

THE FORMATION AND SOME REACTIONS OF (η^6 -PHENYLLITHIUM)TRICARBONYLCHROMIUM *

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Summary

A transmetalation reaction between bis(η^6 -phenyltricarbonylchromium)mercury and n-butyllithium has afforded (η^6 -phenyllithium)tricarbonylchromium in moderate yield. This novel organolithium reagent has been characterized by methanolysis, carbonation, and by reactions with $(\text{CH}_3)_3\text{SiCl}$ and acetyl chloride. Reactions of (η^6 -phenyllithium)tricarbonylchromium with pyridine, $(\text{C}_6\text{H}_5)_2\text{PCl}$, and $\text{C}_6\text{H}_5\text{PCl}_2$ have afforded the corresponding pyridyl- and phosphinobenzene-tricarbonylchromium complexes, respectively. A reaction with PCl_3 produced bis(η^6 -phenyltricarbonylchromium)-n-butylphosphine as the only identifiable product.

Introduction

In contrast to the usual aryllithium compounds ArLi which have played such an important role in the development of organic and organometallic synthesis, lithium derivatives of η^6 -arenetricarbonylchromium complexes of the type $(\eta^6\text{-ArLi})\text{Cr}(\text{CO})_3$ have thus far been limited to one brief communication on the formation of (η^6 -phenyllithium)tricarbonylchromium (III). Complex III was reported to be formed from the reaction of n-butyllithium and $(\eta^6\text{-C}_6\text{H}_6)\text{-Cr}(\text{CO})_3$ (I) in THF at low temperatures: carbonation produced a 19% yield of $(\eta^6\text{-C}_6\text{H}_5\text{COOH})\text{Cr}(\text{CO})_3$ (IV) [2].

It is known, however, from more recent studies that interactions of η^6 -arenetricarbonylchromium complexes with various organolithium reagents can also lead to attack of the latter on carbonyl and η^6 -arene ligands, leading to metal-carbene complexes [3—5] and products of ring alkylation [6—10], respectively. It was therefore of interest to develop an alternate, higher-yield route to III,

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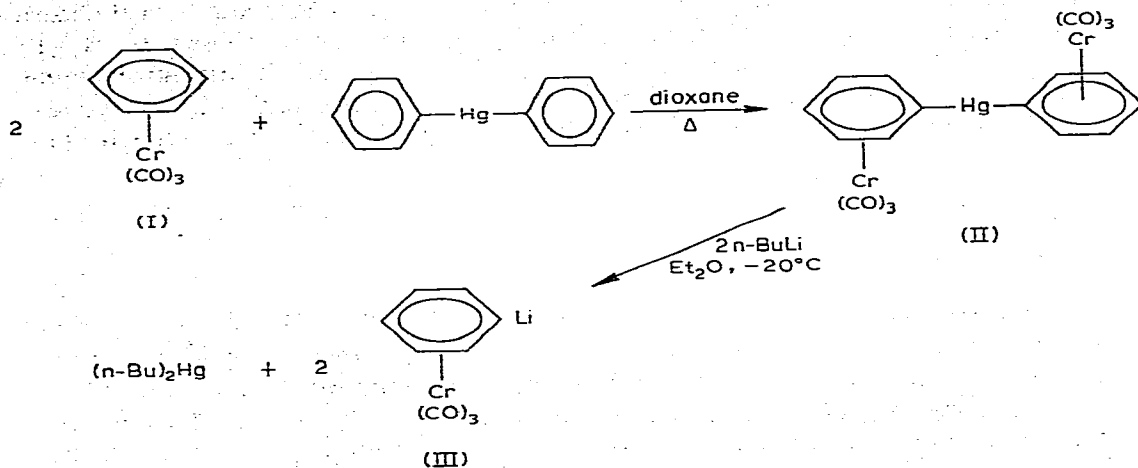
since III and related analogs should prove very valuable to organometallic synthesis, especially in the rapidly expanding area of (η^6 -arene)-transition metal chemistry [11].

One attractive alternative route to III is afforded by the metal-metal exchange (transmetalation) reaction, wherein an arylmercury compound is allowed to react with an alkyllithium derivative. For example, the interactions of either chloromercuriferrocene or diferrocenylmercury and *n*-butyllithium have been shown to produce good yields of ferrocenyllithium by this technique, and side reactions are minimized [12-14].

In this report, we describe a facile preparation of III by transmetalation of bis(η^6 -phenyltricarbonylchromium)mercury (II) with *n*-butyllithium, and some results which illustrate the potential synthetic utility of III*.

Results and discussion

The starting material II was conveniently obtained by a ligand exchange reaction between the readily available η^6 -benzenetricarbonylchromium [16] and diphenylmercury in refluxing dioxane. The mercurial II can be prepared in over 60% yield by this method as an air-stable crystalline solid. Since our original disclosure of II and its reactions [1], II has been independently synthesized in similar yield from a reaction between $\text{Cr}(\text{CO})_6$ and diphenylmercury [17], using a special glass reactor of the type designed by Strohmeier [18]. It should also



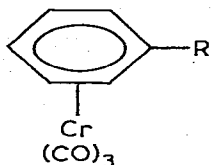
be mentioned that II has subsequently served as a valuable precursor to the formation of stable bis(η^6 -phenyltricarbonylchromium)methylcarbonium ion salts [19].

When an ethereal suspension of II was treated with excess *n*-butyllithium at -20°C, a clear yellow solution of III was produced almost immediately. After methanolysis, I was obtained in 92% yield. The formation of III can also be

* An earlier attempt to produce III by transmetalation of (η^6 -trimethylstannylbenzene)tricarbonylchromium and phenyllithium failed, due probably to attack of the organolithium reagent at a carbonyl group rather than at the carbon-tin bond [15].

carried out using stoichiometric amounts of *n*-butyllithium or at room temperature. However, the yield of I is significantly diminished in each case. As might be expected, solutions of III are extremely sensitive not only to temperature, but also to air and moisture. Although a detailed stability study of III was not undertaken, solutions of it could be kept conveniently for 10–15 min at -20°C without noticeable decompositions.

In order to obtain further evidence for the formation of III, a solution of it was carbonated by the addition of dry ice. Subsequent acidification of the aqueous extract produced (η^6 -benzoic acid)tricarbonylchromium (IV) in ca. 50% yield. A solution of III and chlorotrimethylsilane also readily afforded

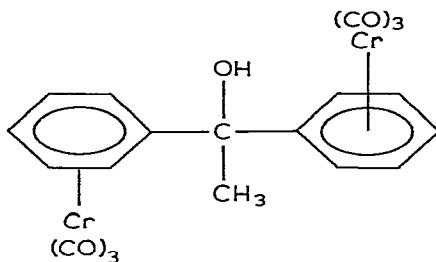


(IV) R = COOH

(V) R = Si(CH₃)₃

(VI) R = C(O)CH₃

(IX) R = P(C₆H₅)₂

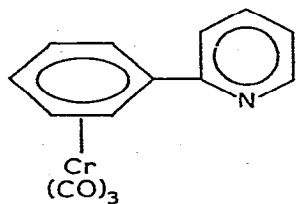


(VII)

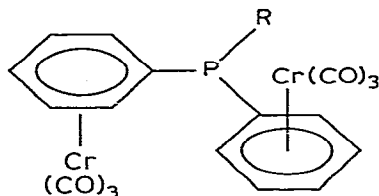
(η^6 -trimethylsilylbenzene)tricarbonylchromium (V) [15] in similar yield.

Addition of a solution of III to an ethereal solution of acetyl chloride produced I, (η^6 -acetophenone)tricarbonylchromium (VI), and bis(η^6 -phenyltricarbonylchromium)methylcarbinol (VII) in yields of 22, 18 and 36%, respectively. The rather large amount of I obtained may indicate that it was formed by proton abstraction of III from VI. The large amount of carbinol VII formed in this reaction is also surprising, since acetyl chloride was always present in large excess.

A reaction between III and pyridine afforded [η^6 -(2-pyridyl)benzene]tricarbonylchromium (VIII). The yield of VIII was low (7%), however, and both I



(VIII)



(X) R = C₆H₅

(XI) R = *n*-C₄H₉

as well as an unidentified by-product were also produced. No attempts were made to maximize the conversion of III to VIII. This reaction may possibly proceed by way of an addition product of III and pyridine, analogous to the formation of 2-phenylpyridine from pyridine and phenyllithium [20].

Several reactions of III with various phosphorus halides were also briefly

investigated, and in each instance phosphinobenzenetricarbonylchromium complexes resulted. Thus, a reaction between III and $(C_6H_5)_2PCl$ produced (η^6 -phenyltricarbonylchromium)diphenylphosphine (IX) in 54% yield, whereas a similar reaction with $C_6H_5PCl_2$ afforded bis(η^6 -phenyltricarbonylchromium)-phenylphosphine (X) in 32% yield. A subsequent attempt to produce tris(η^6 -phenyltricarbonylchromium)phosphine from a reaction between III and PCl_3 produced instead bis(η^6 -phenyltricarbonylchromium)-*n*-butylphosphine (XI) as the only identifiable product, the third P—Cl bond therefore being substituted by the excess *n*-butyllithium present.

The studies described in this paper thus demonstrate that III can be readily prepared by a transmetalation reaction involving II and *n*-butyllithium, and can serve as a useful precursor to a number of substituted arenemetal tricarbonyls which would be extremely difficult to prepare by direct complexation of the tricarbonylchromium moiety to a substituted arene*. Further studies are underway to examine the coordination chemistry of complexes VIII—XI, and to utilize III in the formation of other novel $[(\eta^6-C_6H_5)Cr(CO)_3]$ -substituted complexes.

Experimental

Ethyl ether and hexane were purified by distillation from lithium aluminum hydride. Proton NMR and IR spectra were recorded on Varian A-60 and Beckmann IR-10 spectrometers, respectively. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Melting points were recorded on a Mel-Temp unit and are uncorrected.

Bis(η^6 -phenyltricarbonylchromium)mercury (II)

Into a 500-ml single-necked flask was added 250 ml of deoxygenated dioxane, 6.02 g (17.0 mmol) of diphenylmercury, and 10.9 g (50.9 mmol) of η^6 -benzenetricarbonylchromium (I) [16]. The flask was fitted with a reflux condenser equipped with a 3-way stopcock connected to a mercury overpressure valve, was flushed several times with nitrogen, and heated to reflux under magnetic stirring for 72 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was extracted with acetone, the extracts filtered over a frit, and the filtrate evaporated to dryness. Unreacted starting materials were removed by vacuum sublimation of the residue at $95^\circ/10^{-3}$ mmHg and subsequent extraction with hot benzene. The resulting solid was extracted again with acetone, filtered, and the extracts evaporated to dryness to produce 6.50 g (61%) of II as a yellow crystalline solid. The product is insoluble in ethyl ether, petroleum ether, and methylene chloride; it is soluble in acetone and slightly soluble in boiling benzene. An analytical sample was prepared by a subsequent crystallization from benzene, m.p. $178-179^\circ C$ (dec.). (Found: C, 34.75; H, 1.83; Cr, 16.50; Hg, 32.20; O, 15.37. $C_{18}H_{10}Cr_2HgO_6$ calcd.: C, 34.49; H, 1.61; Cr, 16.59; Hg, 32.00; O, 15.31%). The proton NMR spectrum

* For example, in a recent attempt to prepare IX directly from $Cr(CO)_6$ and triphenylphosphine at elevated temperatures, IX could not be isolated, and a dimeric product of composition $[(C_6H_5)_3PCr(CO)_2]_2$ was formed [21].

in acetone- d_6 exhibited only one broad singlet centered at τ 5.0 ppm, which can be assigned to the η^6 -C₆H₅ protons. The IR spectrum (KBr) contained peaks assignable to carbonyl frequencies at 1970s and 1850s, as well as other absorptions at 1500m, 1450m, 1400m, 1170m, 1150m, 1020m and 810m cm⁻¹. The mass spectrum showed a molecular ion at m/e 626.

Formation of (η^6 -phenyllithium)tricarbonylchromium (III)

Into a flame-dried 250-ml flask equipped with a nitrogen inlet tube was added 80 ml of ethyl ether and 0.80 g (1.28 mmol) of II. The flask was flushed several times with nitrogen, and with rapid stirring, the slurry was cooled to -20°C . n-Butyllithium in hexane (3.0 ml, 6.6 mmol) was added, producing a clear yellow solution which was stirred for 15 min. During this period the solution became slightly cloudy and darkened somewhat.

Methanol (50 ml) was subsequently added slowly and stirring was continued at -20°C for an additional 15 min. The resulting yellow solution was allowed to warm to room temperature, the solvent was evaporated via a water aspirator, and the di-n-butylmercury which had formed removed under high vacuum at room temperature. Sublimation of the residue at 80 – $85^\circ\text{C}/10^{-3}$ mmHg produced 0.50 g (92%) of η^6 -benzenetricarbonylchromium (I), m.p. 160 – 161°C , identified by IR, NMR and mixture melting point comparisons with an authentic sample [16].

When the above reaction was carried out at room temperature, a 61% yield of I was obtained. A similar reaction conducted at -20°C but with a molar ratio of n-butyllithium to II of 3/1 afforded I in 73% yield.

Carbonation of (η^6 -phenyllithium)tricarbonylchromium (III)

A solution of III was prepared under nitrogen in 40 ml of ethyl ether at -20°C from 0.40 g (0.64 mmol) of II and 0.89 ml (1.91 mmol) of n-butyllithium in hexane. After the clear yellow solution had been stirred for 8 min at -20°C , freshly chopped pieces of dry ice were added. The excess dry ice was evaporated as the reaction mixture slowly warmed to room temperature. Evaporation of the solvent yielded a yellow-orange solid which was extracted with 25 ml of 5% aqueous potassium hydroxide. The extract was filtered and 25 ml of 5% hydrochloric acid was slowly added to the filtrate until it was just acidic, at which point orange crystals precipitated. These were filtered and sublimed at $120^\circ\text{C}/10^{-3}$ mmHg to yield 164 mg (50%) of orange (η^6 -benzoic acid)tricarbonylchromium (IV), m.p. 198 – 200°C (lit. [22] 201 – 202°C).

Reaction of (η^6 -phenyllithium)tricarbonylchromium (III) with chlorotrimethylsilane

A solution of III was prepared at -20°C under nitrogen in 80 ml of ethyl ether from 0.8 g (1.27 mmol) of II and 1.77 ml (3.81 mmol) of n-butyllithium in hexane. After stirring for 5 min, a solution of 1.0 ml of (CH₃)₃SiCl in 5 ml of ethyl ether was added and stirring was continued for 30 min at -20°C . The reaction mixture was filtered over a frit containing Celite, the filtrate was evaporated to dryness and the residue was chromatographed on a hexane-packed column of alumina. Elution with hexane/benzene (3/1) afforded two bands. The first band produced 194 mg (53%) of (η^6 -trimethylsilylbenzene)tricar-

bonylchromium (V), m.p. 71–72°C (lit. [15] 72–73°C). The product was further identified by spectral comparisons with an authentic sample. The second band yielded a small amount of I.

Reaction of (η^6 -phenyllithium)tricarbonylchromium (III) with acetyl chloride

A solution of III was prepared under nitrogen at -20°C from 0.8 g (1.27 mmol) of II, 80 ml of ethyl ether and 3.0 ml (6.6 mmol) of n-butyllithium in hexane. After the reaction mixture had been stirred for 5 min, it was added to a stirred mixture of 20 ml acetyl chloride and 20 ml of ethyl ether at -20°C . After an additional 15 min, the reaction mixture was allowed to warm to room temperature, the solvent was evaporated, and the thick orange oil which remained was dissolved in benzene and chromatographed on alumina. Elution with benzene removed a yellow band containing 0.12 g (22%) of I. Elution with a 1/1 mixture of benzene/ethyl ether yielded 0.166 g (18%) of (η^6 -acetophenone)tricarbonylchromium (VI), m.p. 90–91°C (lit. [23] 91–92.5°C) after crystallization from hexane. Further identification was made by mixing melting point and spectral comparisons with authentic VI prepared by the acetylation of I [24,25]. A final elution of the column with acetone produced 0.213 g (36%) of bis(η^6 -phenyltricarbonylchromium)methylcarbinol (VII), m.p. 179°C (dec.). An analytical sample of the same m.p. was prepared by recrystallization of the product from methylene chloride/hexane. (Found: C, 51.00; H, 2.96; Cr, 22.20; O, 23.76. $\text{C}_{20}\text{H}_{14}\text{Cr}_2\text{O}_7$ calcd.: C, 51.08; H, 3.00; Cr, 22.11; O, 23.81%). The proton NMR spectrum (CDCl_3) exhibited bands at τ (ppm) 8.08 (3H, s, CH_3), 7.70 (1H, s, OH), and 4.2–5.0 (10H, m, C_6H_5). The IR spectrum (CHCl_3) contained a weak O–H stretching frequency at 3620 cm^{-1} and strong carbonyl absorptions at 1985 and 1810 cm^{-1} .

[η^6 -(2-Pyridyl)benzene]tricarbonylchromium (VIII)

A clear yellow solution of III was prepared under nitrogen at -20°C in 40 ml of ethyl ether from 0.40 g (0.63 mmol) of II and 0.88 ml (1.90 mmol) of n-butyllithium in hexane and was stirred vigorously for 10 min. Subsequently, 5.0 ml (62 mmol) of pyridine (dried over BaO) was added, and the reaction mixture was stirred for an additional 20 min at -20°C . The resulting cloudy orange solution was allowed to warm to room temperature and stirred for 45 h. Water (100 ml) was slowly added to the orange-brown mixture, which was then stirred for 5 min before being extracted with several portions of ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated. The resulting yellow-orange crystalline residue was dissolved in benzene and chromatographed on alumina. Three bands were eluted with benzene, ethyl ether and acetone, respectively. The first band yielded 19 mg (7%) of I, and the second 23 mg (6%) of VIII, m.p. 120–121°C after recrystallization from hexane. (Found: C, 57.57; H, 3.12; N, 4.91; O, 16.50. $\text{C}_{14}\text{H}_9\text{CrO}_3$ calcd.: C, 57.74; H, 3.12; N, 4.81; O, 16.48%). The IR spectrum (CCl_4) contained two carbonyl absorptions at 1990 and 1920 cm^{-1} . The third band contained trace amounts of a yellow oil which was not further identified, but which exhibited terminal carbonyl bands at 1990 and 1935 cm^{-1} .

(η^6 -Phenyltricarbonylchromium)diphenylphosphine (IX)

A solution of III was prepared in 50 ml of ethyl ether under nitrogen at

−20°C from 0.80 g (1.27 mmol) of II and 1.77 ml (3.81 mmol) of n-butyllithium in hexane. After the solution had been stirred for 8 min, 1.0 ml (5.4 mmol) of chlorodiphenylphosphine in 10 ml of ethyl ether was added slowly. Stirring was continued at −20°C for an additional 30 min before the reaction mixture was warmed to room temperature over a period of 1.5 h. The resulting cloudy yellow solution was filtered under nitrogen over a frit packed with Celite to remove LiCl. Evaporation of the solvent left oily yellow crystals which were recrystallized from methylene chloride/hexane to yield 0.546 g (54%) of IX, m.p. 146–147°C (Found: C, 63.14; H, 4.20; Cr, 13.00; O, 12.05; P, 7.80. $C_{21}H_{15}CrO_3P$ calcd.: C, 63.32; H, 3.80; Cr, 13.06; O, 12.05; P, 7.78%). The proton NMR spectrum ($CDCl_3$) exhibited two multiplets in the ratio of 2/1 at τ 2.62 and 4.82 ppm, assignable to the uncomplexed and complexed phenyl ring protons, respectively. The IR spectrum (Nujol) contained terminal carbonyl bands at 1980 and 1915 cm^{-1} .

Bis(η^6 -phenyltricarboxylchromium)phenylphosphine (X)

A solution of III was prepared in 50 ml of ethyl ether under nitrogen at −20°C from 0.80 g (1.27 mmol) of II and 1.77 ml (3.81 mmol) of n-butyllithium in hexane. After stirring for 8 min, a solution of 1.0 ml (7.4 mmol) of dichlorophenylphosphine in 10 ml of ethyl ether was added. The reaction mixture was stirred for 20 min at −20°C, allowed to warm slowly to room temperature, and filtered under nitrogen over a frit packed with Celite. The solvent was removed via a water aspirator and the resulting yellow oil was left overnight at 10^{-3} mmHg on a vacuum line to remove di-n-butylmercury. A proton NMR spectrum ($CDCl_3$) of the residue indicated multiplets assignable to uncomplexed and complexed phenyl protons between τ 2.1–2.8 and 4.5–5.0 ppm, respectively, but no upfield peaks in the n-butyl region. Recrystallization of the product from benzene/heptane afforded 0.218 g (32%) of X, m.p. 218–220°C (dec.). (Found: C, 54.10; H, 3.07; Cr, 19.40; O, 17.99; P, 5.79. $C_{24}H_{15}Cr_2O_6P$ calcd.: C, 53.94; H, 2.83; Cr, 19.46; O, 17.97; P, 5.80%). The IR spectrum (KBr) contained carbonyl bands at 1900 (broad) and 1980 cm^{-1} .

Reaction of (η^6 -phenyllithium)tricarboxylchromium (III) with phosphorus trichloride

A solution of III was prepared in 40 ml of ethyl ether under nitrogen at −20°C from 0.40 g (0.63 mmol) of II and 0.88 ml (1.90 mmol) of n-butyllithium in hexane. After the yellow solution had been stirred for 8 min, 0.50 ml (5.4 mmol) of PCl_3 in 5 ml of ethyl ether was added. The reaction mixture was stirred at −20°C for an additional 20 min, allowed to warm to room temperature and filtered under nitrogen over a frit packed with Celite. Evaporation of the solvent and crystallization of the product from benzene/heptane afforded 0.224 g (34%) of bis(η^6 -phenyltricarboxylchromium)-n-butylphosphine (XI), m.p. 147–138°C (Found: C, 51.18; H, 3.77; Cr, 20.20; O, 18.70; P, 6.00. $C_{22}H_{19}Cr_2O_6P$ calcd.: C, 51.37; H, 3.72; Cr, 20.22; O, 18.66; P, 6.02%). The proton NMR spectrum ($CDCl_3$) contained the following resonances: τ (ppm) 7.88–8.23, 8.26–8.68, 8.86–9.24 (9H, m, n- C_4H_9), 4.12–4.87 (10H, m, η^6 - C_6H_5). The IR spectrum (CCl_4) exhibited terminal carbonyl bands at 1990 and 1920 cm^{-1} .

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