NCS) were added and the resulting solution was stirred for an additional 60 min at -30°: a 59±1% yield of t-butylbenzene was obtained. After

Figure 2:   The effect of temperature on the yield of
n-butylbenzene from the reaction of benzene-
tricarbonylchromium with n-butyllithium in
tetrahydrofuran
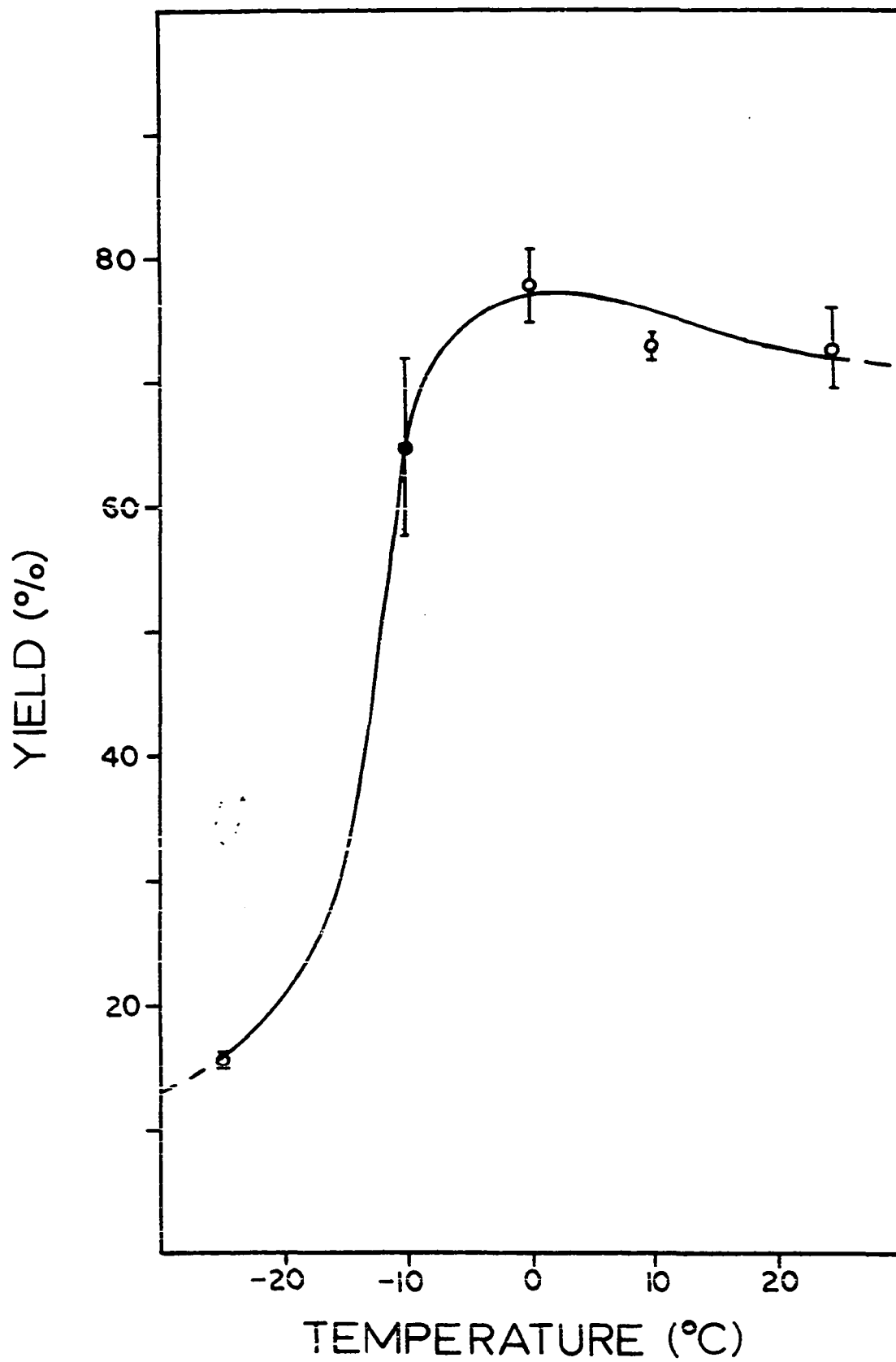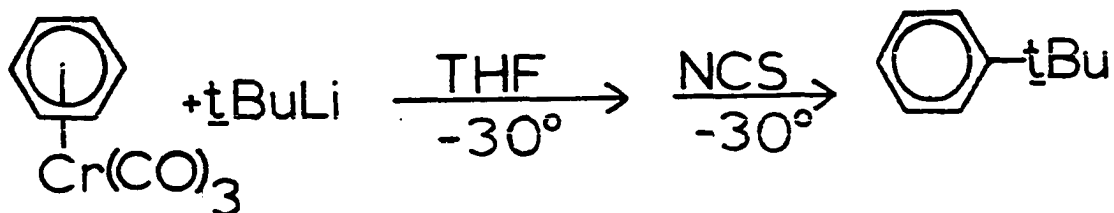
90 min at -30° without the addition of NCS the yield was 36±2%. The product was identified on the basis of its retention time and an nmr spectrum obtained from glpc collected material.

Less than 1% n-butylbenzene was formed from the interaction of phenyllithium with n-butyllithium under conditions similar to those which resulted in an 80±1% yield of butylbenzene from benzenetricarbonylchromium. The addition of hexacarbonylchromium, anhydrous chromium trichloride or benzenetricarbonylchromium to the phenyllithium-butyllithium reaction mixture at 0° failed to catalyze the desired reaction. No coupling, symmetrical or unsymmetrical, was observed under these conditions.

B. (Arene)tricarbonylchromium Complexes

The reaction of a variety of (arene)tricarbonylchromium complexes with n-butyllithium has been examined. The results from this study are presented in Table 1. The reactions were carried out in a manner similar to that described for the conversion of benzenetricarbonylchromium to (toluene)tricarbonylchromium. The crude reaction products were usually

Table 1. Products and yields obtained from the alkylation of (arene)tricarbonylchromium complexes <u>via</u> the addition of an alkyl halide to the solution resulting from the reaction of the (arene)tricarbonylchromium complex with <u>n</u>-butyllithium

Arene	Alkyl Halide	Yield of alkylated Product (%)	
		α	ring (position)
Toluene	CH_3I	14 ± 2	6 ± 1 (o); 41 ± 1 (m); 22 ± 4 (p)
	C_2H_5Br	~8	10 ± 1 (o); 34 ± 3 (m); ~13 (p)
Ethylbenzene	CH_3I	<1	5 ± 0 (o); 49 ± 1 (m); 26 ± 2 (p)
<u>t</u>-Butylbenzene	CH_3I	--	32 ± 2 (m); 22 ± 1 (p)
<u>o</u>-Xylene	CH_3I	28 ± 2	8 ± 2 (3) 50 ± 7 (4)
<u>m</u>-Xylene	CH_3I	45 ± 1	10 ± 2 (4) 33 ± 4 (5)
<u>p</u>-Xylene	CH_3I	20 ± 3	44 ± 3
Mesitylene	CH_3I	75^a	--
	<u>n</u>-C_3H_7I	71^a	--

[a] Isolated yield of alkylated complex.

converted to the arenes by oxidation with ceric ammonium nitrate to facilitate glpc analysis. The reported yields have been corrected for differences in thermal conductivity.

A summary of these data is presented in Figure 3. This figure presents the relative proton abstraction ratios for the various carbon atoms of the substrates studied.

The methylation of (toluene)tricarbonylchromium yielded m-xylene as the major product. Toluene was identified on the basis of its retention time. The other products were collected
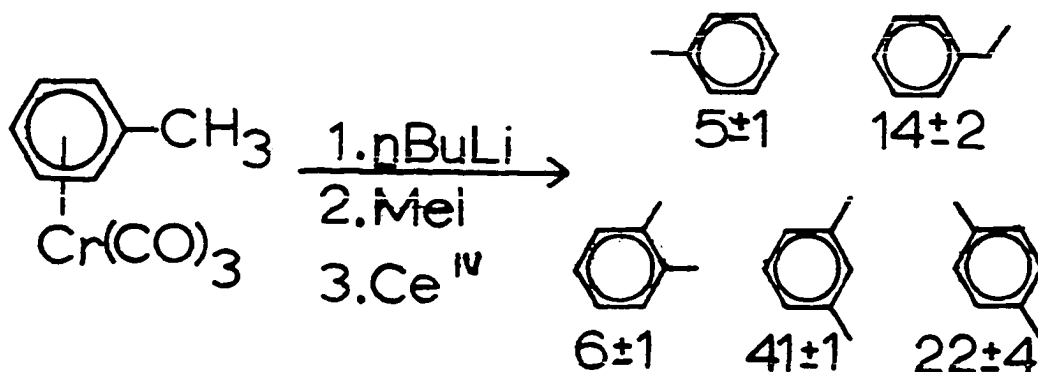
by glpc. meta-Xylene was characterized by its nmr and mass spectra. These spectra and the retention time were identical to that of commercial m-xylene. The other products were shown to be isomers by mass spectral data and were identified primarily by retention time. In addition, one fraction solidified on standing at 0°, consistent with its assignment as p-xylene on the basis of retention time. The nmr spectrum of this species is also consistent with this assignment.

In addition to these products, small amounts of compounds with retention times very similar to butyltoluenes were obtained in a combined yield of ca. 11%. This accounts for greater than 95% of the initial starting material.

Figure 3. Normalized proton abstraction ratios from
the reaction of (arene)tricarbonylchromium
complexes with n-butyllithium
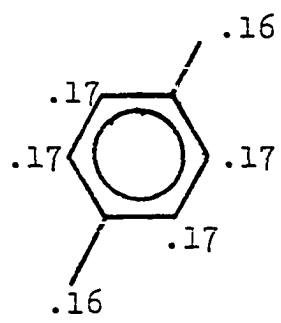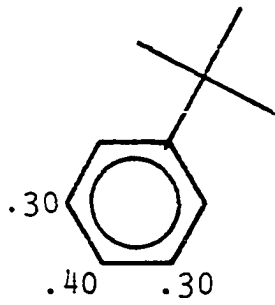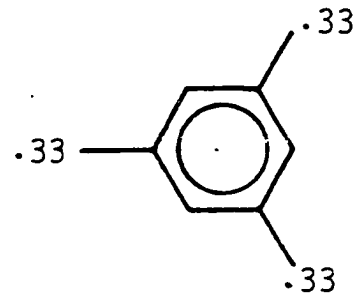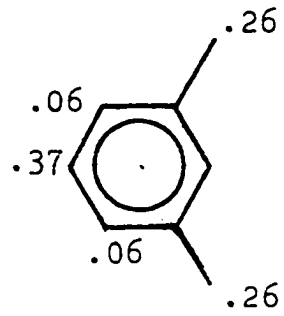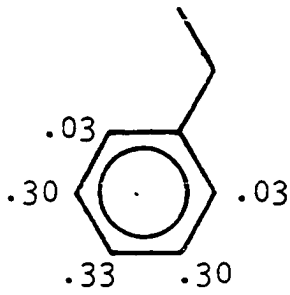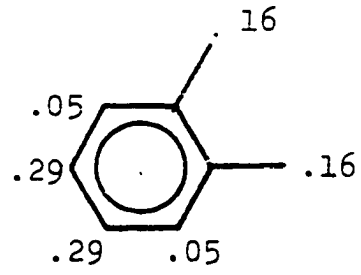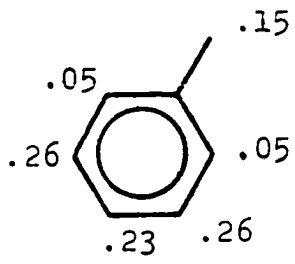
The reaction of (toluene)tricarbonylchromium with n-butyllithium may be quenched by the addition of ethylbromide. Decomplexation resulted in yields of methylethylbenzenes very similar to the yields of xylenes from the sequence above. The products were identified on the basis of retention time and by peak enhancement with commercial materials.

When the reaction of (toluene)tricarbonylchromium with n-butyllithium at -20° was quenched with either i-propyl iodide or t-butyl chloride less than 5% of the desired alkylated toluenes was obtained. Thus, secondary and tertiary alkyl halides do not serve as useful quenching reagents.

Under these reaction conditions arenes failed to alkylate. When a 1:1 mole ratio of (toluene)tricarbonyl-chromium and p-xylene was allowed to react with an excess of n-butyllithium 84±4% of the p-xylene was recovered unchanged. No products resulting from the methylation of p-xylene were observed by glpc. Only 3±1% of the (toluene)tricarbonyl-chromium was recovered as toluene. The recovery of toluene

$Cr(CO)_3$ +

(84±4)   3±1   8±0

6±2   36±1   (19)
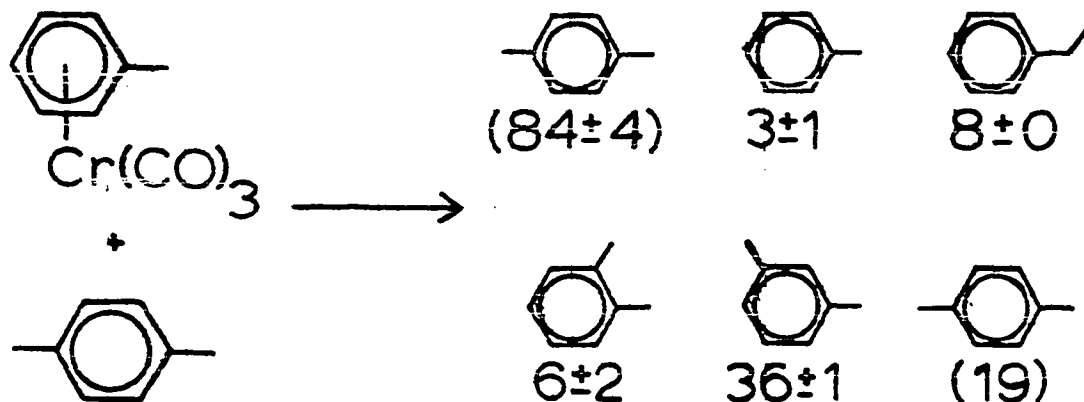
and its methylated derivatives was 71±4%. This is somewhat
less than that obtained from the methylation of the toluene
complex in the absence of p-xylene. The amount of butylated
products was not determined in this reaction. The yields of
ortho- and meta-xylene are similar to but lower than those
obtained in the absence of the initial p-xylene. On this
basis, the p-xylene formed from the alkylation of (toluene)-
tricarbonylchromium was assumed to be obtained in the same
ratio relative to m-xylene as in the absence of initial
p-xylene. This amount was subtracted from the total recovery
to calculate the recovery of unreacted p-xylene. Under
conditions where (toluene)tricarbonylchromium was alkylated
to greater than 95% less than 20% of the uncomplexed p-xylene
was changed.

The methylation of (ethylbenzene)tricarbonylchromium
resulted in the production of m-ethyltoluene in a yield of
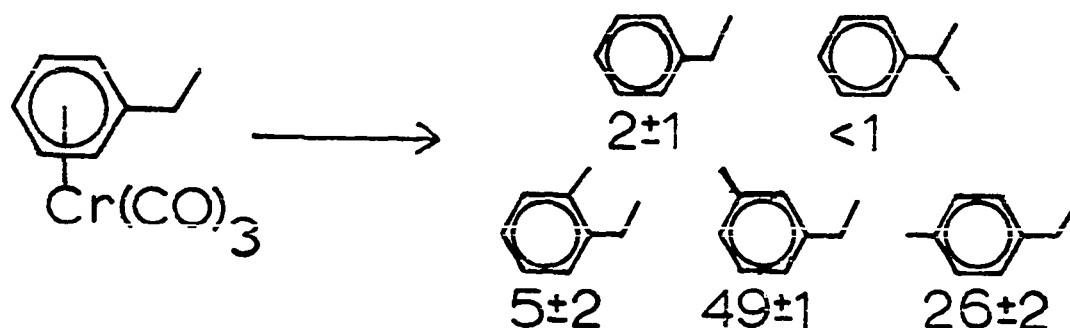
49±1%. The product assignment was on the basis of retention
time. The products gave a glpc trace very similar to that
obtained from the ethylation of (toluene)tricarbonylchromium.

The reaction of (ethylbenzene)tricarbonylchromium with n-butyllithium gave almost identical yields of butylethylbenzenes at 0° and 23°. The yields after 90 min at 0° were 38% meta- and 14% para-butylethylbenzene: after 80 min at 23°, 34% meta- and 16% para-butylethylbenzene was obtained. One run at each temperature was performed. A preliminary report of this work has been published (57).

The addition of N-bromosuccinimide (NBS) at low temperatures resulted in much better yields of the butylated
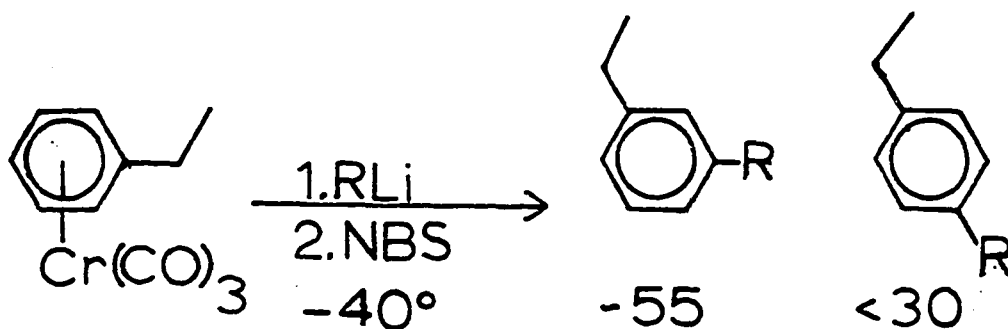
materials. Thus, when N-bromosuccinimide was added to the mixture resulting from the interaction of (ethylbenzene)tricarbonylchromium and butyllithium at -40° an ca. 55% yield of m-butylethylbenzene was obtained. Both n- and t-butyllithium gave similar results. The products were identified on the basis of retention time. An nmr spectrum of the crude reaction products was consistent with this assignment. Ethylbenzene was recovered unchanged (>95%) from the interaction of ethylbenzene with t-butyllithium at 0° for 30 min.

The products from the ethylation of (t-butylbenzene)-
tricarbonylchromium were collected by glpc and identified on
the basis of their mass spectra and nmr spectra. The nearly
identical mass spectra indicate that the two products are
isomers. The nmr spectrum of the minor product shows a phenyl

23±5 32±2 22±1
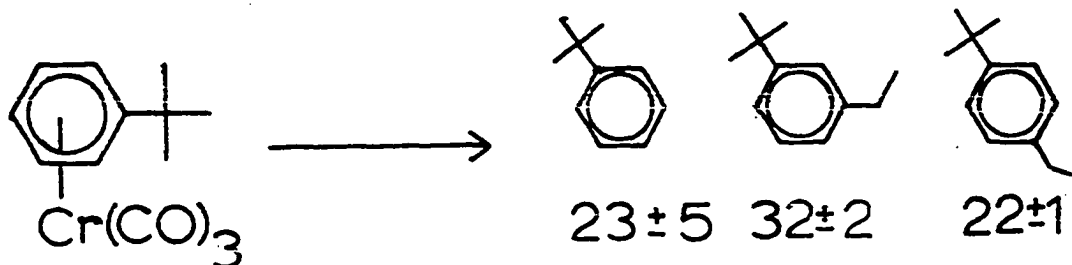
region very similar to that of m-xylene. The phenyl region
of the second isomer consists of two signals. On this basis
the major isomer was assigned as meta-ethyl-t-butylbenzene
and the minor isomer as the para isomer. That the minor
isomer would be the ortho isomer would be unlikely from
steric arguments and would be inconsistent with the isomer
distributions obtained in the other alkylation reactions.
Satisfactory exact mass determinations have been obtained for
these compounds. These products have identical retention
time to the products obtained from the alkylation of (ethyl-
benzene)tricarbonylchromium by t-butyllithium described
above.

The products from the methylation of the xylenes were
identified on the basis of retention time. (para-Xylene)-
tricarbonylchromium gave a 20±3% yield of products derived

from α metalation, (o-xylene)tricarbonylchromium gave a 28±2%
yield and (m-xylene)tricarbonylchromium gave a 45±1% yield of
products resulting from α metalation.

Only α alkylation of (mesitylene)tricarbonylchromium has
been observed. Thus, (mesitylene)tricarbonylchromium has been
converted to (1-ethyl-3,5-dimethylbenzene)tricarbonylchromium
and (1-butyl-3,5-dimethylbenzene)tricarbonylchromium in 75
and 71% isolated yield, respectively.

<div align="center">

C. Heteroatom Substituted Benzenetri-

carbonylchromium Complexes

</div>

The effect of four other substituents on both the
alkylation by addition of alkyl halides and the alkylation by
base has been examined. The results from the methylation of
these complexes are presented in Table 2.

The reaction of (iodobenzene)tricarbonylchromium with n-
butyllithium produced the same products as the analogous
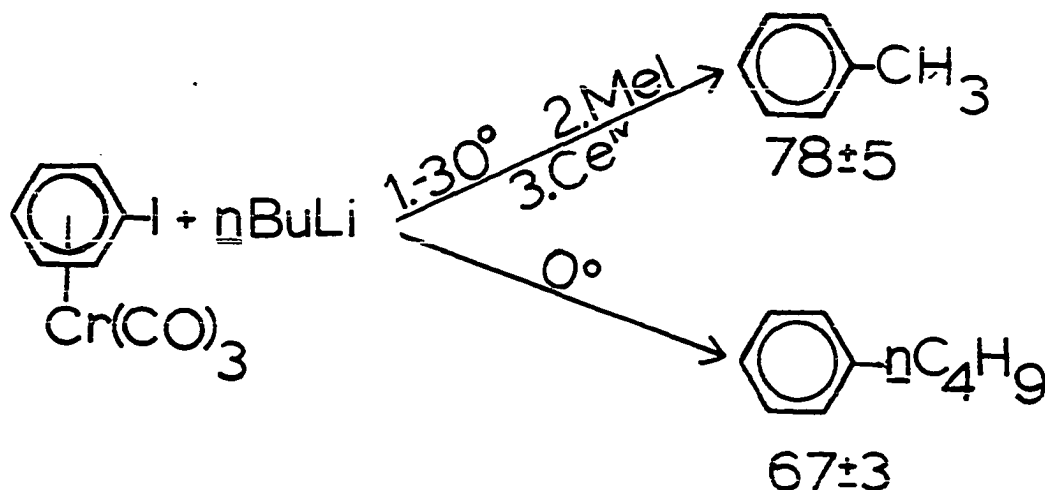
Table 2. Products and yields from the methylation of hetero-
atom substituted benzenetricarbonylchromium complexes
involving the addition of methyl iodide to the
reaction of the complex with n-butyllithium

Benzene derivative	Temp (°C)	Number of equivalents of base	Products (% yield)
Iodobenzene	-30	6	toluene (78±5)
Fluorobenzene	-40	4	o-fluorotoluene (71±3)
Anisole	-40	4	o-methylanisole (14±0) 2,6-dimethylanisole (66±9)
N,N-Dimethylaniline	-40	4	N,N-Dimethyltoluidines: o (19±0); m & p (42±4)

benzenetricarbonylchromium reaction. At -30°, the reaction of
(iodobenzene)tricarbonylchromium with n-butyllithium was
quenched by the addition of methyl iodide to produce, after
oxidation, toluene in 78±5% yield. The reaction with base at
0° produced n-butylbenzene in 67±3% yield. Even the yields
obtained are very similar to those from the analogous benzene-
tricarbonylchromium reactions.

The reaction of (fluorobenzene)tricarbonylchromium with
n-butyllithium at -40° proceeded via directed ortho metalation.
The major product from the sequence below was o-fluorotoluene.
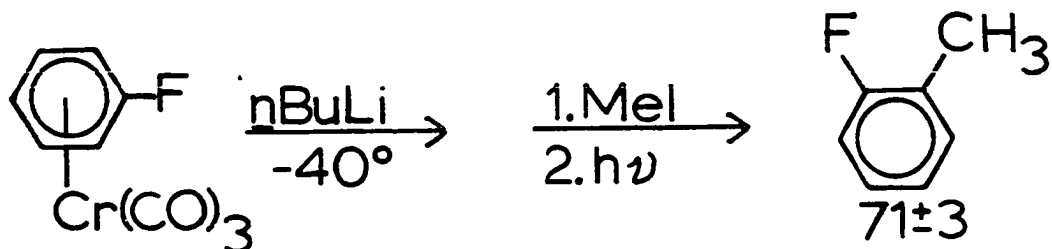
In this and the remaining reactions, photolytic decomposition was found preferable to oxidative decomplexation.

The yield of n-butylbenzene in the above reaction was negligible. It is interesting that nucleophilic displacement of fluoride was not significant under these conditions.

The reaction of (anisole)tricarbonylchromium with n-butyllithium was quenched by the addition of methyl iodide to yield 2,6-dimethylanisole, after photolytic decomposition. Some 2-methylanisole was also obtained. The products were
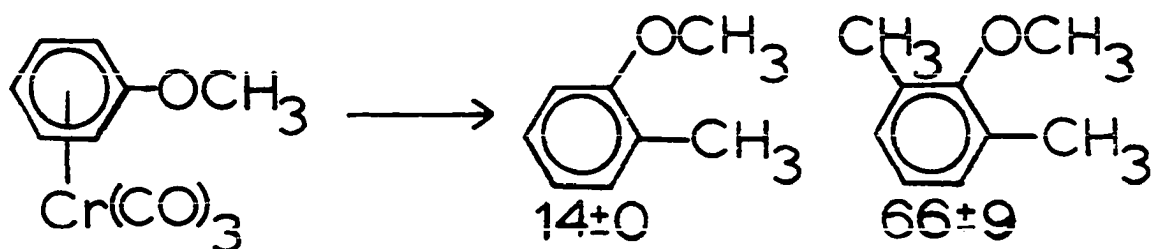
collected by glpc and identified from spectral data. Some (2,6-dimethylanisole)tricarbonylchromium was also isolated from this reaction and was identical spectroscopically to

(2,6-dimethylanisole)tricarbonylchromium prepared by direct complexation of commercial 2,6-dimethylanisole.

Addition of NBS to the reaction mixture at -40° did not result in the formation of any butylanisoles. Nearly quantitative recovery of anisole was obtained after photolytic decomplexation.

The reaction of (N,N-dimethylaniline)tricarbonylchromium with n-butyllithium resulted only in monometalation. The products are shown in the equation. The products were

$$19 \pm 0 \, (o)$$
$$42 \pm 4 \, (m+p)$$
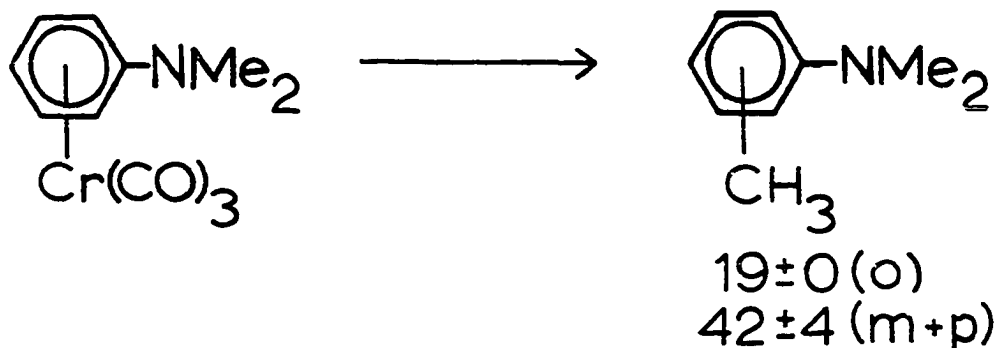
collected by glpc and identified on the basis of spectral data. m- and p-N,N-Dimethyltoluidines were not separable under the glpc conditions used and were collected together. The nmr of the collected mixture was identical to that of a 3:1 mixture of commercial m- and p-N,N-dimethyltoluidines.

Addition of NBS to the reaction mixture at -40° did not result in the formation of significant amounts of butylated materials.

D. Methyllithium

The reaction of benzenetricarbonylchromium with methyllithium has received only superficial attention. The crude results are presented here to illustrate that all systems are not as well-behaved as those previously described.

Benzenetricarbonylchromium was allowed to react with 4 equivalents of methyllithium at 0°. After 60 min, 4 equivalents of methyl iodide were added and the resulting solution was stirred for ca. 40 min. After an aqueous work up, the products were allowed to stand for several days to effect decomplexation. The products were then collected by glpc. The major product from this reaction was o-phenyl-acetophenone. The spectral data for this compound were nearly identical to those of o-phenyl-acetophenone prepared by an independent method. The other major components include biphenyl and methylbiphenyl(s). These products were collected together and were identified on the basis of spectral data and retention time. Minor amounts of other materials were also obtained.

This reaction is extremely sensitive to the reaction conditions. Reliable yield data is not available as duplicate runs have not been performed. Yields have not been maximized. o-Phenyl-acetophenone has been obtained in yields up to 20% and the biphenyl and methylbiphenyl in combined yield of ca. 15%.

A similar reaction was quenched by the addition of deuterium oxide. The crude reaction products were analyzed by mass spectroscopy. These data are consistent with the formation of $\underline{d}_0$- and $\underline{d}_1$-benzenetricarbonylchromium, (toluene)-tricarbonylchromium and (phenylbenzene)tricarbonylchromium. No carbonyl products analogous to that above were observed by glpc.

When a similar reaction mixture was quenched by the addition of ethyl iodide, no ketone products were observed.

IV. DISCUSSION

The reaction of benzenetricarbonylchromium with n-butyl-
lithium gives rise to two different types of products. The
first of these appears to result from proton abstraction by the
base while the second involves net alkylation by the base.
Each of these processes will be discussed in turn.

A. The Proton Abstraction Process

The reaction of benzenetricarbonylchromium with n-butyl-
lithium at $\leq$-20° has been quenched by the addition of methyl
iodide to yield (toluene)tricarbonylchromium, by the addition
of iodine to yield (iodobenzene)tricarbonylchromium and, from
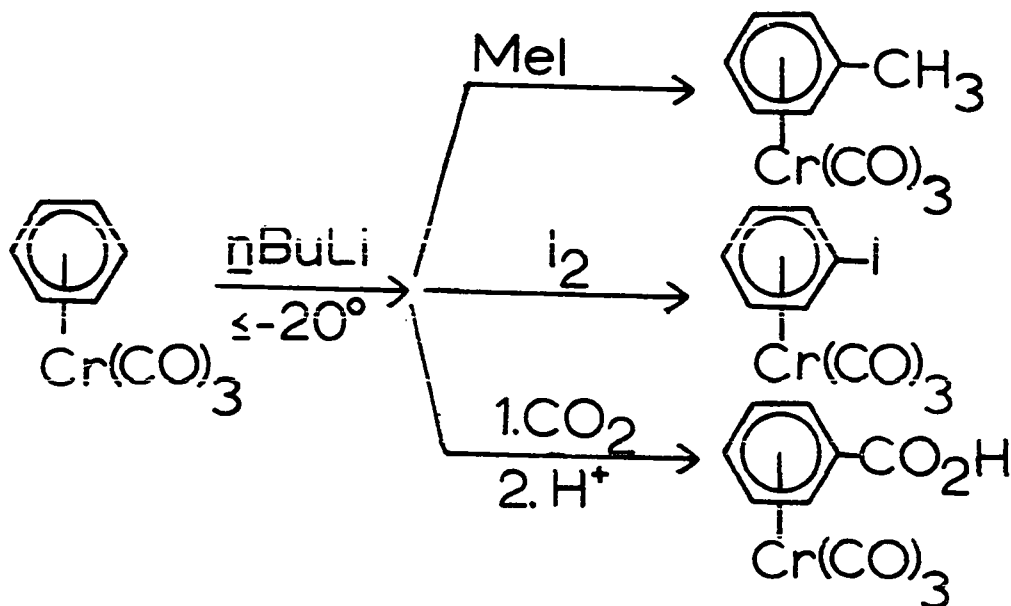
the work of Nesmeyanov et al., by the addition of carbon
dioxide and then acidification to yield (benzoic acid)-
tricarbonylchromium (8). These reactions support the

intermediacy of (phenyllithium)tricarbonylchromium as similar

chemistry has been observed for other organolithium species

(2, 58,59). The formation of (phenyllithium)tricarbonyl-

chromium in this manner is directly analogous to the metalation

of metallocenes by alkyllithium and alkylsodium reagents (2-7).

Additional evidence for the intermediacy of (phenyl-

lithium)tricarbonylchromium comes from the fact that the

intermediate has been generated in a variety of ways. The mode

of generation has little affect on the chemistry of the

intermediate. First, when (iodobenzene)tricarbonylchromium is

allowed to react with n-butyllithium at -20° and the reaction

quenched with methyl iodide toluene is obtained in 78±5%

yield after oxidative decomplexation. Toluene was obtained
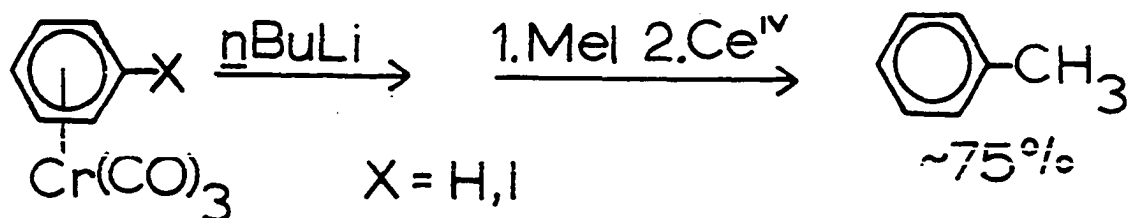
in similar yield from the reaction of benzenetricarbonyl-

chromium with n-butyllithium under identical conditions.

Interaction of phenyl iodide with n-butyllithium results in a

very good yield of phenyllithium (60). A similar halogen-

metal exchange reaction between (iodobenzene)tricarbonyl-

chromium and n-butyllithium would produce (phenyllithium)-

tricarbonylchromium.

Second, Rausch and Gloth have quenched the reaction of
bis(benzenetricarbonylchromium)mercury and n-butyllithium by
the addition of carbon dioxide. Acidification gave a 19% yield
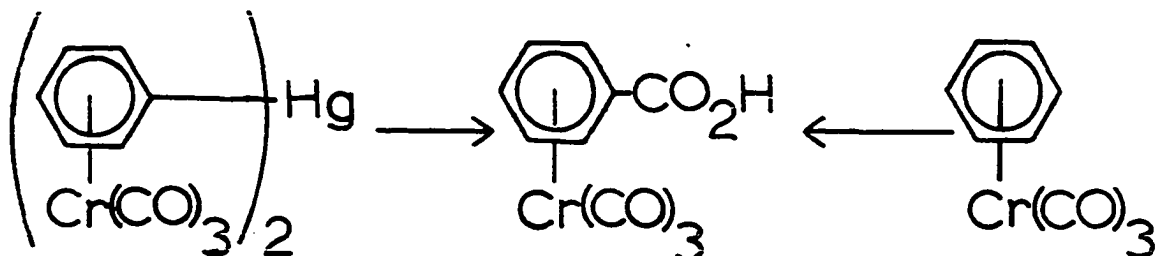
of (benzoic acid)tricarbonylchromium (9). This is nearly
identical to the yield of (benzoic acid)tricarbonylchromium
obtained by Nesmeyanov et al. from the reaction of n-
butyllithium with benzenetricarbonylchromium (8). The
reaction of organomercury compounds with an alkyllithium
reagent is a common method of preparation of organolithium
compounds (61). Thus, in each of these cases, it is entirely
feasible that (phenyllithium)tricarbonylchromium would form
from the initial reagents and this intermediate is entirely
consistent with the chemistry observed.

In addition to the chemical evidence, an intermediate
generated by the addition of n-butyllithium to benzenetri-
carbonylchromium at ca. -20° has been observed by nuclear
magnetic resonance spectroscopy. The spectrum observed for
this species has been presented in Figure 1. This signal
is the first spectrum observed after mixing. No change was
observed after 45 minutes under these conditions. The signal

is relatively sharp and well-defined. This suggests that the intermediate is generated rapidly, in good to excellent yield and with little or no decomposition, even after 45 minutes. It is felt that this spectrum is due to (phenyllithium)tri-carbonylchromium. A spectrum of phenyllithium has been provided in Figure 1 for comparison. The spectrum of phenyl-lithium has been analyzed by other workers (62). The spectrum of phenyllithium is not identical to that of the intermediate; however, there are important similarities. In both cases upfield and downfield multiplets are observed in a relative ratio of 3:2, respectively. This is quite inconsistent with formation of a carbene complex as an intermediate, where a singlet would be expected for the aromatic protons (63). In brief, the spectrum of the intermediate resembles a compressed version of the phenyllithium spectrum. This spectrum would be entirely consistent with the intermediacy of (phenyllithium)-tricarbonylchromium.

The methyl iodide quench of (phenyllithium)tricarbonyl-chromium and subsequent decomplexation leads to toluene in 71% yield as determined by gas chromatography. This is the highest yield of any species obtained from the quenching of (phenyl-lithium)tricarbonylchromium. This means that methyl iodide provides the best indication of the amount of metalation of benzenetricarbonylchromium under these conditions. For this reason, methyl iodide was chosen as the quenching reagent in

studies of the metalation of various substituted benzene-
tricarbonylchromium complexes.

The iodine quench of (phenyllithium)tricarbonylchromium
leads to (iodobenzene)tricarbonylchromium in only 26±2% iso-
lated yield. Nonetheless, this is the best method of prepara-
tion of this material to date. The other methods which have
been reported involve the interaction of phenyl iodide with
(trisammonia)(tricarbonyl)chromium (9b) or (tris-4-picoline)-
(tricarbonyl)chromium (64) to obtain 6 and 14% yields of
(iodobenzene)tricarbonylchromium, respectively. An increased
yield of (iodobenzene)tricarbonylchromium should result from
the use of 1,1,2,2-tetrafluorodiiodoethane in place of iodine
as the quenching agent. This has been used in the preparation
of 1,1'diiodoferrocene from ferrocene in 56% yield (59). The
major problem with this reagent would involve the rather high
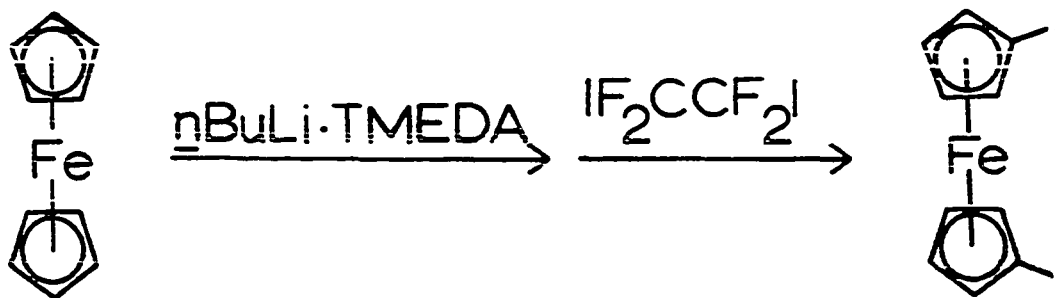
cost. The low yield from the use of iodine as quenching
reagent is probably due to oxidation of the formed (iodo-
benzene)tricarbonylchromium by iodine. Iodine has been used
as a decomplexation agent for (arene)tricarbonylchromium
complexes under conditions very similar to the quenching
conditions (47a).

Direct interaction of benzenetricarbonylchromium with n-butyllithium provides the best method of generation of (phenyllithium)tricarbonylchromium. This method involves readily available starting materials and provides a relatively stable solution of (phenyllithium)tricarbonylchromium in good yield. Use of bis(benzenetricarbonylchromium)mercury is hindered by difficulties in obtaining the starting material and by the fact that the solution of (phenyllithium)-tricarbonylchromium which is obtained begins decomposing after 10-15 minutes, even after rigorous precautions to exclude oxygen and moisture (9a). (Iodobenzene)tricarbonylchromium is best prepared from (phenyllithium)tricarbonylchromium and would, therefore, not usually be the reagent of choice for the synthesis of (phenyllithium)tricarbonylchromium.

The metalation of (toluene)tricarbonylchromium by n-butyllithium proceeds to yield almost exclusively ring lithiation. Products resulting from α metalation are received in only ca. 10% yield. It has been established that the α anionic type species is thermodynamically more stable than the ring anionic species (28). The low yield of α metalation received in the n-butyllithium reaction clearly demonstrates that proton abstraction is kinetically controlled and that transmetalation is not important under these conditions.

Kinetic control and the lack of transmetalation have previously been observed in the interaction of toluene with

the n-butyllithium-tetramethylethylenediammine (TMEDA) adduct
(65). In this reaction toluene gives an 89% yield of products
derived from α metalation.

The large difference in the conditions necessary for the
metalation of toluene relative to those used in the metalation
of (toluene)tricarbonylchromium again demonstrates the strong
activating influence of the tricarbonylchromium moiety to this
type of reaction. This is also illustrated by the interaction
of ca. equimolar quantities of (toluene)tricarbonylchromium
and p-xylene with excess n-butyllithium. Under conditions
where greater than 90% of the (toluene)tricarbonylchromium
is consumed, greater than 80% of the p-xylene was recovered
unchanged. The loss of p-xylene is probably due to the work up
as no species which would have resulted from the methylation of
p-xylene were observed by glpc.

The extent of α vs. ring metalation may be affected by
many factors. One of these is the large steric bulk of the
tricarbonylchromium moiety which effectively blocks one face
of the arene from attack by base. This factor is probably
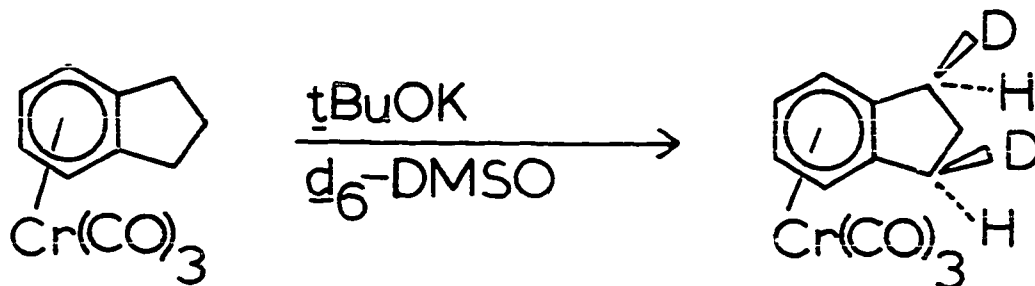
responsible for the stereoselectivity of hydrogen-deuterium exchange observed for (indane)tricarbonylchromium (28). However, it does not seem reasonable that this factor alone would be sufficient to account for the amazingly low extent of α metalation.

Broaddus observed that the metalation of toluene with the n-butyllithium-TMEDA adduct occurred with less α proton abstraction than the base catalyzed isotopic exchange of toluene (65). This was rationalized in terms of the principle that the C-H bond will be broken to the largest extent in the transition state involving the weakest base. Therefore, it may be reasonably proposed that electron delocalization factors will be largest with the weakest base. When more charge is developed on carbon, delocalization is a more important factor and thus the reaction is favored at benzylic positions relative to ring positions (65). An additional effect may involve initial coordination of the lithium atom of the alkyllithium reagent to a carbonyl oxygen. The importance of coordination of lithium to oxygen atoms of organic molecules has long been recognized (66). It has recently been suggested that the interaction of hexacarbonyl-chromium with methyllithium proceeds via an adduct which involves such lithium-oxygen interaction (67). Such an adduct from interaction of an (arene)tricarbonylchromium complex with an alkyllithium reagent might prefer a conformation where the

ring alkyl substituent and the carbonyl-butyllithium adduct are as far apart as possible for steric reasons. This should lead to preferential meta and para proton abstraction. This type of interaction would provide a conducted tour of the alkyllithium to the ring protons of least steric hindrance and could explain the increased rate of ring relative to α proton abstraction.

The presence of some α metalation provides a contrast with ferrocene chemistry. The α anion of either methylferrocene or 1,1'dimethylferrocene has not been generated (12, 2, 25). This difference is probably due to the fact that the π electron system of the cyclopentadienyl ring is already electron rich relative to the π electron system of benzene. In addition, the ($\underline{h}^5$-cyclopentadienyl)iron substituent may be less electron withdrawing than the tricarbonylchromium substituent. Both of these factors would result in a decreased ability of ferrocenes to accept additional electron density relative to the (arene)tricarbonylchromium complexes. Abstraction of the ring protons would involve the σ electron density, and should be less affected by these factors. The facts that ring proton abstraction from ferrocenes occurs under more rigorous conditions than from (arene)tricarbonylchromium complexes (68) and that electrophilic substitution occurs more readily for ferrocenes than for (arene)tricarbonylchromium complexes (68, 69) are consistent with these electronic arguments.

The regioselectivity of ring proton abstraction is
similar for the arene, (arene)tricarbonylchromium and analogous
ferrocene systems. Comparative data from these systems are
presented in Table 3. It should be noted that due to the
difference in acidities each system was examined under
different conditions. (Ethylbenzene)tricarbonylchromium yields
less ortho substitution than ethylbenzene. Although the
magnitude of this difference is not great, it is outside of
experimental error. The difference in the yield of ortho

Table 3. The regioselectivity of ring proton abstraction from
ethyl- and t-butylbenzene and the analogous
tricarbonylchromium and (h^5-cyclopentadienyl)iron
complexes

| Compound | Relative yield of ring proton abstraction (%) | | | |
| | Ring position | | | |
	2	3	4	Ref.
Ethylbenzene	15	58	27	65
(Ethylbenzene)tricarbonyl- chromium	6	61	33	This work
Ethylferrocene	7	93	--	12
t-Butylbenzene	0	68	32	65
(t-Butylbenzene)tri- carbonylchromium	0	59	41	This work
t-Butylferrocene	<2	>98	--	12

metalation in these systems may be due to the difference in structure of the butyllithium under the different conditions used. The n-butyllithium should be tetrameric in THF (70): a 1:1 adduct is formed with TMEDA (71). Some recent results have suggested that the TMEDA adduct is smaller than the n-butyllithium tetramer and therefore less subject to steric interactions (72a). This difference in steric size may be sufficient to allow the increased amount of ortho metalation observed for ethylbenzene relative to the tricarbonylchromium substituted derivative.

The metalation of (xylene)tricarbonylchromium complexes occurs with substantial amounts of α proton abstraction. But, the amount of α metalation in these cases is still less than the amount of α metalation observed for toluene. The decreased number of ring protons and the increased steric hindrance to ring proton abstraction would both help increase the amount of α proton abstraction for the (xylene)tricarbonylchromium complexes relative to (toluene)tricarbonylchromium. This is brought to an extreme in the metalation of (mesitylene)- tricarbonylchromium where only α proton abstraction is observed. The isolation of alkylated derivatives of (mesitylene)tricarbonylchromium from this reaction clearly demonstrates the very good yield of alkylated complexes which may be obtained. Admittedly, this is an exceptional example in that only one product is obtained. In other cases several

isomers are formed and separation problems prevent this method from being of general synthetic use.

This reaction is also limited by the observation that secondary or tertiary alkyl halides are not satisfactory quenching agents.

The presence of methoxy, fluoro or dimethylamino substituents on benzenetricarbonylchromium results in directed ortho metalation. The dimethylamino substituent is the poorest ortho director of the three. This is true for the uncomplexed benzene derivatives (72 - 74) as well as for the tricarbonylchromium substituted derivatives. Metalation of N,N-dimethylaniline by n-butyllithium results in ca. 70% ortho metalation (74) while nearly quantitative ortho metalation of fluorobenzene and anisole is observed (75). Whether the regioselectivity is due to inductive effects or to interaction of the lithium atom of the alkyllithium with a lone electron pair of the hetero atom is still under discussion (72).

The dimetalation of (anisole)tricarbonylchromium again demonstrates the activating influence of the tricarbonyl-chromium moiety on the proton abstraction process. Cleavage of tetrahydrofuran by n-butyllithium occurs more readily than proton abstraction from anisole (73) while dimetalation of (anisole)tricarbonylchromium occurs under such mild conditions that tetrahydrofuran is unaffected.

The dimetalation of (anisole)tricarbonylchromium was quite unexpected. It is interesting that both metalations occur ortho to the methoxy substituent. This result may prove to be of some synthetic value, perhaps allowing synthesis of some complexed metacyclophanes.

The reaction of (fluorobenzene)tricarbonylchromium with n-butyllithium is also interesting. First, it is interesting that proton abstraction occurs almost exclusively. Nucleophilic displacement of fluoride is known to be especially facile (46, 47). But, this process does not compete with the proton abstraction process.

The weakest activator and ortho director is the dimethylamino substituent. But, even in this case it is obvious that some ortho direction is important. (Ethylbenzene)tricarbonylchromium yields less than 10% ortho metalation; (N,N-dimethylaniline)tricarbonylchromium yields 19%.

As mentioned, these results show a rather close correlation with the results observed for the analogous uncomplexed systems. The major exception being the mildness of conditions which may be used. This similarity of results suggests that similar mechanisms are involved in the ortho directing abilities in these cases. This mechanism is still under discussion (72) and these results do not add any special insight into this problem.

B. The Net Alkylation by Base

The formation of n-butylbenzene from the interaction of
benzenetricarbonylchromium and n-butyllithium is an interesting
and intriguing reaction. Perhaps one of the most obvious
mechanistic possibilities would involve competitive proton
abstraction from and nucleophilic attack on benzenetricarbonyl-
chromium by butyllithium. Were this the case, the relative
importance of the two processes would have to be temperature
dependent with nucleophilic attack becoming more important as
the temperature is increased.

We have observed that (phenyllithium)tricarbonylchromium
is generated in very good yield at -20°. When this inter-
mediate is allowed to warm to 0° in the presence of butyl-
lithium, butylbenzene is obtained in very good yield.
Operation of the above mechanism would require conversion of
the (phenyllithium)tricarbonylchromium back to benzene-
tricarbonylchromium, presumably through proton abstraction
from solvent. This mechanism would predict that conversion
of d_6-benzenetricarbonylchromium to butylbenzene under these
conditions should proceed with substantial loss of deuterium
incorporation. In the simplest case, substantial amounts of
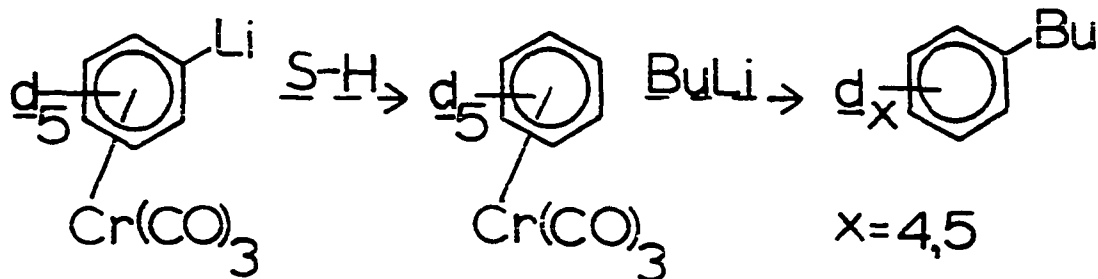
$\underline{d}_4$-butylbenzene should be formed. Only $\underline{d}_5$-butylbenzene was obtained. This result illustrates that the (phenyllithium)-tricarbonylchromium does not abstract a proton under these conditions. But, under these conditions, butylbenzene is formed in 80% yield. Therefore, (phenyllithium)tricarbonylchromium itself must be an important intermediate in this process. Also, unless ring hydrogen migration is important, this result indicates that the carbon bearing the lithium ends up with the butyl group. This conclusion is consistent with the observation that (ethylbenzene)tricarbonylchromium yields nearly identical amounts of meta substituted product from alkylation both $\underline{via}$ alkyl halide and $\underline{via}$ butyllithium. It is not likely that butyllithium would nucleophilically attack
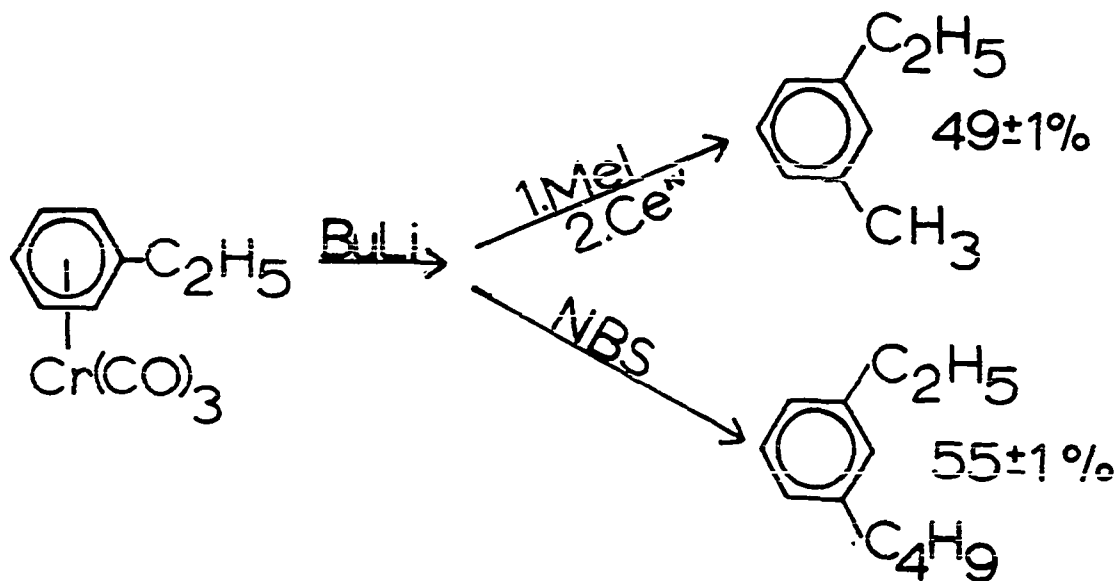
(phenyllithium)tricarbonylchromium derivatives at the carbon of highest electron density.

Alternatively, the (phenyllithium)tricarbonylchromium
could lose the elements of lithium hydride to yield a benzyne
intermediate, either complexed or uncomplexed, which would then
add butyllithium to yield, for example, o-lithiobutylbenzene.
Abstraction of a proton by this anionic species would then
yield butylbenzene. But again, such a mechanism would convert
$\underline{d}_6$-benzenetricarbonylchromium to $\underline{d}_4$-butylbenzene. This was not
observed.
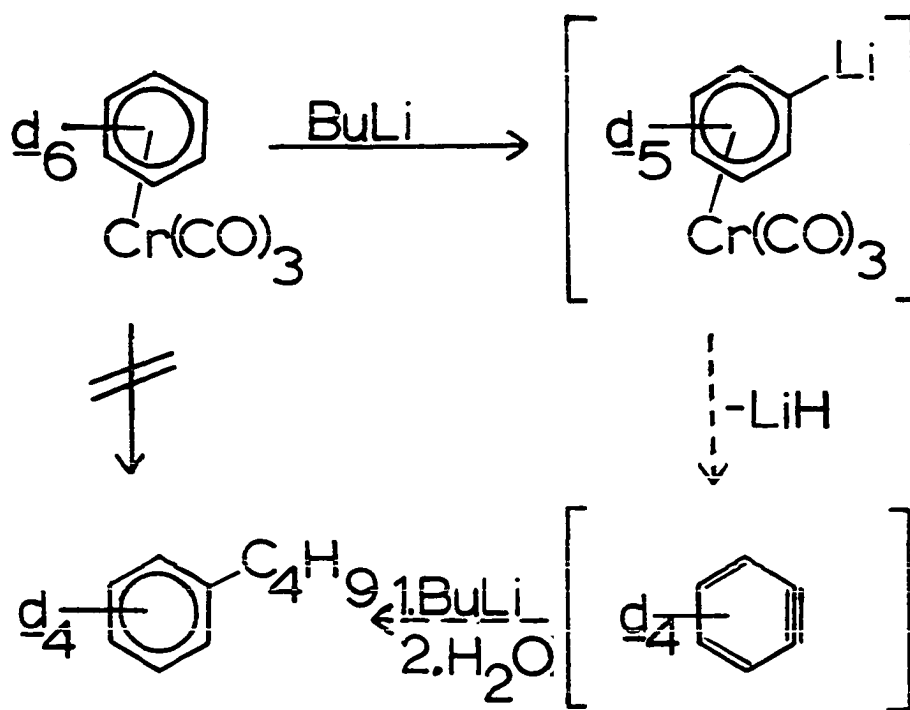
In addition to these results, the pattern of chemistry
observed in these reactions is much different from that
observed for reactions which appear to involve nucleophilic
attack on the ring. First, uncomplexed materials are received

from these reactions. Nucleophilic displacement of halide substituents from (halobenzene)tricarbonylchromium complexes yields new (substitutedbenzene)tricarbonylchromium complexes (46, 47). Second, a fluoride substituent is very readily displaced from (fluorobenzene)tricarbonylchromium by nucleophiles (46, 47). If nucleophilic addition to the organic ligand were important substantial amounts of (butylbenzene)-tricarbonylchromium would be expected from the reaction of n-butyllithium with (fluorobenzene)tricarbonylchromium. Very little of this was observed. This result is totally inconsistent with a mechanism involving nucleophilic attack on the arene ligand.

Thus, nucleophilic attack on the arene ligand appears to be inconsistent with the experimental results. Nucleophilic attack on either the metal or the carbonyl ligands is still possible. Of these, attack on the metal would be more likely to lead to the observed products. Indeed, there is considerable precedence for products of this nature to arise from σ-organometallic complexes.

The formation of butylbenzene appears to be very similar to the coupling of alkyllithium reagents in the presence of

$$C_6H_5Li + \underline{t}-C_4H_9Li + CuBr_2 \xrightarrow[-78°]{THF} \xrightarrow[-78°]{O_2} \underline{t}-C_4H_9-C_6H_5 \quad 73\%$$

cupric bromide (76). This reaction almost certainly proceeds through a σ-organocopper complex (76).

The coupling of aryl Grignard reagents has been observed in the presence of halides of many transition metals (77). The mechanism of this process is not understcod at present, but σ complexes are believed to play an important role. Reaction of mesitylmagnesium bromide with 0.5 equivalents of chromium(II) chloride led to the isolation of a THF adduct of bis($\underline{h}^1$-mesityl)chromium. This species yielded 2,2',4,4',6,6'-hexamethylbiphenyl when resubjected to the
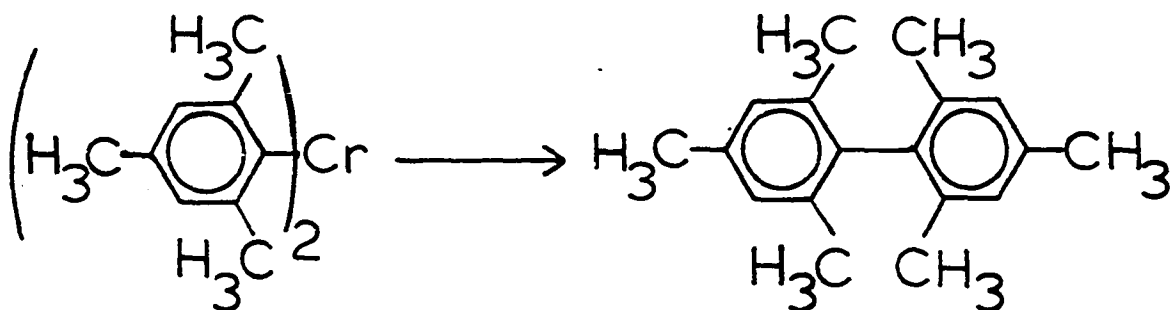
reaction conditions (78). Similar reaction of phenylmagnesium bromide with chromium(III) chloride led to biphenyl in good yield, but the σ adduct was not isolable (79). Side products in this reaction include bisbenzenechromium and (benzene)-(phenylbenzene)chromium (80). The formation of these latter products probably involves the conversion of σ to π complexes. Whether a π complex is an intermediate in the formation of biphenyl or merely a competing pathway is not understood.

Alkyl transfer from a metal to a π bonded ligand has been observed in other systems. Pyrolysis of ($\underline{h}^5$-cyclopentadienyl)-(tricarbonyl)(ethyl)molybdenum led to formation of the (($\underline{h}^5$-ethylcyclopentadienyl)tricarbonylmolybdenum) dimer (81).
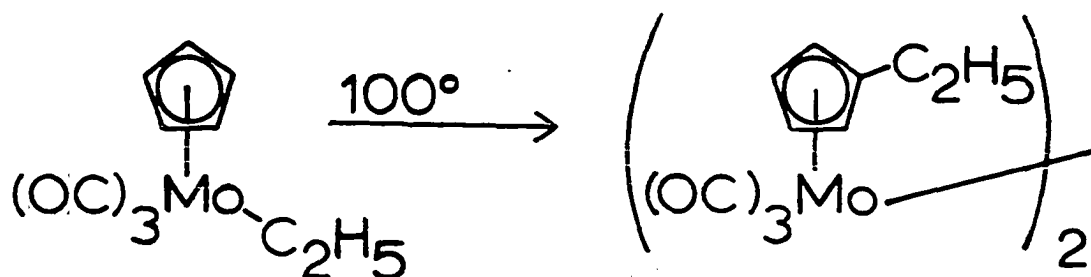
($\underline{h}^5$-Cyclopentadienyl)(triphenylphosphine)(phenyl)nickel yields 1-phenylcyclopentadiene in the presence of carbon monoxide (82). It is expected that the original product is
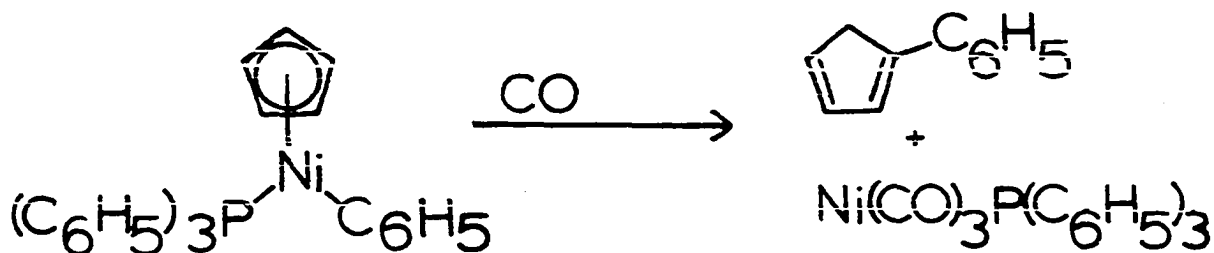
5-phenylcyclopentadiene which could then undergo a thermally allowed 1,5 hydrogen shift to yield the conjugated isomer.

These results by other workers demonstrate that coupling may occur $\underline{via}$ a complex involving only σ ligands or a complex containing a σ and a π ligand. Formation of each of these

types of intermediates is possible in the formation of n-butylbenzene. The formation of the former would involve attack on the metal with loss of carbon monoxide. The
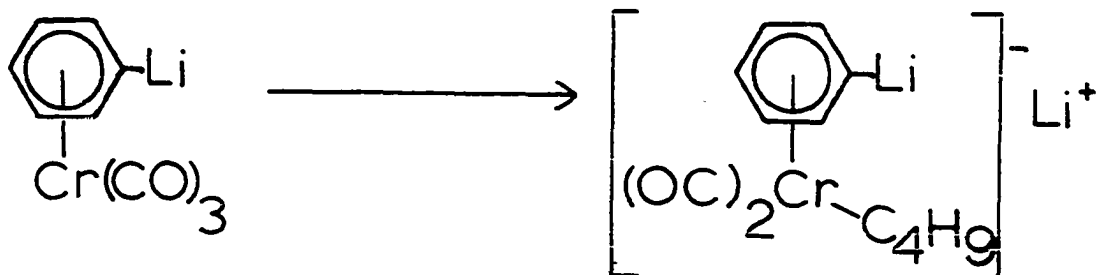
photolytic displacement of a carbon monoxide ligand from arenetricarbonylchromium complexes has often been observed (83). The analogous thermal ligand exchange process has not. Although it is unlikely that this intermediate would arise through direct displacement of a carbonyl, a more complicated pathway may be operative. Formation of the latter type of intermediate would require rearrangement of the metal arene bonding. This could occur before, after or during nucleophilic attack by butyllithium. This process would appear to be just
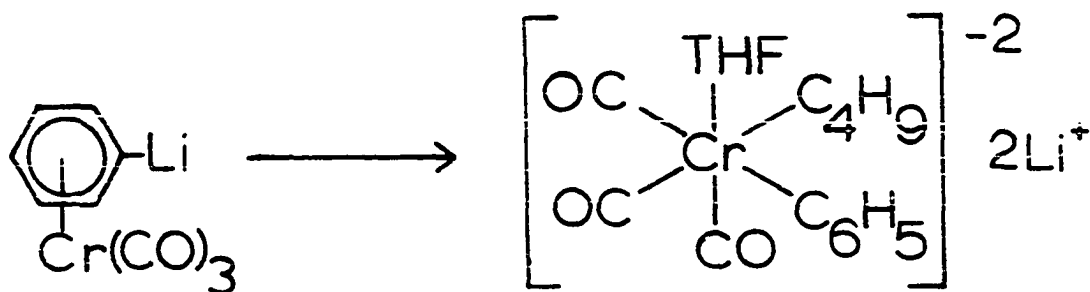
the reverse of that involved in the formation of bisbenzene-
chromium from phenylmagnesium bromide and chromium(II)
chloride. The formation of the (phenyl)(butyl)chromium inter-
mediate would place chromium in a formal oxidation state of
negative two. This should not be disconcerting. The reaction
of phenyllithium with chromium(III) chloride has been observed
to yield an ether adduct of trilithio hexaphenylchromium, in

$$CrCl_3 + C_6H_5Li \longrightarrow Li_3Cr(C_6H_5)_6 \cdot 4(C_2H_5)_2O$$
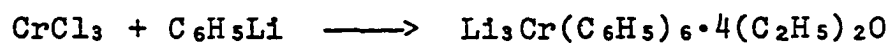
which chromium has a -3 formal oxidation state (84). And
recently, the pentacarbonylchromium dianion has been synthe-
sized and shown to be quite stable in tetrahydrofuran (85).

The formation of butylbenzene from (phenyllithium)-
tricarbonylchromium and n-butyllithium requires a net two
electron oxidation. This could occur in several ways. Were
butylbenzene to be generated directly from either intermediate,
chromium would be left, at least momentarily, in a -2 formal
oxidation state. An alternative would involve the generation
of the radical anion of butylbenzene and would leave chromium
in a -1 formal oxidation state. Present experimental results
and literature precedence do not allow resolution of the
mechanistic questions. The main point is that an intermediate
involving a chromium-butyl bond fits most comfortably with
both the experimental data and the literature.

This wor.cing hypothesis of a mechanism also allows some rationalization of observed differences in reactivity of n-vs. t-butyllithium and of the effect of ring substituents on this alkylation reaction.

The reaction of benzenetricarbonylchromium with n-butyllithium to produce butylbenzene occurs in very good yield at 0°. The reaction with t-butyllithium must be conducted at relatively low temperatures or a very poor mass balance is received. This difference in conditions is most likely due to the different thermal stabilities of the different alkyl-chromium bonds. It has been demonstrated that the t-alkyl-chromium bond undergoes homolytic cleavage and β-elimination at lower temperatures than an n-alkyl-chromium bond (86,87). Thus, the lower temperature probably minimizes these competing side reactions of the alkyl-chromium bond.

The reaction of (ethylbenzene)tricarbonylchromium with either base also requires low temperatures. It is unlikely that the inductive or steric effects of the ethyl group are sufficient to cause such a change. Perhaps, again, some side reaction, presumably involving the α hydrogens becomes important. This could involve homolytic cleavage of the alkylchromium bond followed by abstraction of a benzylic hydrogen atom leading to radical type products.

The importance of an oxidizing agent is consistent with the overall balanced equation for this process. Where the

oxidizing agent becomes involved in the mechanism is not clear at present.

Again, it is interesting to note the mild conditions underwhich this reaction proceeds. Uncomplexed arenes have been alkylated under much more forcing conditions (88). For example, a 15% yield of t-butylbenzene was obtained by heating a 1:1 mixture of benzene and t-butyllithium in decalin at 165° for 20 hr (88a). A 59% yield of t-butylbenzene was obtained from benzenetricarbonylchromium after less than 2 hr at -30°.

This reaction may prove to be of more synthetic value than the alkylation involving the addition of alkyl halides to the generated anion. This reaction appears to be much more general in that primary and tertiary alkyl groups may be added. The yield for either base is greater than 50% where the reaction has been found to work. A recent publication has suggested that a variety of carbon anions may be used to alkylate benzenetricarbonylchromium (47b).

It is interesting that the tricarbonylchromium complexes of anisole, fluorobenzene and N,N-dimethylaniline do not undergo this reaction under similar conditions. In the first two cases, mostly ortho metalation is observed. It is possible that the ortho substituent provides sufficient steric hindrance to prevent the reaction. If the reaction were to proceed through the sigma aryl-chromium intermediate previously mentioned, it is possible that interaction of the

lithium with the heteroatom sufficiently increases the stability of the phenyllithium intermediate that rearrangement to form the aryl-chromium sigma bond is no longer favorable. In the case of (N,N-dimethylaniline)tricarbonylchromium a very low mass balance is received after addition of NCS at low temperature. It could be that oxidation of the complex is occurring and the desired butylation would be observed if milder oxidants were employed.

The reaction of methyllithium with benzenetricarbonyl-chromium does not proceed in a manner similar to the analogous n-butyllithium reaction, at least when quenched with methyl iodide. So little is presently known about the methyllithium reaction that it is very difficult to understand why the reactions are different. Good mass balance has not been realized. The effect of temperature, so important in the n-butyllithium reaction, has not been explored. The minimum data presently available do suggest that the quenching reagent is important. No ketone products were observed when the reaction was quenched by the addition of ethyl bromide. The results obtained from this system merely suggest that this question is worth further study.

V. EXPERIMENTAL

A. Commercial Compounds

Most of the organic chemicals used in this study were obtained from the Aldrich Chemical Company. Common solvents and inorganic reagents were obtained from Aldrich Chemical Company, J. T. Baker Chemical Company and/or Mallincrodt Chemical Works. Exceptions are presented in Table 4.

Table 4. Source of commercial compounds

Compound	Source
d_6-Benzene	Columbia Organic Chemicals Co.
n-Butyllithium in hexane	Foote Mineral Co.
t-Butyllithium in pentane	Foote Mineral Co.
Chromium trichloride	Research Organic/Inorganic Chemical Co.
Hexacarbonylchromium	Strem Chemicals Inc.
Methyllithium in ethyl ether	Foote Mineral Co.
Lithium aluminum hydride	Ventron Corporation
Petroleum ether	Skelly Petroleum Co.
Phenyllithium in benzene	Foote Mineral Co.
m-Xylene	Eastman Kodak Co.
p-Xylene	Eastman Kodak Co.

B. Equipment

The equipment used in all complexations was constructed according to the instructions of Strohmeier (89).

Nuclear magnetic resonance (nmr) spectra were obtained using a Varian Associates A-60b or HA-100 Nuclear Magnetic Resonance Spectrometer. When there was no reasonable alternative, the Hitachi R-20B Nuclear Magnetic Resonance Spectrometer was employed.

Infrared (ir) spectra were obtained on a Beckman IR-12 Infrared Spectrophotometer.

Routine mass spectra were obtained on an Atlas CH-4 Mass Spectrometer. An AEI MS-902 Mass Spectrometer was used to obtain high resolution mass spectral data which were used to obtain the exact mass of a compound and in the analysis of deuterium content of d_6-benzenetricarbonylchromium.

Melting points were taken on a Thomas Hoover Capillary Melting Point Apparatus.

The gas chromatographic work utilized a Varian Aerograph 200 Gas Chromatograph with a thermal conductivity detector and a Beckman Model 1005 Recorder with disc integration.

C. Prepared Compounds

All melting points are uncorrected.

Glyme, diglyme and tetrahydrofuran (THF) were distilled over calcium hydride and stored under nitrogen over molecular sieves until needed.

Hexacarbonylchromium was stored in a desiccator between uses and was occasionally sublimed.

Elemental analyses were carried out by Spang Micro-analytical Lab (Ann Arbor, Michigan).

1. Complexation method

In the general procedure, 2.2 g hexacarbonylchromium (10 mmol) was added to a dry 50 ml round bottom flask equipped with a side arm. Toluene (5 ml, 47 mmol), 10 ml glyme and 15 ml diglyme were added. The flask was fitted onto a Strohmeier apparatus. The system was purged with nitrogen and the solution refluxed under nitrogen. The reflux was maintained for at least 24 hrs after hexacarbonylchromium was no longer observed in the condenser (ca. 3 days) unless significant decomposition was observed before this time. A bright yellow to orange solution was usually obtained. The solution was filtered into ether-water. The filtration at this point helped to minimize emulsion formation during work up. The layers were separated, the ethereal layer was washed thoroughly with water, dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure.

Purification of the resulting yellow material was conducted by a variety of methods. Often, the arene used was sufficiently volatile to be removed at reduced pressure. The resulting complex was washed with pentane and sublimed.

Alternatively, the material could be chromatographed on silica gel. The arene was eluted with petroleum ether or hexane and the complex was eluted with ether.

(Toluene)tricarbonylchromium was obtained in ca. 65% yield by this method. The physical properties of (toluene)-tricarbonylchromium and other complexes prepared are presented in Table 5.

2. Decomplexation methods

Three methods of decomplexation were employed during this study. Of these, Methods A and B were used for all arene work. Method C was used when the organic substrate was not stable to ceric ammonium nitrate (CAN), specifically, substrates containing fluoro, methoxy or amino groups.

a. __Method A__   The material to be decomplexed (ca. 50 mg) was added to 2 ml acetonitrile. A 0.2 N CAN solution (1 g CAN was dissolved in 2 ml water and 8 ml acetonitrile) was added dropwise until the solution turned nearly colorless and then slightly yellow. The solution was allowed to stand for 10 min. The solution was extracted with 10 ml pentane, the pentane solution washed with water and dried over anhydrous magnesium sulfate. The resulting solution was ready for glpc analysis.

b. __Method B__   This method is identical to Method A except that an aqueous 0.2 N solution of CAN is added dropwise

Table 5. The yields and physical properties of prepared (substituted benzene)-
tricarbonylchromium complexes

Substrate	Yield (%)	Melting Point			NMR Data (CCl₄; δ)
		Obs.	Lit.	(Ref.)	
Benzene[a]	50,56,62	161-163	165.5-166.5	(49)	5.30(s)
d₆-Benzene[a,b]	26	161-163	---	--	---
Toluene	65	79-81	82.5-83.5	(49)	5.18(m,5), 2.20(s,3)
Ethylbenzene	50,70	47-49	48-49	(90)	5.20(m,5), 2.48(m,2), 1.15(m,3)
t-Butylbenzene	54	79.5-80	83.5-84.5	(49)	5.22(m,5), 1.30(s,9)
o-Xylene	52	88-89	90-91.4	(49)	5.03(s,4), 2.11(s,6)
m-Xylene	82	104-106	107-108.5	(49)	5.20(m,1), 4.79(m,3), 2.40(s,6)
p-Xylene	60	95.5-97	99-100	(49)	5.15(s,4), 2.10(s,6)
Mesitylene	68	166-168	∼165	(91)	4.75(s,3), 2.18(s,9)
Anisole	64	82-83	86-87	(49)	5.60-4.60(m,5), 3.66(s,3)
N,N Dimethylaniline[c]	61,85	142-143	145.8-146.5	(49)	5.52(m,2), 4.75(m,3), 2.85(s,6)
2,6 Dimethylanisole[c,d]	46	63-64	---	--	5.03(m,3), 3.68(s,3), 2.22(s,6)
Fluorobenzene[e]	20,25	116-118	116-117	(46b)	5.27(m,4), 4.70(m,1)

[a]Solvent for complexation was 15 ml glyme and 10 ml diglyme.

[b]See Table 6 for mass spectral data.

[c]Chloroform was NMR solvent.

[d]Exact mass calculated for $C_{12}H_{12}{}^{52}CrO_4$: 272.0141; Obs: 272.0135.

[e]Freshly sublimed hexacarbonylchromium was used.

Table 6. Mass spectral data for natural and deuterated benzenetricarbonylchromium

m/e	Intensity of natural sample[a]	Intensity of deuterated sample[a]	Calculated peaks for						
			d_0	d_1	d_2	d_3	d_4	d_5	d_6
P-2 212	7	.6	.8						
P 214	100	10.8	10.8						
P+1 215	25	2.3	2.5	0					
P+2 216	7	.5	.8	0	0				
P+3 217		.1		0	0	.1			
P+4 218		4.4			0	0	0		5.8
P+5 219		2.0				0	0	2.0	
P+6 220		84.0					0	.5	83.5
P+7 221		15.6						0	22.5

[a]Ionization voltage was 70 eV.

to an ethereal solution of the complex to be oxidized. This method involves a two-phase oxidation and is free of acetonitrile.

c. Method C   An ethereal solution (50 mg/10 ml) is irradiated using a sun lamp and water filter. After 1 hr the green solution was filtered. The resulting solution was ready for glpc analysis.

3. **m-Butyltoluene**

m-Xylene (2 ml, 16 mmol) was added to the solution resulting from the interaction of 12 ml 1.6 $\underline{M}$ (19 mmol) n-butyllithium in hexane with 20 mmol TMEDA under argon at room temperature. The solution was stirred for $\underline{ca}$. 15 min before 5 ml (54 mmol) n-propyl bromide was added. The resulting solution was washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The product was not further purified. The nmr spectrum and glpc data are consistent with a 2:1 mixture of m-n-butyltoluene and m-xylene; nmr (CCl₄; δ) 6.90(m, 72 units), 2.55(m,21), 2.28(s,71), 1.40(m,48) and 0.92(m,35); exact mass calculated for $C_{11}H_{16}$: 148.125194: observed: 148.125509.

D. The Proton Abstraction Process

1. Methylation of benzenetricarbonylchromium

Benzenetricarbonylchromium (50 mg, 0.23 mmol) was added to 3 ml cold tetrahydrofuran in an argon atmosphere at -30°. The desired temperature was maintained with a Dry Ice-ethanol-water bath. It is assumed that the reaction temperature is closely approximated by the bath temperature. To the cold, stirred solution was added 0.8 ml 1.6 $\underline{M}$ (1.3 mmol) n-butyllithium in hexane by syringe. The resulting solution was stirred at -30° for 30 min. Methyl iodide (1 ml, 10 mmol) was added. After 15 min, 13 mg (0.12 mmol) ethylbenzene was

added by syringe and weighed by difference. The resulting
solution was added to 25 ml ether, washed with 3x60 ml aqueous
sodium chloride, dried over anhydrous magnesium sulfate,
filtered and the solution reduced in volume to 3 ml under
reduced pressure. The resulting solution was decomplexed by
Method A.

Gas chromatographic analysis of the resulting solution
was performed using a 2 m column packed with 5% bentone 34,
5% diisodecylphthalate on chromosorb W at 65°. Toluene was
identified by retention time. The relative peak areas were
determined by disc integration. The relative thermal
conductivities (TC) of toluene and ethylbenzene were
determined using a known mixture of these compounds. The
relative thermal conductivity of toluene to ethylbenzene was
1 to 1.2.

To determine this value, an ethereal solution containing
0.47 mmol toluene and 0.42 mmol ethylbenzene was subjected to
glpc analysis. The compounds were added by syringe and
weighed by difference. The relative integration of the two
peaks were 13.3:13.6 and 13.3:13.9 for two traces,
respectively. From these data, the relative thermal conduc-
tivity of toluene to ethylbenzene was 1:1.14 and 1:1.17 from
the two runs, respectively. The average was rounded off to
obtain the 1:1.2 value used in the calculations as illustrated
below.

The yield calculation was performed according to the formula presented below. In the two runs performed, the

$$\% \text{ yield of cpd} = \frac{\text{rel. area of cpd}}{\text{rel. area of std}} \times \frac{\text{no. mmol std}}{\text{theoretical no. mmol cpd}} \times \frac{\frac{\text{rel. TC std}}{\text{rel. TC cpd}}}{} \times 100$$

relative areas of the peaks due to toluene and ethylbenzene were 7.5 to 6.6 and 10 to 8.2, respectively. The calculations were performed as shown below. Thus, from these data toluene

$$\% \text{ yield toluene} = \frac{7.5 \text{ units toluene}}{6.6 \text{ units ethylbenzene}} \times$$

$$\frac{.12 \text{ mmol ethylbenzene}}{.23 \text{ mmol toluene}} \times 1.2 \times 100 = 71\%$$

$$= \frac{10 \text{ units}}{8.8 \text{ units}} \times \frac{.12 \text{ mmol}}{.23 \text{ mmol}} \times 1.2 \times 100 = 71\%$$

was obtained in 71% yield.

2. (Toluene)tricarbonylchromium

(Toluene)tricarbonylchromium was obtained from benzene-tricarbonylchromium essentially as described above. The reaction was scaled up to use 200 mg (.91 mmol) benzene-tricarbonylchromium and 2 ml 1.6 M (3.2 mmol) n-butyllithium. The reaction was quenched by the addition of 2 ml (20 mmol) methyl iodide. After the aqueous work up the solvent was removed and the resulting yellow solid was sublimed. (Toluene)tricarbonylchromium (109 mg) was received in 50%

yield. The melting point and nmr spectrum of this material were identical to that of the material prepared by direct complexation of toluene (Table 5).

3. (Iodobenzene)tricarbonylchromium

n-Butyllithium (2 ml, 1.6 M solution in hexane, 3.2 mmol) was added to a cold stirred solution of 500 mg (2.3 mmol) benzenetricarbonylchromium in 20 ml THF under argon at -78°. The solution was stirred at -78° for 60 min and then 500 mg (2 mmol) iodine was added and the solution stirred for 120 min at ca. -70°. The solution was taken up in ether. The ethereal solution was washed with aqueous sodium bisulfite, aqueous sodium chloride, water and then aqueous sodium chloride. The ethereal solution was dried over anhydrous magnesium sulfate, filtered and the solvent removed at reduced pressure. The yellow solid was sublimed under vacuum to yield 220 mg (iodobenzene)tricarbonylchromium (26%). Similar runs yielded 23 and 26%; mp 110-111°; lit. mp 111° (64); nmr (DCCl$_3$,δ) 5.57(m,2), 5.21(m,3). An nmr of the crude reaction mixture indicated the presence of substantial amounts of phenyl iodide.

4. Methylation of substituted benzenetricarbonylchromium complexes

In the space to follow, three examples of the general procedure used in the methylation of substituted benzene-tricarbonylchromium complexes are presented. The reaction of

(toluene)tricarbonylchromium presents the general manner in which the alkylation of the (arene)tricarbonylchromium complexes was conducted. Alkyl halides other than methyl iodide were included in this study. The reaction of (anisole)-tricarbonylchromium presents the general conditions for the methylation of the heteroatom substituted benzenetricarbonyl-chromium complexes. The reaction of (iodobenzene)tricarbonyl-chromium is presented because it is unique. The conditions and products from all these runs are presented in Table 7. Several products were collected by glpc and spectral data were obtained. These compounds and their spectral data are presented in Table 8. In cases where the nmr spectral data are published, the reference is provided without repeating the data. In each of these cases the nmr spectrum obtained from glpc collected material is very nearly identical to the published spectrum. The mass spectra of these products were used only to indicate that a variety of collected products were isomers. For this reason, only the molecular ion region and other characteristic peaks are reported. Again, references to literature data have been listed where available.

a. Methylation of (toluene)tricarbonylchromium

(Toluene)tricarbonylchromium (50 mg, .22 mmol) was added to 3 ml cold THF in an argon atmosphere. The temperature was maintained with a Dry Ice-ethanol-water bath, in this case at -20°. n-Butyllithium (1 ml 1.6 M in hexane, 1.6 mmol) was added to the cold, stirred solution by syringe. (The final

solution concentration listed in Table 7 was calculated from
the label concentration of n-butyllithium and the solution
volume. The concentration of the n-butyllithium was monitored
periodically by titration (92) and did not deviate by more
than 5% over the period of use.) The resulting solution was
stirred at -20° for 10 min before 1 ml (10 mmol) methyl
iodide was added. Mesitylene was weighed by difference and
added as standard. The amount of standard added was close to
half the original number of mmol of (arene)tricarbonylchromium
complex used. In this case, 13 mg (.11 mmol) mesitylene was
added. The solution was worked up as described for the
methylation of benzenetricarbonylchromium. After decomplexa-
tion by either Method A or B, the resulting pentane solution
was subjected to glpc analysis.

In this case, the analysis was performed using a 2 m
column packed with 5% diisodecylphthalate, 5% bentone 34 on
chromosorb W at 40°. The assignment of all products is
consistent with their retention time. In addition, ethyl-
benzene and the xylenes were collected and spectral data
were obtained (Table 8). The identification of m-xylene is
on the basis of nmr and mass spectral data in addition to the
retention time. The yields of products were determined by
the method illustrated for the methylation of benzene-
tricarbonylchromium. The relative peak areas were determined
by disc integration or, occasionally by the cut and weigh

method. The relative thermal conductivity ratios were determined from a solution of known composition of toluene, p-xylene and mesitylene. It was found that the TC of these compounds were directly proportional to the molecular weight of the compounds. (In one run, a mixture containing .20 mmol toluene, .20 mmol p-xylene, and .19 mmol mesitylene yielded an integration ratio of 38:44:47 for the three compounds, respectively. This indicates thermal conductivity ratios of 1:1.2:1.3.) The data presented in Table 7 have been corrected for these differences in thermal conductivity.

A blank run was performed as above but without the (arene)tricarbonylchromium complex at -10° to show that there are no side products which would interfere with product analysis or yield determination.

In order to collect many of the arenes produced in the reaction, the reaction was scaled up to consume 150-300 mg of the (arene)tricarbonylchromium complex. No complications were encountered.

b. Methylation of (anisole)tricarbonylchromium

(Anisole)tricarbonylchromium (50 mg, .20 mmol) was added to 3 ml cold THF at -40° under an argon atmosphere. n-Butyl-lithium (0.5 ml, 1.6 M in hexane, .8 mmol) was added and the solution was stirred at -40° for 25 min. Methyl iodide (1 ml, 10 mmol) was added and the resulting solution was stirred at -40° for 25 min. The solution was poured into ether-water,

worked up in the usual manner and decomplexed by Method C.
(The photolytic decomplexation was used for reactions
involving the tricarbonylchromium complexes of anisole,
fluorobenzene and N,N-dimethylaniline.) N,N-dimethylaniline
(13 mg, .11 mmol) was added as standard. The resulting solu-
tion was analyzed by glpc. The peak areas were determined by
disc integration. The relative thermal conductivities were
determined using a known mixture of anisole, 2-methylanisole
and N,N-dimethylaniline. The thermal conductivity ratio of
anisole to N,N-dimethylaniline was 1. The ratio of anisole
to 2-methylanisole was 1:1.1, again the same ratio as the
ratio of the molecular weights of the two compounds. The
yields were calculated in the manner previously described.
The data are presented in Table 7. The data are corrected for
thermal conductivity differences. The products were collected
and identified on the basis of spectral data (Table 8).

In addition, in this particular reaction, the crude
reaction product was chromatographed on silica gel. The
column was eluted with pentane-ether. This led to the
isolation of (2,6-dimethylanisole)tricarbonylchromium. This
material was nearly identical by nmr and ir spectroscopy to
the complex obtained on interaction of commercial 2,6-
dimethylanisole with hexacarbonylchromium. The data has been
presented in Table 5. The melting point of the material
obtained from the chromatography was lower than that of the

material prepared by direct complexation. The observed mp for the chromatographic material was 42-50°. Addition of pure material resulted in an increase in the melting point.

c. Toluene   Toluene was obtained from (iodobenzene)-tricarbonylchromium in a manner very similar to the methylation of benzenetricarbonylchromium. (Iodobenzene)tricarbonyl-chromium (70 mg, .20 mmol) was added to 3 ml THF at -30° under an argon atmosphere. n-Butyllithium (0.8 ml 1.6 M in hexane, 1.3 mmol) was added and the resulting solution was stirred at -30° for 30 min. Methyl iodide (1 ml, 10 mmol) was added and the resulting solution was stirred at -30° for 15 min. The solution was poured into ether-water and worked up in the usual manner. The resulting solution was decomplexed by Method B and analyzed by glpc using a 2 m column packed with 5% diidodecyl-phthalate, 5% bentone 34 on chromosorb W at 65°. Mesitylene (13 mg, .11 mmol) was used as standard. Toluene was obtained in 78±5% yield. A 2±1% yield of butylbenzene was also obtained. The products were identified on the basis of retention time. The yields were calculated in the manner already described. The data are the result of two runs.

5. Competition study

(Toluene)tricarbonylchromium (54 mg, .24 mmol) and 23 mg (.22 mmol) p-xylene were added to 3.5 ml THF. The solution was purged with argon and cooled to -20°. n-Butyllithium (0.5 ml 1.6 M in hexane, 0.8 mmol) was added and the resulting

Table 7. Reaction conditions, products and yields for the reactions of substituted benzenetricarbonylchromium complexes with n-butyllithium which were quenched by the addition of an alkylhalide

Substituted Benzene (mmol;$\underline{M}$)	Temp (°C)	Alkyl Halide[a]	Conc. of n-BuLi ($\underline{M}$)	Standard
Toluene (.22;.06)	-20		.4	Mesitylene
Toluene (.22;.06)	-10	C_2H_5Br	.4	Mesitylene
Toluene (.22;.06)	-10	$\underline{i}$-C_3H_7I	.4	Mesitylene
Toluene (.22;.06)	-10	$\underline{t}$-C_4H_9Br	.4	$\underline{i}$-Propylbenzene
Ethylbenzene (.21;.05)	-10		.4	Mesitylene

[a]Methyl iodide was used unless otherwise indicated.

[b]The following columns were used: I:2 m 5% diisodecylphthalate, 5% bentone 34 on chromosorb W; II:2 m 10% Lac 446 on chromosorb W; and, III:4 m 5% diisodecylphthalate, 5% bentone 34 on chromosorb W.

[c]All products were identified on the basis of retention time and peak enhancement unless otherwise indicated.

[d]Mass spectral data were obtained.

[e]Mass and nmr spectral data were obtained.

GLPC Conditions		Products[c]	Yield (%)	Glpc Peak Integrations	
Column[b]	Temp (°C)			Run 1	Run 2
I	40	Toluene	5±1	5	4
		Ethylbenzene[d]	14±2	16	15
		p-Xylene[e]	22±4	25	22
		m-Xylene[e]	41±1	51	40
		o-Xylene[d]	6±1	6	6
		Standard		112(.17 mmol)	40(.08 mmol)
I	70	Toluene	8±3	14	30
		n-Propylbenzene	∿8	59	88
		p-Ethyltoluene	∿13		
		m-Ethyltoluene	34±3	100	139
		o-Ethyltoluene	10±1	34	36
		Standard		169(.12 mmol)	210(.12 mmol)
I	70	i-Propyltoluenes	<3		
I	70	t-Butyltoluenes	<3		
I	70	Ethylbenzene	2±1	3	2
		p-Ethyltoluene	26±2	26	25
		m-Ethyltoluene	49±1	46	47
		o-Ethyltoluene	5±2	5	5
		Standard		48(.11 mmol)	52(.11 mmol)

Table 7. (Continued)

Substituted Benzene (mmol;M)	Temp (°C)	Alkyl Halide	Conc. of n-BuLi (M)	Standard
t-Butylbenzene (.40;.05)	-15	C_2H_5Br	.2	i-Propylbenzene
o-Xylene (.21;.05)	-20		.4	Durene
m-Xylene (.21;.05)	-20		.2	Indane
p-Xylene (.21;.05)	-10		.4	s-Butylbenzene
Iodobenzene	-30		.4	Ethylbenzene

[f]Exact mass was determined.

GLPC Conditions Column	Temp (°C)	Products	Yield (%)	Glpc Peak Integrations Run 1	Run 2
II	80	t-Butylbenzene	23±5	4	5
		m-Ethyl-t-butyl-benzene[e,f]	32±2	8.5	7
		p-Ethyl-t-butyl-benzene[e,f]	22±1	5.3	5
		Standard		8.8(.19 mmol)	8(.19 mmol)
II	75	o-Xylene	2±1	.4	.2
		o-Ethyltoluene	28±2	4.5	3.9
		1,2,3-Trimethyl-benzene	8±2	1.0	1.3
		1,2,4-Trimethyl-benzene	50±7	8.5	6.6
		Standard		9(.11 mmol)	8.6(.11 mmol)
II	75	m-Xylene	2±1	.3	.5
		m-Ethyltoluene	45±1	6	8.1
		1,2,4-Trimethyl-benzene	10±2	1.1	2
		1,3,5-Trimethyl-benzene	33±3	4.1	6.3
		Standard		7.0(.11 mmol)	9.3(.11 mmol)
II	75	p-Xylene	3±1	2	3
		p-Ethyltoluene	20±3	13	31
		1,2,4-Trimethyl-benzene	44±3	32	59
		Standard		22.5(.06 mmol)	75(.10 mmol)
I	65	Toluene	78±5	3.8	6
		Standard		3.2(.12 mmol)	6.5(.14 mmol)

Table 7. (Continued)

Substituted Benzene (mmol;$\underline{m}$)	Temp (°C)	Alkyl Halide	Conc. of n-BuLi $(\underline{M})$	Standard
Fluorobenzene (.21;.05)	-40		.4	Mesitylene
Anisole (.20;.05)	-40		.2	N,N-Dimethylaniline
N,N-Dimethyl-aniline (.20;.05)	-40		.2	Anisole

GLPC Conditions		Products	Yield (%)	Glpc Peak Integrations	
Column	Temp (°C)			Run 1	Run 2
III	55	o-Fluorotoluene[e]	71±3	10.7	10.9
		n-Butylbenzene	<1		
		Standard		8.3(.11 mmol)	9.0(.11 mmol)
II	90	2-Methylanisole[e]	14±0	2.2	3.5
		2,6-Dimethyl- anisole[e]	66±9	11.5	15
		Standard		8.6(.12 mmol)	13.6(.12 mmol)
II	125	N,N-Dimethyl- aniline	8±3	1	.7
		o-N,N-Dimethyl- toluidine[e]	19±0	2	2.5
		m+p-Dimethyl- toluidine[e]	42±4	4.7	5.2
		Standard		4.7(.10 mmol)	6.0(.10 mmol)

Table 8. Spectral and physical data of glpc collected products which were obtained from the alkylation sequence involving the addition of alkyl halides

Product	NMR (CCl₄;δ)	Mass Spectral Data (m/e) 70 ev	16 ev	(Ref.)	Other
m-Xylene	6.89(m,4) 2.38(s,6) (94a)	106 105 91	106 105 91	(93)	
p-Xylene	6.92(s,4) 2.30(s,6)	106 105 91		(93)	Solidified on standing at 0° (Lit. mp 13-14° (95))
o-Xylene		106 105 91	106 105 91	(93)	
Ethylbenzene		106 105 91	106 91	(93)	
m-Ethyl-t-butylbenzene	7.06(s,4) 2.62(m,2) 1.34(s,9) 1.26(m,3)	162 147	162 147		Exact mass: $C_{12}H_{18}$ Calc: 162.140843 Obs: 162.138883
p-Ethyl-t-butylbenzene	7.08(m,2) 7.00(m,2) 2.57(m,2) 1.30(s,9) 1.18(m,3)	162 147			Exact mass: $C_{12}H_{18}$ Calc: 162.140843 Obs: 162.138283

Table 8. (Continued)

Product	NMR (CCl₄;δ)	Mass Spectral Data (m/e) 70 ev 16 ev (Ref.)			Other

Product	NMR (CCl$_4$;δ)	Mass Spectral Data (m/e)	Other
o-Fluorotoluene	6.95(m,4) 2.27(d,3 J=2.5 cps) (94b)	111(08) 110(100) 109(03)	
o-Methylanisole	6.85(m,4) 3.78(s,3) 2.18(s,3) (94c)	123(10) 122(100) 107(04)	
2,6-Dimethyl- anisole	6.86(m,3) 3.63(s,3) 2.23(s,6) (94d)	137(10) 136(100) 121(07)	
o-N,N-Dimethyl- toluidine	7.0-6.75(m,4) 2.62(s,6) 2.26(s,3)	136(11) 135(100) 134(06) 120(06) 105(06)	
m- + p-N,N- Dimethyl- toluidine	7.1-6.3(m)[a] 2.86(s) 2.80(s) 2.27(s) 2.21(s)	136(10) 135(150) 134(10)	

[a] The nmr spectrum is presented in Figure 4.

Figure 4. Nuclear magnetic resonance spectra of glpc
           collected (top) and a 3:1 mixture of
           commercial (bottom) m- + p-N,N-dimethyltoluidine
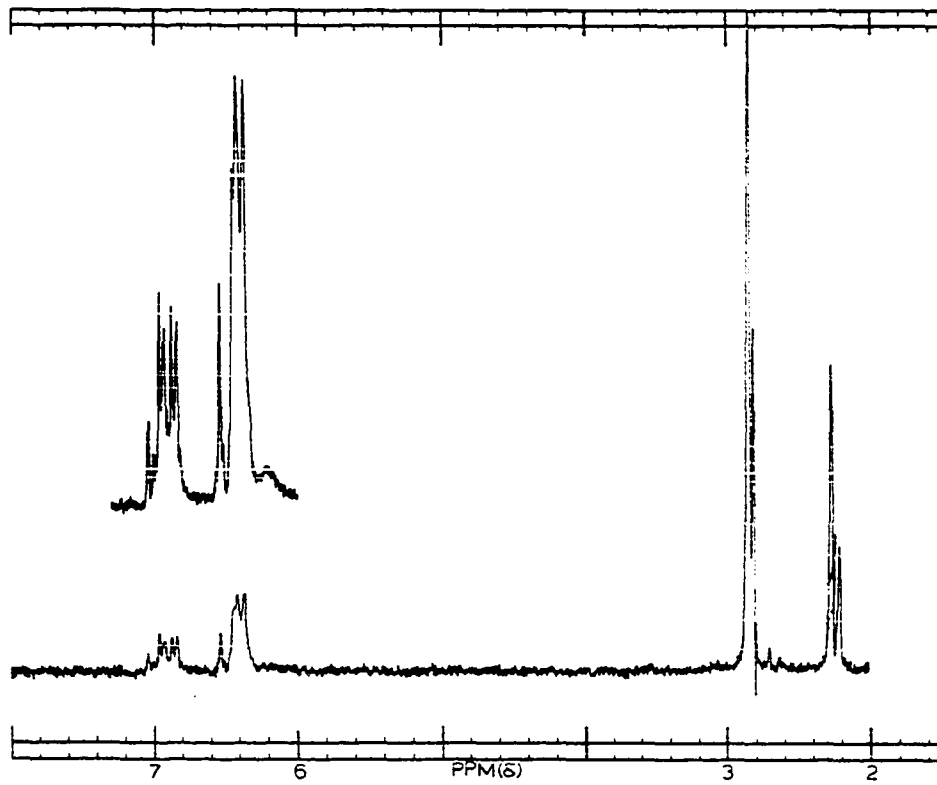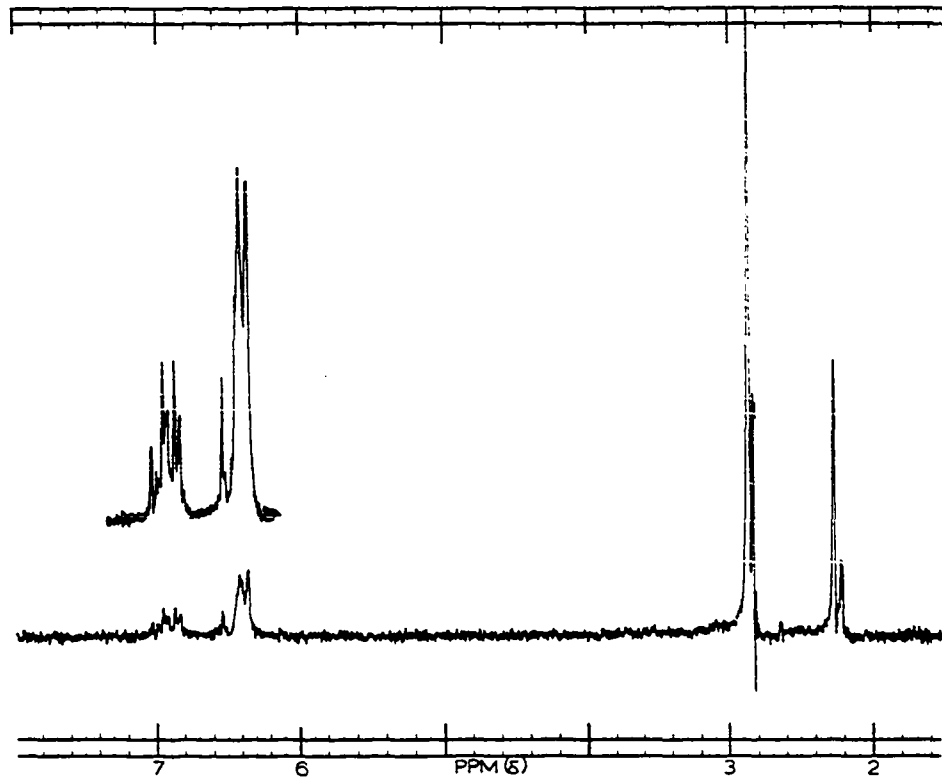
solution stirred at -15° for 10 min. Methyl iodide (1 ml, 10 mmol) was added, the solution stirred at -15° for 10 min and then worked up in the usual manner. Mesitylene (16 mg, .13 mmol) was added as standard. The solution was treated with ceric ammonium nitrate as described in Method A. The resulting solution was analyzed by glpc using a 2 m column packed with 5% diisodecylphthalate and 5% bentone 34 on chromosorb W at 50°. The relative glpc peak integrations for ethylbenzene:p-xylene: m-xylene:o-xylene:mesitylene were 8:93:34:5:60 and 10:106:42: 9:71 for two runs, respectively. From these data, the following yields were obtained: ethylbenzene, 8±0%; p-xylene, 93±2%; m-xylene, 36±1%; and, o-xylene, 6±2%. The yields of products listed are based on the consumption of 0.24 mmol of (toluene)tricarbonylchromium. The yields (omitting p-xylene) are somewhat lower than in similar runs in the absence of initial p-xylene. Assuming that the ratio of m- to p-xylene formed from the (toluene)tricarbonylchromium is the same in both cases, a 19% yield of p-xylene is expected. Thus, unreacted p-xylene was recovered in 74% yield, based on .24 mmol of starting material. Only .22 mmol of p-xylene was used. Correction for this results in an 84±4% recovery of p-xylene. To obtain the deviation, the math was conducted in the manner indicated for each run. In this way, the recovery of p-xylene was 81 and 87% for the two runs, respectively. No products which could be due to the alkylation of p-xylene were observed by glpc.

6. (1-Ethyl-3,5-dimethylbenzene)tricarbonylchromium

(Mesitylene)tricarbonylchromium (199 mg, .78 mmol) was added to 12 ml dry THF. The solution was cooled with stirring under argon to -30°. $\underline{n}$-Butyllithium (1.5 ml 1.6 $\underline{M}$ in hexane, 2.4 mmol) was added and the resulting solution was stirred at -30° for 15 min. Methyl iodide (2 ml, 20 mmol) was added, the resulting solution was stirred for 15 min and then taken up in ether. The ethereal solution was washed thoroughly with aqueous sodium chloride, dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The yellow solid was sublimed at room temperature at 0.1 torr. A yellow solid (158 mg) was obtained in 75% yield. The melting point was 107-110°. Recrystallization yielded crystals of melting point 109-110°. This material was indistinguishable from the product obtained from the sublimation by nmr spectroscopy: nmr (DCCl$_3$;δ) 4.82(s,3), 2.46(q,2 J=7.5 cps), 2.20(s,6), 1.34(t,3 J=7.5 cps); the analysis calculated for C$_{13}$H$_{14}$CrO$_3$: C, 57.78; H, 5.19; observed: C, 57.72; H, 5.08.

7. (1-Butyl-3,5-dimethylbenzene)tricarbonylchromium

(1-Butyl-3,5-dimethylbenzene)tricarbonylchromium was obtained in 71% yield under the conditions described above with the exception that $\underline{n}$-propyl iodide was used as the quenching agent. The physical data are: nmr(DCCl$_3$;δ) 4.90(s,3), 2.30(m,2), 2.20(s,6), 1.52(m,4), 0.96(m,3); mp 80-82°:

analysis calculated for $C_{15}H_{16}CrO_3$: C, 60.40; H, 6.04;
observed: C, 60.28; H, 6.18.

8. Deuterium oxide quench of the reaction of (toluene)tricarbonylchromium with n-butyllithium

In a manner similar to that described for the methylation of (toluene)tricarbonylchromium, 150 mg (.66 mmol) (toluene)-tricarbonylchromium was allowed to react with 2.8 ml 2.2 M n-butyllithium (6.2 mmol) at -15°. After 25 minutes the reaction was quenched by the addition of 5 ml (.28 mol) deuterium oxide. The resulting solution was added to ether-water. The ethereal layer was washed with water, dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The resulting solid was washed with hexane and residual amounts of hexane were removed under reduced pressure. The resulting yellow solid was analyzed by mass spectroscopy. The data are presented in Table 9a. These data are most consistent with a mixture of 3% d_0, 84% d_1 and 13% d_2 species.

Table 9a. Mass spectral data for (toluene)tricarbonylchromium obtained from the deuterium oxide quench of the reaction of (toluene)tricarbonylchromium with n-butyllithium

	m/e	Intensity of natural sample[a]	Intensity of deuterated sample	d_0	d_1	d_2
P-2	126	7.5				
P-1	127	---	8		8	
P	128	100	6	4.3		1.7
P+1	129	27.5	144	1.2	142.8	
P+2	130	8	62		39.3	22.7
P+3	131		20		11.4	6.1

[a]Ionization voltage was 70 eV.

E. The Net Alkylation by Base

1. Butylation of benzenetricarbonylchromium

n-Butyllithium (0.8 ml 1.6M in hexane, 1.3 mmol) was added to a stirred solution of 48 mg (.22 mmol) benzene-tricarbonylchromium in 3 ml THF at 0° under argon. The resulting solution was stirred at 0° for 30 min, added to ether-water and worked up as previously described. No decomplexation procedure was employed. The solution from the aqueous work up was reduced in volume to ca. 3 ml. Mesitylene (13 mg, .11 mmol) was weighed by difference and added as standard. The solution was analyzed by glpc using a 2 m column packed with 10% Lac 446 on chromosorb W at 80°. The same method of yield determination was used as described for the methylation of benzenetricarbonylchromium. The peak areas were corrected for differences in thermal conductivity. As discussed previously, it was assumed that the thermal conductivities of all arenes were proportional to the molecular weight of the arenes. Data from two runs indicate that a 78±3% yield of n-butylbenzene was obtained. The n-butylbenzene was collected by glpc: nmr (DCCl$_3$; δ) 7.18(m,5), 2.60(m,2), 1.7-1.1(m,4), 0.95(m,3). This spectrum was nearly identical to commercial material (94e). The retention time was identical to commercial material.

2. Temperature study

Temperature study of this reaction was conducted as described above except that the temperature was varied. The temperature was maintained by an appropriate bath. The reaction temperature was assumed to be closely approximated by the bath temperature. The conditions of these reactions and the yield of butylbenzene in each case are presented in Table 9b. In all cases but the one presented above, the data are the result of two runs.

Table 9b. The effect of temperature on the yield of n-butyl-benzene from the reaction of benzenetricarbonyl-chromium with n-butyllithium

No.	Temp (°C)	Time (min.)	Yield (%)	Glpc Integrations	
				Run 1 $n\text{-BuC}_6H_5$: $(\overline{CH}_3)_3C_6H_3$	Run 2 $n\text{-BuC}_6H_5$: $(CH_3)_3C_6H_3$
1	-25	85	17±1	9.3:26.0	8.0:20.1
2	-25	30	16±0	15.2:42.1	7.0:19.2
3	-10	30	65±7	10.0:6.4	20.2:15.0
4	0	30	78±3	33.0:19.5	24.0:13.5
5	10	30	73±1	12.6:7.7	12.0:7.4
6	25	30	73±3	22.1:14.0	28.5:17.1
7	-20	30			
and then	0	30	80±1	30.6:17.0	17.6:10.0

3. The reaction of d_6-benzenetricarbonylchromium with n-butyllithium

The reaction of d_6-benzenetricarbonylchromium with n-butyllithium was conducted according to the procedure outlined above. The temperature was maintained at -30° for 20 min and the temperature was then allowed to increase to 15° over the period of 100 min. The work up was as described above and the deuterated butylbenzene was collected by gas chromatography and analyzed by mass spectroscopy: m/e (int) 14 ev: 140(11), 139(100), 138(03), 137(00), 136(00), 135(03), 134(24). Clearly, there are no d_3 or d_2 species. These data are tabulated below (Table 10). These data are most consistent with 79% d_5-, 2% d_4- and 19% d_0-butylbenzene.

Table 10. Mass spectral data for butylbenzene obtained from d_6-benzenetricarbonylchromium

	m/e	Intensity of natural sample	Intensity of deuterated sample	Calculated peaks for					
				d_0	d_1	d_2	d_3	d_4	d_5
P	134	100	18	18					
P+1	135	11	2	2	0				
P+2	136		0		0	0			
P+3	137		0			0	0		
P+4	138		2				0	2	
P+5	139		74					0	74
P+6	140		8						8

4. __Effect of TMEDA on the butylation of benzenetricarbonyl-__
__chromium__

This reaction was performed as described for run 7 of
Table 9. The only exception was that TMEDA was added to the
reaction solution before it was brought to 0°. Thus, the
reaction was conducted as usual at -20° for 30 min, 1 equi-
valent TMEDA relative to initial n-butyllithium was added at
-20°, after stirring for ca. 20 additional min at -20° the
solution was brought to 0° and stirred at 0° for 30 min.
From two runs, the yield of n-butylbenzene was 16±8%.

5. __Attempted reaction of n-butyllithium with phenyllithium__

This reaction was conducted in the manner described for
the butylation of benzenetricarbonylchromium with the
exception that phenyllithium was used in place of benzene-
tricarbonylchromium. Less than 1% of butylbenzene was
indicated by glpc analysis under the conditions previously
described. The data are the result of two runs.

The addition of anhydrous chromium trichloride (1 equi-
valent), hexacarbonylchromium (1 equivalent) or benzene-
tricarbonylchromium (1 equivalent) did not significantly alter
the amount of butylbenzene obtained. The conditions of these
reactions were not greatly varied and these negative results
certainly do not eliminate the possibility of finding
catalytic conditions for this process.

6. Reaction of benzenetricarbonylchromium with t-butyllithium

Reaction of benzenetricarbonylchromium with t-butyllithium was carried out as described for the analogous n-butyllithium reactions. The ethereal solution obtained after the usual work up procedure was analyzed by glpc using a 2 m column packed with 10% Lac 446 on chromosorb W at 80°. n-Butylbenzene was used as the standard; ca. .10 mmol was used per run. The t-butylbenzene was collected and identified on the basis of the nmr spectrum: (CCl₄;δ) 7.15(m,5), 1.30(s,9). This spectrum is nearly identical to that of commercial t-butylbenzene (94f). The data from these runs are presented in Table 11. The data at each temperature are the result of two runs.

Table 11. The effect of temperature on the yield of t-butylbenzene from the reaction of benzene-tricarbonylchromium with t-butyllithium[a]

				Glpc Integrations	
No.	Temp(°C)	Time(min)	Yield(%)	Run 1 t-Bu:n-Bu	Run 2 t-Bu:n-Bu
1	-30	90	36±2	6.5:8.5	7.0:8.5
2	0	30	27±1	12.1:20.1	6.0:10.4
3	25	30	25±3	18:30	6.1:11.7

[a]The concentration of benzenetricarbonylchromium was 0.06 M and of t-butyllithium was 0.42 M.

7. t-Butylbenzene

Benzenetricarbonylchromium (50 mg, 0.23 mmol) was added to 3 ml THF at -30° in an argon atmosphere. To this cold, stirred solution was added 0.8 ml 2M (1.6 mmol) t-butyllithium in pentane. After 30 min at -30°, 200 mg (1.5 mmol) N-chlorosuccinimide was added and the resulting solution was stirred at -30° for 60 min. The solution was worked up in the usual manner. n-Butylbenzene (13 mg, .10 mmol) was added as standard and the resulting solution was analyzed by glpc (Lac 446 at 80°). The data from two runs indicate a yield of 59±1% t-butylbenzene. Characterization of this material was discussed above. (Glpc ratio of n- to t-butylbenzene: 8.8:12 and 8.5:11.3.)

8. m-t-Butylethylbenzene

(Ethylbenzene)tricarbonylchromium (50 mg, 0.21 mmol) was added to 3 ml THF at -40° under argon. t-Butyllithium (0.6 ml 2.0 M in pentane, 1.2 mmol) was added and the resulting solution was stirred for 2 hr at -40°. N-bromosuccinimide (200 mg, 1.1 mmol) was added and the resulting solution allowed to warm to room temperature over the period of 60 min. Mesitylene (13 mg, .11 mmol) was added as standard. The solution was taken up in ether and the ethereal solution was washed successively with .3 N hydrochloric acid, saturated aqueous sodium bicarbonate and three portions saturated aqueous sodium chloride. The work up of this reaction is

accompanied by emulsion formation and the presence of a dark solid which is not soluble in either the ethereal or aqueous solutions. The organic layer is dried over anhydrous magnesium sulfate, filtered and the volume reduced to ca. 5 ml under reduced pressure. This solution was analyzed by glpc (Lac 446, 90°). m-t-Butyl-ethylbenzene was obtained in 58±1% yield (2 runs). Other products include ethylbenzene (12±1%) and p-t-butyl-ethylbenzene (5±1%). The retention time of the alkylated products was identical to that of m- and p-t-butyl-ethylbenzene which had been characterized from the ethylation of (t-butylbenzene)tricarbonylchromium. An nmr of the crude reaction mixture was consistent with this assignment. The glpc integration ratios of ethylbenzene:m-ethyl-t-butyl-benzene:p-ethyl-t-butylbenzene:mesitylene were 3:20:2:13.5 and 3:23:2:15 for the two runs, respectively.

When this reaction was conducted at temperatures above -40° low mass balance was received.

When the reaction was conducted as above but without the addition of NBS, a 36% yield of m-t-butyl-ethylbenzene was received.

9. m-n-Butyl-ethylbenzene

m-n-Butyl-ethylbenzene was obtained from (ethylbenzene)-tricarbonylchromium in 55±1% yield in the manner described above except that n-butyllithium (.6 ml 1.6 M in hexane,

1 mmol) was the base. Other products include p-n-butyl-ethylbenzene (29±6%) and ethylbenzene (4±1%). The alkylated products were collected by glpc. m-n-Butyl-ethylbenzene was characterized from: nmr (CCl₄;δ) 6.9(m,4), 2.55(m,4) and 1.8-.8(m,10); mass spectrum in m/e(int) at 16 ev: 163(18), 162(P,100), 132(10), 120(68), 119(38), 104(14) and 91(14). p-Ethyl-n-butylbenzene was characterized from: nmr (CCl₄,δ) 6.88(m,4), 2.54(m,4), 1.8-.8(m,10); mass spectrum in m/e(int) at 16 ev: 163(14), 162(P,85), 132(8), 120(30), 119(100), 104(11) and 91(11). The nmr spectrum was nearly identical to an nmr published for this material (96). The relative glpc integrations for mesitylene:m-ethyl-n-butylbenzene:p-ethyl-n-butylbenzene were 10:14.2:9 and 12.5:17.5:8.5 for two runs, respectively.

10. n-Butylbenzene

n-Butylbenzene was obtained from (iodobenzene)-tricarbonylchromium in the manner as described for the butylation of benzenetricarbonylchromium. In this reaction, .20 mmol (iodobenzene)tricarbonylchromium and 0.12 mmol mesitylene were used. A 67±3% yield of butylbenzene was obtained. The glpc integrations for butylbenzene:mesitylene were 9.3:7.7 and 10.5:8.2 for the two runs, respectively.

11. Attempted reaction of ethylbenzene with t-butyllithium

This reaction was conducted in the manner described for the formation of m-t butyl-ethylbenzene from (ethylbenzene)

tricarbonylchromium except that ethylbenzene was substituted for (ethylbenzene)tricarbonylchromium. The same standard and glpc conditions were used. Greater than 95% recovery of ethylbenzene was observed.

12. Attempted butylation of (anisole)tricarbonylchromium

Attempted butylation of (anisole)tricarbonylchromium was conducted in a manner similar to that described for the butylation of (ethylbenzene)tricarbonylchromium. (Anisole)-tricarbonylchromium (50 mg, .21 mmol) was added to 3 ml cold, stirred THF at -30° in an argon atmosphere. n-Butyllithium (0.8 ml 1.6 M, 1.3 mmol) was added. After 30 min, 200 mg (1.1 mmol) N-bromosuccinimide was added and the resulting solution was stirred at -30° for 80 min, allowed to come to room temperature and poured into ether-water. The usual work up was employed and the resulting solution was analyzed by glpc (Lac 446 at 90°). No products were observed at longer retention time than anisole. No evidence for formation of any butylated materials was observed. A good recovery of (anisole)tricarbonylchromium was obtained from this reaction.

13. Attempted butylation of (N,N-dimethylaniline)-tricarbonylchromium

Attempted butylation of (N,N-dimethyaniline)-tricarbonylchromium was conducted as described immediately above. After the usual aqueous work up, the solution was

subjected to the decomplexation conditions of Method C. Glpc analysis of the material obtained from this procedure indicated no recognizable products; i.e., a very low mass balance was obtained. The glpc analysis was conducted as indicated for the methylation of this complex. There was no indication of any butylated materials by glpc.

F. The Methyllithium Reaction

1. <u>Reaction of methyllithium with benzenetricarbonylchromium</u>

Benzenetricarbonylchromium (1 g, 4.7 mmol) was dissolved in 50 ml dry THF. The solution was purged with argon and cooled to 0°. Methyllithium (10 ml 2 <u>M</u> in ether, 20 mmol) was added to the stirred solution over <u>ca</u>. 1 min. The solution darkened from a pale clear yellow to an orange after <u>ca</u>. 1 min, and continued to darken to a clear brown solution after 45 min. The solution appeared to be homogeneous at this point. After an additional 15 min (60 min after the addition of methyl-lithium), 2 ml (20 mmol) methyl iodide was added in portions over <u>ca</u>. 2 min. The solution became very dark and no longer appeared clear or homogeneous. The solution was stirred for 40 min over which time the temperature was allowed to slowly increase to 10°. Water was added and the solution was allowed to warm to room temperature. The material was worked up in the standard manner. A yellow-orange solution was obtained. This solution was allowed to stand at room temperature for several days. The resulting solution was filtered and

analyzed by glpc using a 2 m column packed with SE-30 on chromosorb W at 140°. Four fractions were collected.

The first fraction was the second largest fraction and appeared to be more than one component by glpc. The following data were obtained: nmr (DCCl₃;δ) 7.7-7.1(m) and 2.24(m); mass spectrum at 16 ev in m/e (int) 168(15) and 154(33); the ir showed no carbonyl group. These data are consistent with a ca. 2:1 mixture of biphenyl and methylbiphenyl(s). The retention time of this material is also consistent with this assignment.

The second fraction was ca. half as large as the first and clearly contained at least two components. The following data were obtained: mass spectrum at 16 ev in m/e (int) 196(10), 182(85), 180(85). 168(85), 154(52); ir (CCl₄; cm⁻¹) 1720, 1695 and 1680. The products are tentatively assigned as phenylbenzaldehyde and a methyl substituted derivative.

The third fraction was ca. half as large as the second. The following data were obtained: ir (CCl₄; cm⁻¹) 1735, 1700; mass spectrum at 16 ev in m/e(int) 200(06), 198(11), 196(20), 195(05), 182(08), 181(11), 180(08), 168(11), 157(09), 155(09), 154(15). It is tentatively suggested that the major component of this mixture is some isomer of phenyl-acetyl-cyclohexadiene.

The fourth fraction was the major component. The following data were obtained: nmr (DCCl₃;δ) 7.7-7.13(m,9),

2.0(s,3); ir (DCCl₃, cm⁻¹) 1690 and 1685; mass spectrum at 16 ev in m/e(int) 197(17), 196(100), 195(29), 194(13), 182(14), 181(44), 154(14). The nmr of this material was nearly identical to that of o-phenylacetophenone prepared by an independent method (see Figure 5).

The reaction was scaled down to consume 50 mg (.23 mmol) benzenetricarbonylchromium and a limited amount of changes in conditions were investigated. The only methods which allowed any o-phenylacetophenone to be observed by glpc involved decomplexation as described above or by irradiation with 350 nm light in a Rayonet reactor. The best conditions of those examined were as presented above. In one run, 20% o-phenyl-acetophenone and 16% biphenyl and methylbiphenyl(s) were obtained. The reaction mixture was analyzed under the glpc conditions described above. Benzoin (14 mg, .07 mmol) was used as standard and was added after the decomplexation procedure. The other products were obtained in a combined yield of ca. 15% in this reaction.

2. o-Phenylacetophenone

o-Phenylacetophenone was prepared by the method of Tegner (97). o-Phenylbenzoic acid (792 mg, 4 mmol) was dissolved in 15 ml ether which had been freshly distilled over lithium aluminum hydride. Methyllithium (7.5 ml 2.0 M in ether, 15 mmol) was added dropwise to the stirred solution under argon. The solution was stirred for 30 min and then

Figure 5. Nuclear magnetic resonance spectra of
o-phenylacetophenone obtained from the
reaction of methyllithium with benzene-
tricarbonylchromium (top) and with
o-phenylbenzoic acid (bottom)

HCCl₃
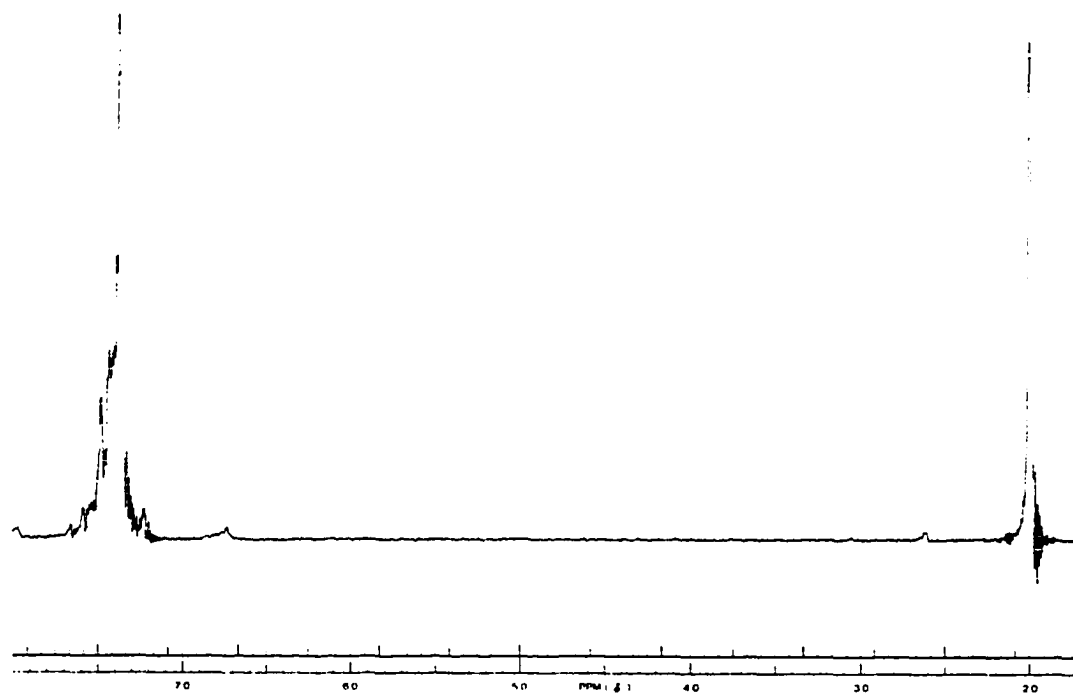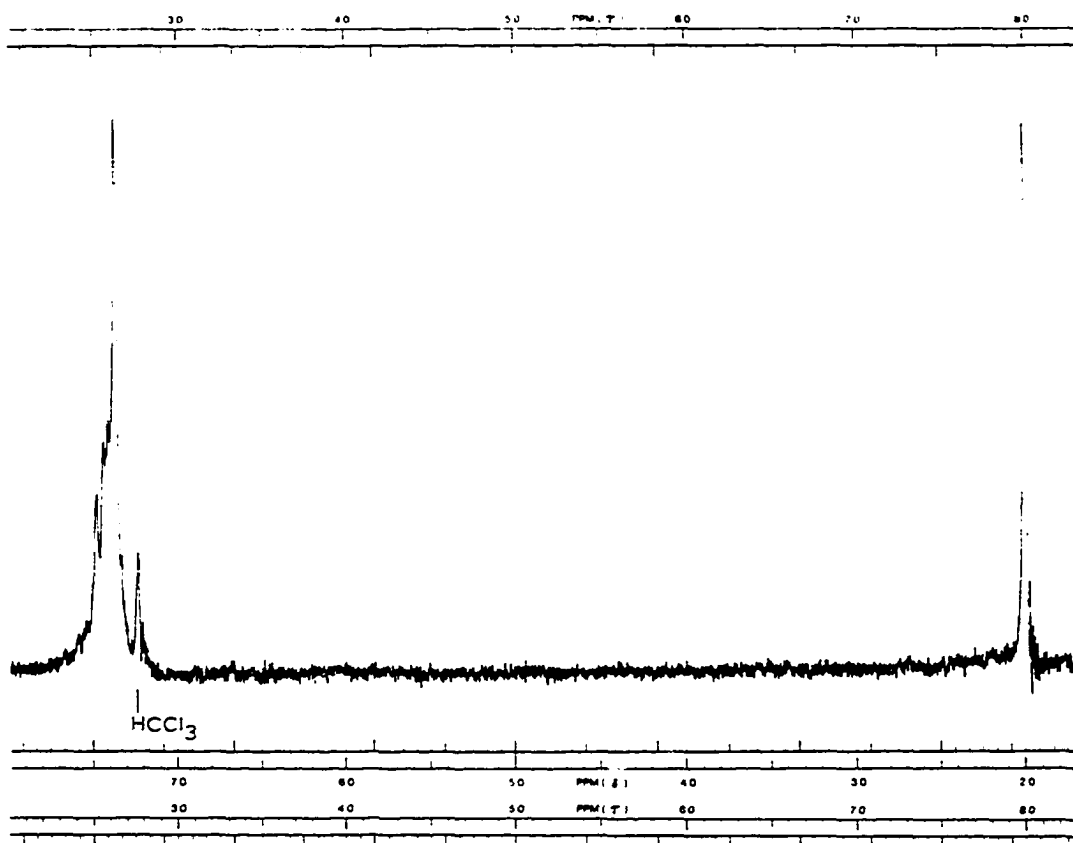
quenched with water. The resulting solution was worked up in the usual manner. The solution was analyzed by glpc (SE-30, 140°). The o-phenylacetophenone was collected: nmr (DCCl$_3$;δ) 7.37(m,9) and 1.98(s,3), lit nmr (CCl$_4$,δ) 7.27(m,9) and 1.87(s,3) (98); ir (DCCl$_3$, cm^{-1}) 1690 and 1685.

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