THE JOURNAL OF Organic Chemistry®

VOLUME 45, NUMBER 13 | JUNE 20, 1980

Arene-Metal Complexes. 12. Reaction of (η^6-Benzene)tricarbonylchromium with *n*-Butyllithium[1]

Roger J. Card and Walter S. Trahanovsky*

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received July 3, 1979

The reaction of (η^6-benzene)tricarbonylchromium with *n*-butyllithium in tetrahydrofuran at −20 °C results in the formation of an intermediate which may be quenched by the addition of methyl iodide or iodine to yield (toluene)tricarbonylchromium or (iodobenzene)tricarbonylchromium in 50 or 26% yield, respectively. The chemistry and the ^{1}H NMR spectrum of this intermediate are consistent with its assignment as (η^6-phenyllithium)tricarbonylchromium. If this intermediate is allowed to warm to 0 °C in the presence of an excess of *n*-butyllithium, *n*-butylbenzene is obtained in 80% yield. Mechanistic details are discussed.

Introduction

The reaction of (benzene)tricarbonylchromium and its derivatives with nucleophiles and bases is of interest for two major reasons. First, a wide range of chemistry is observed in these reactions. Although accurate prediction of the reaction pathway is not yet possible, the reactions appear to be controlled by the nature of the nucleophile or base. For example, Fischer has reported the formation of carbene complexes in low yield from the nucleophilic attack of phenyllithium on the carbonyl ligands of $Cr(C_6H_6)(CO)_3$.[2] Reaction of $Cr(C_6H_6)(CO)_3$ with *n*-butyllithium may be followed by addition of carbon dioxide and then acidification to produce fair yields of $Cr(CO)_3C_6H_5COOH$, presumably through the formation of $Cr(PhLi)(CO)_3$.[3] $Cr(arene)(CO)_3$ complexes appear to be unique in that they undergo selective, thermodynamically controlled α-proton abstraction in the presence of mild base.[4] This is in sharp contrast to the chemistry of simple alkylmetallocenes where only ring proton abstraction is observed.[5,6] The net nucleophilic displacement of ring fluoride and chloride substituents by mild nucleophiles has received considerable study,[7] and a wide range of carbon nucleophiles will add to the benzene nucleus of $Cr(C_6H_6)(CO)_3$ to yield alkylated products under mild conditions.[1b,8]

Second, these latter reactions have potential synthetic utility in that they allow a mild functionalization of the benzene nucleus and often result in a regioselectivity not observed in the reactions of uncomplexed analogues.[1b,8]

The mechanism of formation of these alkylated materials is not fully understood. Semmelhack's work is consistent with initial, reversible addition of mild nucleophiles to the complexed benzene π system;[8] but this work involves the use of relatively mild bases under conditions where ring proton abstraction cannot compete with nucleophilic ad-

---

(1) (a) Part 11: Trahanovsky, W. S.; Hall, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 4850. (b) A preliminary account of this work has appeared: Card, R. J.; Trahanovsky, W. S. *Tetrahedron Lett.* **1973**, 3823. (c) Based on work by R. J. Card in partial fulfillment of the requirements for the Ph.D. degree at I.S.U.

(2) Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407.

(3) (a) Nesmeyanov, A. N.; Kolobova, N. E.; Anisimov, K. N.; Makarov, Yu. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 2665. (b) Rausch, M. D. *Adv. Chem. Ser.* **1944**, *No. 130*, 263. (c) See also: Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *101*, 768. This study appeared after submission of the present paper and is closely related to the work described in our paper.

(4) Trahanovsky, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2897.

(5) Slocum, D. W.; Engelmann, T. R.; Ernst, C.; Jennings, C. A.; Jones, W.; Koonsvitsky, B.; Lewis, J.; Shenkin, P. *J. Chem. Educ.* **1969**, *46*, 144.

(6) Selective α-proton abstraction has been observed in other systems only when an additional anion stabilizing substituent is present on the α carbon. For examples, see: (a) Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1963**, *85*, 2030. (b) Maltz, H.; Kelly, B. A. *J. Chem. Soc.* **1971**, 1390. (c) Marr, G.; Ronayne, J. *J. Organomet. Chem.* **1973**, *47*, 417. (d) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 688.

(7) (a) Brown, D. A.; Raju, J. R. *J. Chem. Soc. A* **1966**, 40. (b) Bunnett, J. F.; Hermann, H. *J. Org. Chem.* **1971**, *36*, 4081. (c) Tchissambou, L.; Jaouen, G.; Debard, R. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1972**, *274*, 806. (d) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7091, 7092.

(8) (a) Semmelhack, M. F.; Hall, H. T.; Yoshifugi, M.; Clark, G. *J. Am. Chem. Soc.* **1975**, *97*, 1247. (b) Semmelhack, M. F.; Hall, H. T.; Yoshifugi, M. *Ibid.* **1976**, *98*, 6387. (c) Semmelhack, M. F.; Clark, G.; Yoshifugi, M., Abstracts, The First Chemical Congress of the North American Continent, Mexico City, 1975. (d) Semmelhack, M. F.; Hall, H. T.; Yoshifugi, M.; Clark, G. *J. Am. Chem. Soc.* **1977**, *99*, 1246. (e) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1976**, *295*, 36. (f) Semmelhack, M. F. In "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed.; Elsevier: Amsterdam, The Netherlands, 1976; pp 361–395. (g) See also: Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. This study appeared after submission of our paper.

0022-3263/80/1945-2555$01.00/0

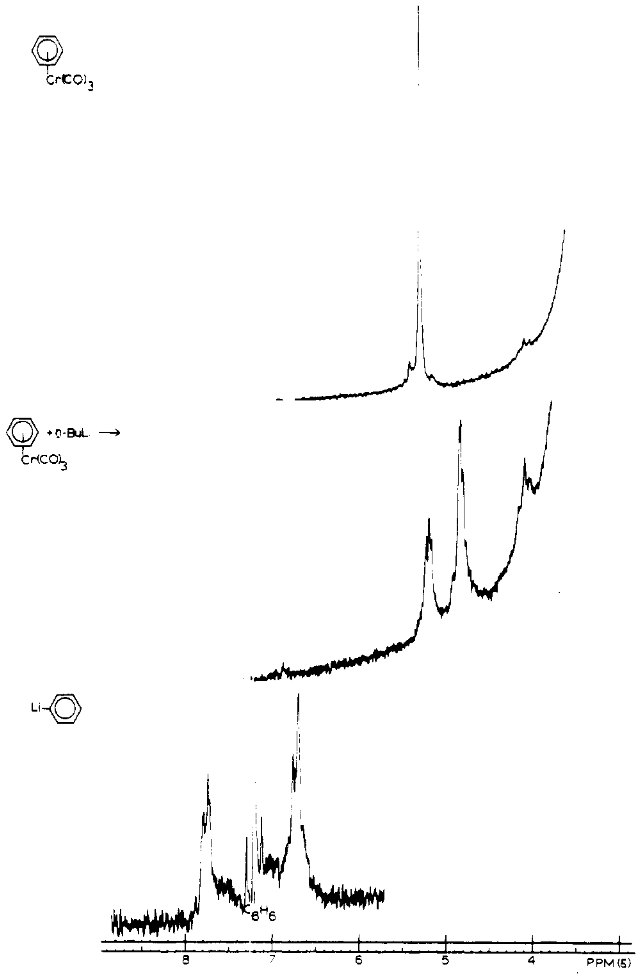
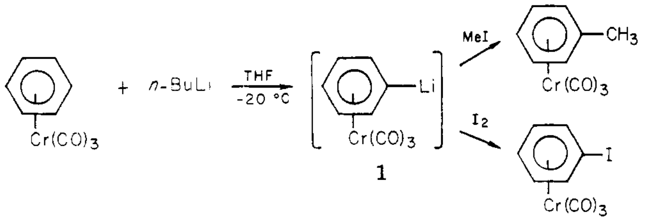


Figure 1. NMR spectra of (benzene)tricarbonylchromium (top), (phenyllithium)tricarbonylchromium (middle), and phenyllithium (bottom) in tetrahydrofuran at -20 °C.

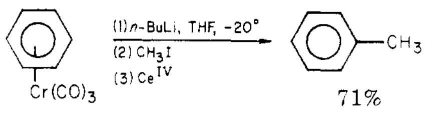
dition. Our work shows that use of more basic reagents results in an entirely different mechanistic pathway than that observed by Semmelhack. We present the results of this work here.

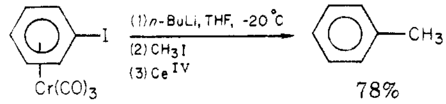
Results and Discussion

The reaction of n-butyllithium with $Cr(C_6H_6)(CO)_3$ is carried out at -20 °C in dry tetrahydrofuran (THF) under argon. This reaction may be quenched by the addition of methyl iodide or iodine to obtain (toluene)- or (iodobenzene)tricarbonylchromium in an isolated yield of 50 or 26%, respectively. The poor yield of (iodobenzene)tricarbonylchromium probably results from competing decomplexation caused by the iodine.[7b]



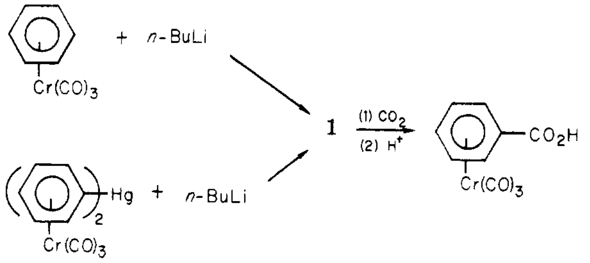
Since some of the (toluene)tricarbonylchromium formed in the sequence above is lost through decomposition during the workup, a more realistic evaluation of the efficiency of this reaction is obtained from GLC analysis of the reaction solution after oxidation by ceric ammonium nitrate. A 71% yield of toluene is obtained in this manner. A similar yield of toluene is obtained from the reaction of (iodobenzene)tricarbonylchromium with n-butyllithium in the sequence below.[9]





The chemistry observed is consistent with initial formation of (phenyllithium)tricarbonylchromium (**1**) in good yield under these conditions. The reactions of alkyl- and aryllithium reagents with methyl iodide or iodine are often used to produce methylated or iodide-containing derivatives.[5,10] The formation of toluene in nearly identical yield from similar sequences starting with either (benzene)tricarbonylchromium or (iodobenzene)tricarbonylchromium is consistent with the formation of a common intermediate. Moreover, the corresponding Grignard reagent can be prepared from (iodobenzene)tricarbonylchromium and magnesium.[11]

(Phenyllithium)tricarbonylchromium has been previously suggested as the common intermediate in the formation of (benzoic acid)tricarbonylchromium from (benzene)tricarbonylchromium[3] and bis[(benzene)tricarbonylchromium]mercury[12] in the sequences below. In



each case (benzoic acid)tricarbonylchromium was isolated in 20 to 60% yield. The substantially higher yield received in the methylation sequence indicates that the low yield of acid is due to inefficiencies in the carbonylation process rather than in the initial formation of (phenyllithium)tricarbonylchromium. Low yields are not atypical in this type of sequence.[5]

The intermediate formed from the reaction of (benzene)tricarbonylchromium with n-butyllithium has been observed by ^1H NMR. A series of three spectra is presented in Figure 1. The top spectrum is of (benzene)tricarbonylchromium in THF at ca. -20 °C. The middle spectrum resulted from the addition of n-butyllithium to the solution from which the top spectrum was obtained. The singlet of (benzene)tricarbonylchromium has been transformed into two multiplets, both upfield from the original signal. It is not known how much of this upfield shift is the result of the solvent change on addition of the hexane solution of butyllithium. The bottom spectrum is of phenyllithium generated from the reaction of n-butyllithium with diphenylmercury under conditions nearly identical with those of the middle spectrum.

---

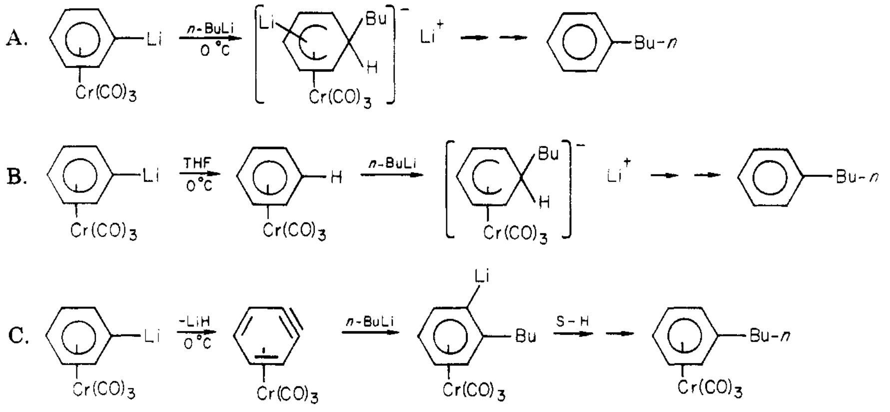
(9) This is reported in the accompanying paper: Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.*, following paper in this issue.

(10) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974; pp 144–158, 196–198.

(11) Moser, G. A.; Rausch, M. D. *Synth. React. Inorg. Met. Org. Chem.* **1974**, *4*, 37.

(12) (a) Rausch, M. D. *Pure Appl. Chem.* **1972**, *30*, 523. (b) Rausch, M. D.; Gloth, R. E. *J. Organomet. Chem.* **1978**, *153*, 59.

Scheme I

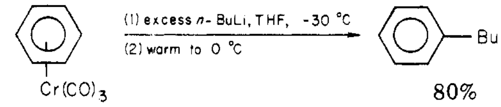


The middle spectrum was the first spectrum observed after mixing, and no further change was observed after an additional 45 min. The fact that the new signal is relatively sharp and well-defined is consistent with rapid, quantitative formation of the intermediate without significant amounts of decomplexation.

The similarity of this spectrum to that of phenyllithium is quite striking. In each case two multiplets are observed in an integral ratio of 2:3 with the downfield multiplet, due to the ortho protons,[13] being the smaller. This spectrum is inconsistent with the formation of significant amounts of a carbene complex, as a singlet would be expected for this type of species.[14] We believe that this spectrum is best interpreted as being due to (phenyllithium)tricarbonylchromium.

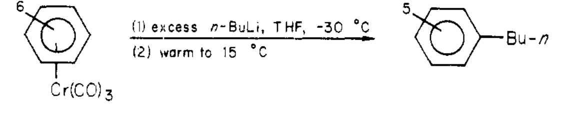
In summary, both the chemistry observed in our laboratory and others and the spectral data are entirely consistent with the rapid, nearly quantitative formation of (phenyllithium)tricarbonylchromium from the reaction of (benzene)tricarbonylchromium with *n*-butyllithium in THF at -20 °C.

When the solution resulting from the reaction of (benzene)tricarbonylchromium and *n*-butyllithium at -20 °C was allowed to warm to 0 °C, *n*-butylbenzene was obtained in 80% yield. A similar yield of *n*-butylbenzene



was obtained from the addition of *n*-butyllithium to a THF solution of (benzene)tricarbonylchromium at 0 °C. Butylbenzene was obtained directly from the reaction; no additional oxidation step was required.[15]

Reaction of (benzene-d_6)tricarbonylchromium with *n*-butyllithium under similar conditions led to the exclusive formation of butylbenzene-d_5. Mass spectroscopic analysis



of this material indicates the presence of less than 2% d_4 and no d_3 or d_2 species.

Table I. Effect of Temperature on the Yield of *n*-Butylbenzene from the Reaction of (Benzene)tricarbonylchromium with *n*-Butyllithium

no.	temp, °C	time, min	yield,[a] %
1	-25	85	17 ± 1
2	-25	30	16 ± 0
3	-10	30	65 ± 7
4	0	30	78 ± 3
5	10	30	73 ± 1
6	25	30	73 ± 3
7	-20	30	
	and then 0	30	80 ± 1

[a] Each yield based on two runs.

The reaction of (benzene)tricarbonylchromium with *n*-butyllithium is temperature dependent. As the reaction temperature is increased from -20 to 0 °C the yield of butylbenzene increases from 16 to 78% (see Table I).

From these data it is apparent that butylbenzene arises from the reaction of the initially formed (phenyllithium)tricarbonylchromium with additional *n*-butyllithium at temperatures above -20 °C. The nearly exclusive formation of butylbenzene-d_5 in the reaction of *n*-butyllithium with (benzene-d_6)tricarbonylchromium is inconsistent with mechanisms involving nucleophilic addition of the butyllithium to the complexed organic π system with concomitant loss of a ring hydrogen atom. Three different examples of this type of process are illustrated in Scheme I. In each case, reaction of (benzene-d_6)tricarbonylchromium would be expected to result in production of substantial amounts of *n*-butylbenzene containing less than 5 deuterium atoms per molecule. In addition, it is not obvious why only uncomplexed butylbenzene would result from any of these processes.

Mechanism B in Scheme I is the closest to that proposed by Semmelhack for the reaction of mild nucleophiles with (benzene)tricarbonylchromium.[8] Consistent with the postulation of a change of mechanism upon the use of stronger base is the observation of different chemistry from the two systems under otherwise nearly identical conditions. The reaction of (benzene)tricarbonylchromium with 2-lithio-2-cyanopropane may be quenched by the addition of methyl iodide to yield (benzene)tricarbonylchromium and 2-methyl-2-cyanopropane as the only products and by the addition of iodine to yield 2-phenyl-2-cyanopropane.[8] In contrast, the reaction of (benzene)tricarbonylchromium with *n*-butyllithium may be quenched by methyl iodide or iodine to yield (toluene)- or (iodobenzene)tricarbonylchromium, respectively. The NMR spectra of the intermediates of the two systems are different.[8b] Thus, there can be little doubt that different mechanisms are involved.

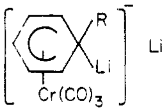
---

[13] Parker, J.; Ladd, J. A. *J. Organomet. Chem.* **1969**, *19*, 1.

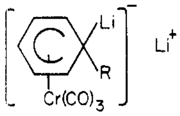
[14] Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799.

[15] Recently it was reported that treatment of (*N*-methylindole)tricarbonylchromium with carbanionic reagents produces substituted arenes directly without the use of an oxidant: Kozikowski, A. P.; Isobe, K. *J. Chem. Soc., Chem. Commun.* **1978**, 1076.

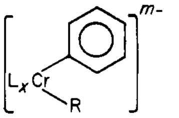
With the assumption that there are no deuterium atom migrations, an assumption which is reasonable, the results of the labeling experiment indicate that formation of *n*-butylbenzene involves the direct conversion of the carbon–lithium bond of (phenyllithium)tricarbonylchromium to the carbon–butyl bond of *n*-butylbenzene. Possible intermediates which would allow such a conversion are **2**, **3**, and **4**. The isomeric intermediates **2** and **3** are variations of the intermediate drawn for mechanism A with the R group being attached to the carbon atom bearing the lithium atom. Conversion of either **2** or **3** to *n*-butylbenzene would require a two-electron oxidation and decomplexation, two processes which cannot be easily rationalized at this time.



2



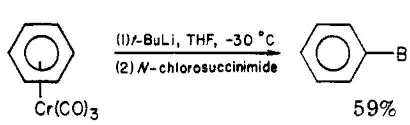
3



4

Production of *n*-butylbenzene from **4**, i.e., some chromium species having a σ-bonded butyl group and a σ-bonded phenyl group, is reasonable since there is ample literature precedence for reductive elimination of two alkyl or aryl groups σ-bonded to a chromium atom.[16-20] However, some species must be reduced to compensate for this overall two-electron oxidation, and the identity of this or these species is not obvious. An additional problem is the formation of **4**. A few examples of transfer of an alkyl group from a metal atom to a π-bonded carbocyclic ligand have been reported,[21] but these reactions involve forcing conditions or low yields, and loss of the metal–ligand π bonding was observed in only one example.[21b] Possibly production of **4** is initiated by formation of a butyl–chromium σ bond with simultaneous release of one of the phenyllithium π bonds. Clearly there are many unanswered questions concerning the exact formulation of **4** and its formation and decomposition. However, a mechanism involving such an intermediate does account for the results of the deuterium labeling experiment and the direct production of uncomplexed *n*-butylbenzene.

Proposal of an intermediate containing a alkyl–chromium σ bond is also consistent with changes in chemistry observed on use of *tert*-butyllithium in place of *n*-butyllithium. The reaction of (benzene)tricarbonylchromium with *tert*-butyllithium at 0 or 25 °C resulted in only an ~25% yield of *tert*-butylbenzene, in sharp contrast to an 80% yield of *n*-butylbenzene received under similar conditions. Homolytic cleavage and β-elimination are much more facile for *tert*-butyl–chromium systems than for *n*-butyl–chromium systems[22,23] and could provide competing reaction pathways for the intermediate. The yield of *tert*-butylbenzene can be more than doubled by conducting the reaction at ≤-30 °C and adding an oxidizing agent. The lower reaction temperature should minimize the competing reactions,[22,23] and the use of an oxidizing agent to initiate reductive elimination from organometallic alkyl σ complexes has been reported by other workers.[24] Of course, an alternative explanation for the difference between *tert*-butylation and *n*-butylation is that the *tert*-butylation proceeds through a different mechanism, such as one involving nucleophilic addition to the complexed ring.



Experimental Section

Most equipment and methods have been described previously.[25] Solvents were distilled over calcium hydride and stored over molecular sieves. Hexacarbonylchromium (Strem Chemicals, Inc.) was stored in a desiccator and occasionally sublimed.

(Benzene)tricarbonylchromium was prepared from benzene and hexacarbonylchromium in glyme and diglyme by the method described previously.[25b] The crude complex was washed with pentane and sublimed to give the pure complex in 50–60% yield: mp 161-163 °C [lit.[26] mp 165.5-166.5 °C]; NMR (CDCl$_3$) δ 5.30 (s).

(Benzene-d_6)tricarbonylchromium was prepared from benzene-d_6 (Columbia Organic Chemicals Co.) in 26% yield by the procedure used to prepare the light compound; mp 161-163 °C. The mass spectral data for this material are presented in Table II.

Methylation of (Benzene)tricarbonylchromium. Cr(CO)$_3$(C$_6$H$_6$) (50 mg, 0.23 mmol) was added to 3 mL of cold tetrahydrofuran in an argon atmosphere at -30 °C (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 of 1.6 M (1.3 mmol) *n*-butyllithium in hexane (Foote Mineral Co.) by syringe. The resulting solution was stirred at -30 °C for 30 min. Methyl iodide (1 mL, 10 mmol) was then added, and after 15 min, 13 mg (0.12 mmol) of ethylbenzene was added by syringe and weighed by difference. The resulting solution was added to 25 mL of ether, washed with three 60-mL portions of aqueous sodium chloride solution, dried (MgSO$_4$), filtered, and concentrated to 3 mL under reduced pressure. This material was added to 2 mL of acetonitrile, and a 0.2 N ceric ammonium nitrate (CAN) solution (1 g of CAN in 2 mL of water and 8 mL of 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 of pentane; the pentane solution was washed with water, dried (MgSO$_4$), and analyzed by GLC (2-m column, 5% Bentone 34, 5% diisodecyl phthalate on Chromosorb W at 65 °C). The relative peak areas were determined by disc integration and corrected for differences in thermoconductivity. The yield for each of two runs was 71%.

(Toluene)tricarbonylchromium was obtained from (benzene)tricarbonylchromium essentially as described above. The reaction was scaled up to use 200 mg (0.91 mmol) of (benzene)tricarbonylchromium and 2 mL of 1.6 M (3.2 mmol) *n*-butyllithium. The reaction was quenched by the addition of 2 mL (20 mmol) of methyl iodide. After the initial aqueous workup the solvent was removed, and the resulting yellow solid was sublimed to give 109 mg (50% yield) of (toluene)tricarbonylchromium: mp 79-81 °C [lit.[26] mp 82.5-83.5 °C]; NMR (DCCl$_3$) δ 5.18 (m, 5) and 2.20 (s, 3).

Iodination of (Benzene)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) of (benzene)tricarbonylchromium in 20 mL of THF under argon at -78 °C. The solution was stirred at -78 °C for 60 min; 500 mg (2 mmol) of iodine was added, and the solution was stirred for 120 min at ca. -70 °C. The solution was taken up in ether, and the ethereal

---

(16) (a) Tsutsui, M. *Ann. N.Y. Acad. Sci.* **1961**, *93*, 135. (b) Morell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.

(17) Tsutsui, M.; Zeiss, H. *J. Am. Chem. Soc.* **1960**, *82*, 6255.

(18) Bennett, G. M.; Turner, E. E. *J. Chem. Soc.* **1914**, 1057.

(19) Herwig, W.; Zeiss, H. H. *J. Am. Chem. Soc.* **1957**, *79*, 6561.

(20) Glocking, F.; Sneeden, R. P. A.; Zeiss, H. *J. Organomet. Chem.* **1964**, *2*, 109.

(21) (a) McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 4096. (b) Yamazaki, H.; Nishido, T.; Matsumoto, Y.; Sumida, S.; Hagihara, N. *J. Organomet. Chem.* **1966**, *6*, 86. (c) Shilova, A. E.; Shilova, A. K.; Kvashina, E. F.; Vorontsova, T. A. *J. Chem. Soc. D* **1971**, 1590.

(22) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1970**, *22*, 713; *26*, 101.

(23) Green, M. L. H. "Organometallic Compounds"; Methuen: London, 1968; Vol. II, Chapter 7.

(24) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1634.

(25) (a) Howell, B. A.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1975**, *97*, 2136. (b) Trahanovsky, W. S.; Hall, R. A. *J. Organomet. Chem.* **1975**, *96*, 71.

(26) Nichols, B.; Whiting, M. C. *J. Chem. Soc.* **1951**, 551.

Table II. Mass Spectral Data for Natural and Deuterated (Benzene)tricarbonylchromium

	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	0.6	0.8						
P	214	100	10.8	10.8						
P + 1	215	25	2.3	2.5	0					
P + 2	216	7	0.5	0.8	0	0				
P + 3	217		0.1		0	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	0.5	83.5
P + 7	221		15.6						0	22.5

[a] Ionization voltage was 70 eV.

Table III. Mass Spectral Data for *n*-Butylbenzene Obtained from (Benzene-d_6)tricarbonylchromium

	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

Table IV. Effect of Temperature on the Yield of *tert*-Butylbenzene from the Reaction of (Benzene)tricarbonylchromium with *tert*-Butyllithium

no.	temp, °C	time, min	yield, %[b]
1	−30	90	36 ± 2
2	0	30	27 ± 1
3	25	30	25 ± 3

[a] The concentration of (benzene)tricarbonylchromium was 0.06 M and of *tert*-butyllithium was 0.42 M. [b] Two runs at each temperature.

solution was washed with aqueous sodium bisulfite, aqueous sodium chloride, water, and then aqueous sodium chloride. The ethereal solution was dried ($MgSO_4$), filtered, and concentrated. The yellow solid was sublimed under vacuum to yield 220 mg (28% yield) of (iodobenzene)tricarbonylchromium (similar runs yielded 23 and 26%): mp 110–111 °C [lit.[27] mp 111 °C]; NMR ($DCCl_3$) δ 5.57 (m, 2), 5.21 (m, 3). An NMR spectrum of the crude reaction mixture indicated the presence of substantial amounts of phenyl iodide.

***n*-Butylation of (Benzene)tricarbonylchromium.** *n*-Butyllithium (0.8 mL, 1.6 M in hexane, 1.3 mmol) was added to a stirred solution of 48 mg (0.22 mmol) of $Cr(CO)_3C_6H_6$ in 3 mL of THF at 0 °C under argon. The resulting solution was stirred at 0 °C for 30 min, added to ether–water, and worked up as previously described. No decomplexation procedure was employed. The solution from the aqueous workup was concentrated to ca. 3 mL. Mesitylene (13 mg, 0.11 mmol) was weighed by difference and added as a standard. The solution was analyzed by GLC (2-m column, 10% Lac 446 on Chromosorb W at 80 °C). Data from two runs indicate that a 78 ± 3% yield of *n*-butylbenzene (retention time identical with that of commercial material) was obtained. The *n*-butylbenzene was collected by GLC; 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 with that of commercial material.[28a]

Temperature study of this reaction was conducted, using the procedure described above except that the temperature was varied. The temperature was maintained by an appropriate bath, and the reaction temperature was assumed to be closely approximated by the bath temperature. The conditions of these reactions and the yields of butylbenzene are presented in Table I.

The reaction of (benzene-d_6)tricarbonylchromium with *n*-butyllithium was conducted according to the procedure outlined above. The temperature was maintained at −30 °C for 20 min, and the temperature was then allowed to increase to 15 °C over the period of 100 min. The workup was as described above, and the deuterated butylbenzene was collected by GLC and analyzed by mass spectroscopy: *m*/*e* (relative intensity, 14 eV) 134 (24), 135 (03), 136 (00), 137 (00), 138 (03), 139 (100), 140 (11). Clearly, there are no d_3 or d_2 species. These data are presented in Table III and are most consistent with 79% d_5, 2% d_4, and 19% d_0 butylbenzene.

***tert*-Butylation of (Benzene)tricarbonylchromium.** Reaction of $Cr(CO)_3C_6H_6$ with *tert*-butyllithium in pentane (Foote Mineral Co.) was carried out as described for the analogous *n*-butyllithium reactions. The ethereal solution obtained after the usual workup procedure was analyzed by GLC (2-m column, 10% Lac 446 on Chromosorb W at 80 °C). *n*-Butylbenzene was used as the standard. The *tert*-butylbenzene was collected and identified on the basis of the NMR spectrum: (CCl_4) δ 7.15 (m, 5), 1.30 (s, 9). This spectrum is nearly identical with that of commercial *tert*-butylbenzene.[28b] The data from these runs are presented in Table IV.

(Benzene)tricarbonylchromium (50 mg, 0.23 mmol) was added to 3 mL of THF at −30 °C in an argon atmosphere. To this cold, stirred solution was added 0.8 mL of 2 M (1.6 mmol) *tert*-butyllithium in pentane. After 30 min at −30 °C, 200 mg (1.5 mmol) of *N*-chlorosuccinimide was added, and the resulting solution was stirred at −30 °C for 60 min. The solution was worked up in the usual manner. *n*-Butylbenzene (13 mg, 0.10 mmol) was added as standard, and the resulting solution was analyzed by GLC (Lac 446 at 80 °C). The data from two runs indicate a 59 ± 1% yield of *tert*-butylbenzene.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research by Grant No. 6605-AC. We also thank Dr. D. J. Kowalski for his very able assistance in obtaining the low-temperature NMR spectra.

Registry No. (Benzene)tricarbonylchromium, 12082-08-5; (benzene-d_6)tricarbonylchromium, 38095-88-4; butyllithium, 109-72-8; (toluene)tricarbonylchromium, 12083-24-8; toluene, 108-88-3; (iodobenzene)tricarbonylchromium, 12082-06-3; butylbenzene, 104-51-8; *tert*-butylbenzene, 98-06-6; (η^6-phenyllithium)tricarbonylchromium, 67421-16-3; butylbenzene-d_5, 20329-91-3; *tert*-butyllithium, 594-19-4.

---

[27] Öfele, K. *Chem. Ber.* **1966**, *99*, 1732.

[28] Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1974: (a) *4*, 2a; (b) *4*, 5B.