π-COMPLEXES OF THE TRANSITION METALS
XVII. BENZYLCHROMIUM[1]

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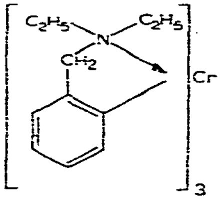
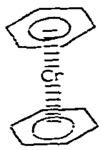
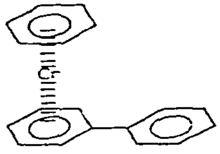
In addition to forming π-complexes with aromatic hydrocarbons, chromium also forms under carefully controlled experimental conditions, σ-bonds to carbon. Examples of the latter type which have been obtained as pure crystalline compounds include $(C_6H_5)_3Cr(THF)_3$ (ref. 2), the anionic complex[3] $Li_3[(C_6H_5)_6Cr]\cdot 2.5Et_2O$** and the "chelate" (I)[4]. There is indirect evidence for the existence of analogous trialkyl- and trinaphthylchromium(III) compounds[5]. The mesitylchromium derivatives are unusual in that blue trimesitylchromium(III) and violet dimesitylchromium(II) exist and are stable toward rearrangement. Whereas these latter substances could not be rearranged to π-complex[6], removal of the solvating molecules from triphenylchromium tristetrahydrofuranate, by washing with diethyl ether etc., results in a profound rearrangement to a black pyrophoric intermediate from which the π-complexes (II) and (III) may be isolated by subsequent hydrolysis. By contrast the hydrolysis of compounds containing σ-chromium to carbon bonds is rapid and quantitative at least for the three examples quoted above. One exception appears to be the benzylchromium salt, $[C_6H_5CH_2Cr(H_2O)_5]^{2+}$ which has only been obtained in aqueous solution, and undergoes slow hydrolysis at room temperature[7].



(I)



(II)



(III)

The present work is concerned with the reactions of chromium(III) chloride as its tetrahydrofuranate, with benzylmagnesium chloride in pure diethyl ether and in tetrahydrofuran–ether mixtures. It was considered unlikely that this reaction would parallel closely the phenyl analog since (i) scission of a σ-benzyl–chromium bond

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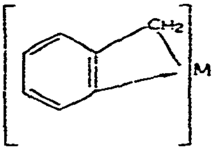
** Our analysis of this compound indicates that it should be formulated as $Li_3[C_6H_5)_6Cr]\cdot 4Et_2O$ (*cf.* EXPERIMENTAL).

would give rise to the more stable benzyl radical and (ii) it might be possible for the benzyl anion to act as a bidentate ligand (IV)*.



(IV)

The addition of an ethereal solution of benzylmagnesium chloride to a suspension of the purple complex, $CrCl_3(THF)_3$ in tetrahydrofuran at —60° causes a rapid reaction giving an intensely colored (yellow-brown) solution containing suspended material. The Gilman color test I becomes positive only after 2.8–3.0 equivalents of benzyl Grignard have been added.

The course of the reaction was first studied using equimolar ratios of reactants and was strikingly influenced by temperature. At room temperature reductive coupling to bibenzyl occurs almost quantitatively (Eqn. 1).

$$2C_6H_5CH_2MgCl + 2CrCl_3 \longrightarrow (C_6H_5CH_2)_2 + 2CrCl_2 \qquad (1)$$

Chromium(II) chloride, which separates from the solution as its tetrahydrofuranate, was characterized as the stable bipyridyl complex, $(bipy)_3Cr(ClO_4)_2$. It seems probable that coupling is preceded by the formation of σ-benzylchromium(III) intermediates which are unstable at room temperature. However, if the mixture resulting from equimolar ratios of the reactants is maintained between —60° and —78° and decomposed with methanol without any intermediate warming, over 90% of the benzyl groups appear as toluene and one half of the chromium(III) chloride tetrahydrofuranate may be recovered unchanged.

These observations may be interpreted if the main, though not exclusive, species present at —78° is one of the benzylchromium(III) chlorides, namely, σ-dibenzylchromium(III) chloride, $(C_6H_5CH_2)_2CrCl$, together with one half of unreacted chromium(III) chloride. Methanolysis at —78° then gives toluene without concurrent reduction of Cr(III) → Cr(II).

$$CrCl_3 + 2C_6H_5CH_2MgCl \longrightarrow (C_6H_5CH_2)_2CrCl \xrightarrow{CH_3OH} 2C_6H_5CH_3 \qquad (2)$$

On warming to room temperature dibenzylchromium chloride interacts with remaining $CrCl_3$ to give monobenzylchromium dichloride, the latter undergoing homolysis to benzyl radicals (and hence bibenzyl) and $CrCl_2$.

$$(C_6H_5CH_2)_2CrCl + Cr^{III}Cl_3 \rightarrow 2C_6H_5CH_2CrCl_2 \rightarrow 2[C_6H_5CH_2^{\bullet} + Cr^{II}Cl_2] \rightarrow (C_6H_5CH_2)_2 + 2CrCl_2 \qquad (3)$$

However, the reaction of two equivalents of benzylmagnesium chloride with one of chromium(III) chloride at —78° resulted in a clear dark orange solution which, on

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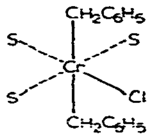
* This concept could account for some of the anomalous reactions of benzyl Grignard reviewed by Kharasch[8].

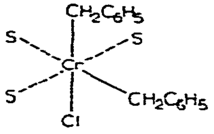
methanolysis without warming, gave toluene almost exclusively and only traces of bibenzyl and unreacted chromium(III) chloride. Similar reactions carried out at room temperature gave on hydrolysis, *hydrogen*, more than half of the benzyl groups as *toluene* and most surprisingly, *2-benzyltoluene* containing traces of bibenzyl. 2-Benzyltoluene was characterized by its infrared and NMR spectra, and by oxidation to 2-benzoylbenzoic acid. Since there is little or no chromium(III) chloride recovered, it can be assumed that these reactions proceed via dibenzylchromium(III) chloride.

$$CrCl_3 + 2C_6H_5CH_2MgCl \rightarrow (C_6H_5CH_2)_2CrCl \rightarrow \text{Intermediates} \rightarrow \text{2-Benzyltoluene} + \text{Toluene} + H_2 \quad (4)$$

There are two possible structures for this compound, (V) and (VI), and the ratio in which they may be formed may be supposed to depend largely upon the reaction temperature and the solvent used. However, it can be anticipated that on hydrolysis both forms will give toluene and that on warming to room temperature some structural changes will occur. Whereas structure (V) may suffer thermal and hydrolytic cleavage to give benzyl radicals and subsequent products, bibenzyl and toluene*, structure (VI) can either undergo similar cleavage of the $C_6H_5CH_2$–Cr bond or rearrange internally to either 2-benzylbenzyl-Cr(H)Cl or 2-benzyltoluene and Cr^ICl. The ultimate "hydrolysis" product of dibenzylchromium(III) chloride can be therefore either bibenzyl and $CrCl_2$, if excess $CrCl_3$ is present (Eqn. 3), or 2-benzyltoluene, hydrogen and toluene (Eqn. 4) depending upon the reaction conditions and the relative concentrations of (V) and (VI).



(V)



(VI)

Attempts were made to obtain crystalline dibenzylchromium chloride, but the intensely dark orange solutions gave only oily deposits from a variety of mixed solvents. Triphenylphosphine, tributylphosphine and 2,2'-bipyridyl failed to produce crystalline complexes.

Reaction between three equivalents of benzylmagnesium chloride and chromium (III) chloride tristetrahydrofuranate yielded final products which were dependent not only on temperature but more strikingly upon whether pure diethyl ether or a mixture of diethyl ether and tetrahydrofuran was used as solvent. In diethyl ether, toluene, 2-benzyltoluene, hydrogen, a small amount of *trans*-stilbene and a yellow π-complex were consistently and reproducibly formed. The latter, isolated as the highly stable tetraphenylboron salt, $C_{45}H_{42}BCr$, m.p. 189–190°, was demonstrated to be π-(2-benzyltoluene)-π-toluene-chromium(I) by physical methods, chemical reduction and thermal decomposition**. There are two structures, (VII) and (VIII), possible for this

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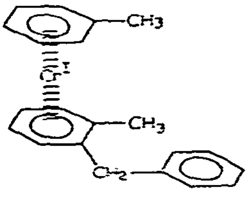
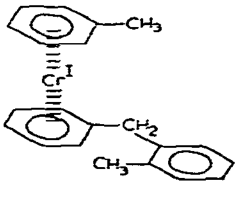
* It is known that the thermal decomposition of dibenzyltin gives bibenzyl[9], and more recently it has been shown that tribenzylgermane gives bibenzyl and much toluene[10].

** During the progress of our work an abstract appeared[11] stating that an apparently similar reaction had given bibenzyl, *trans*-stilbene and a π-bibenzyl-π-toluene-chromium complex. In the absence of experimental details no comment can be made about this result.

complex. Assuming free rotation about the methylene group in 2-benzyltoluene, only compound (VII) should be resolvable into optically active forms. However, at present we are unable to differentiate between (VII) and (VIII); but it can be said that the π-complex is homogeneous. The explosive perchlorate of π-(2-benzyltoluene)-π-toluene-chromium(I) has also been prepared. However, attempts to obtain the corresponding chromium(0)-π-complex directly from the reaction mixture were fruitless.



(VII)



(VIII)

In ether–tetrahydrofuran mixtures the results were erratic, the products being either toluene, bibenzyl and no bis-arene-chromium(I) complex, or, toluene, 2-benzyltoluene, traces of bibenzyl and a small amount of the yellow π-complex already described. The reaction products depend critically on the ratio of diethyl ether to tetrahydrofuran.

In the absence of isolable intermediates any mechanistic proposal is speculative. However, the present observations can be rationalized in a reaction sequence which is based upon known facts concerning σ-bonded arylchromium compounds. Reference has already been made to the profound structural changes engendered by the displacement or removal of tetrahydrofuran (*e.g.* by diethyl ether) from triphenylchromium(III) tristetrahydrofuranate[2]; and there is indirect evidence that the displacement or removal of this solvent from solvated σ-triallylchromium occasions a change to a volatile σ-π-triallylchromium complex[13]*. For these reasons the initial step of the reaction between benzylmagnesium chloride and chromium(III) chloride tristetrahydrofuranate at —78° is considered to be the formation of *trans*-tribenzylchromium(III) solvated by tetrahydrofuran (IX). In solutions of pure diethyl ether this tetrahydrofuran is readily lost, and the σ-tribenzylchromium(III) becomes *trans*-σ-π-tribenzylchromium (X). In the latter, two of the benzyl groups are suitably situated for *ortho*-coupling—there is ample evidence supporting the role of chromium in promoting this type of synthesis[12]—to (2-benzylbenzyl)-benzyl-chromium hydride (XII) or by a 1,3-hydrogen shift (promoted by the chromium center) to π-(2-benzyltoluene)-σ-benzyl-chromium(I) complex (XIII). Hydrolysis of (XII) or (XIII) accounts for the observed products, hydrogen**, toluene and 2-benzyltoluene, and seem to be favorable structures leading to π-complex. The transitory existence of both of these intermediates and/or others cannot be precluded at this time. In any case *hydrogen transfer* processes such as have been observed here and in previous work with organometallic complexes[12] are believed to be of sufficient significance to warrant

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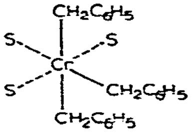
* It is known that the allyl anion can act as a bidentate ligand[14], that is, by forming a σ-π-bond.

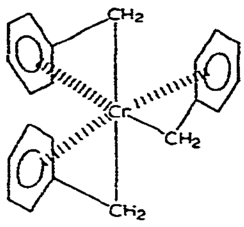
** The volume of hydrogen evolved is in excess of that which could be liberated by hydrolysis of (XII) or (XIII); hence some of the gas must arise from the reduction of water by Cr^{I} or Cr^{II}.

detailed examination. Deuterolytic studies are in progress for this purpose and will be reported in due course.

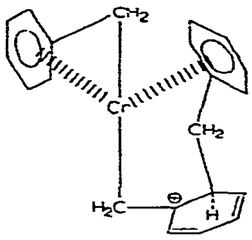
It is evident that the course of the reaction of benzylmagnesium chloride with chromium(III) chloride tristetrahydrofuranate and its products are highly sensitive to (i) the stoichiometry, (ii) the mode of addition of the reactants, (iii) the temperature and (iv) the solvent or solvent mixture. The influence of these factors has been demonstrated separately in earlier work[12], but here for the first time their effects are seen in one system of reagents.



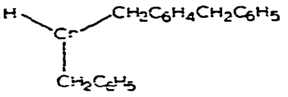
(IX)



(X)

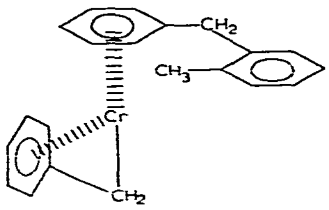


(XI)



$$H-Cr(CH_2C_6H_5)-CH_2C_6H_4CH_2C_6H_5$$

(XII)



(XIII)

EXPERIMENTAL

All operations were carried out under pure dry nitrogen. Diethyl ether and tetrahydrofuran were freshly distilled from lithium aluminum hydride. Vapor phase chromatographic analyses were made in a Beckman G-C-2 apparatus. Toluene product was determined using a 6 ft. silicone 550/firebrick column.

Analysis of Grignard solution

An aliquot of the ethereal solution of benzylmagnesium chloride used (50 ml, 53.25 mmoles) was hydrolyzed at 0° and the ether layer separated and dried over sodium sulfate. The product toluene (44.2 mmoles) was estimated by vapor phase chromatography, isolated by fractional distillation, and purified by vapor phase chromatography. The residue from the distillation was chromatographed on silica gel to give bibenzyl (0.1 g) m.p. and mixed m.p. 52–53°, and an unidentified oil (0.1 g).

Ratio of 1:1 of chromium(III) chloride and benzylmagnesium chloride

(*a*) *Isolation of bibenzyl and chromium(II) chloride.* Ethereal benzylmagnesium chloride (10 ml, 11.3 mmoles) was added slowly to a stirred suspension of the purple complex, $CrCl_3(THF)_3$ (ref. 15) (4.23 g, 11.3 mmoles) in tetrahydrofuran (30 ml) at

—60°. The resulting dark orange-brown mixture, containing much suspended material (negative Gilman color test I), was kept at room temperature for 3 h and then filtered. After washing with ether the white solid, chromium(II) chloride tetrahydrofuranate, was dissolved in air-free water and treated with an excess of bipyridyl in methanol and dilute (5 %) perchloric acid. The black complex $[(bipy)_3Cr](ClO_4)_2$ crystallized from the violet solution and excess bipyridyl was separated by sublimation *in vacuo* at 50°. An X-ray powder photograph of this material was identical with an authentic specimen.

The orange-brown filtrate from the separation of chromium(II) chloride was hydrolyzed with air-free sulphuric acid (5 %). Bibenzyl (1.00 g, 97 %), m.p. 50–52°, was isolated from the colorless organic extract.

(*b*) *Isolation of toluene and unreacted $CrCl_3(THF)_3$*. The reaction mixture as in (*a*) was maintained at —78° either for 1 or 24 h (negative Gilman I) and methanolyzed using an air-free tetrahydrofuran–methanol mixture at —78°. The deep yellow-brown color was slowly discharged with the reappearance of the purple $CrCl_3(THF)_3$ complex (2.06 g). Toluene (10.0 mmoles) was isolated as described above together with a strong smelling green oil (0.1 g) containing bibenzyl. Addition of sodium tetraphenylboron to the aqueous solution gave no π-complex.

Ratio of 1:2 of chromium(III) chloride and benzylmagnesium chloride

(*a*) *With intermediate reduction to chromium(II)*. Benzylmagnesium chloride (11.3 mmoles) was added to the complex, $CrCl_3(THF)_3$ (4.23 g, 11.3 mmoles) in tetrahydrofuran (500 ml) at room temperature. Reduction to $CrCl_2$ occurred and after 30 min the mixture was cooled to —78° and a further equivalent of benzylmagnesium chloride added. After warming to room temperature the clear deep orange-brown solution was hydrolyzed with air-free water. The aqueous layer contained chromium(II) and after exposure to air, did not give any π-complex with sodium tetraphenylboron. (Hydrolysis using an aqueous solution of the latter salt likewise did not yield any π-complex.) The organic layer gave toluene (12 mmoles) and bibenzyl containing a small proportion of 2-benzyltoluene (combined yield 5 mmoles). Crystallization from methanol gave pure bibenzyl (3.25 mmoles), m.p. 52.5°.

(*b*) *At —78°*. A similar reaction to (*a*) in which $CrCl_3(THF)_3$ (13 mmoles) and two equivalents (25.9 mmoles), of benzylmagnesium chloride were used at —78° for 4 h, gave a clear dark orange-brown solution. In duplicate experiments methanolysis without allowing the solution to warm (Gilman test I negative) gave toluene (24.65, 23.9 mmoles). A trace of bibenzyl was detected in each of two experiments and a small proportion (5 %) of the complex $CrCl_2(THF)_3$ remained unreacted. No π-complex was formed.

(*c*) *At 20°*. Two equivalents of benzylmagnesium chloride (25.9 mmoles) were stirred at room temperature with the complex, $CrCl_3(THF)_3$ (4.85 g) for 4 h. Treatment with methanol (2 ml) gave hydrogen (16 ml, STP, 0.725 mmole). Work up in the normal way gave toluene (17.7 mmoles) and 2-benzyltoluene (0.65 g, 3.6 mmoles) containing traces of bibenzyl. No π-complex was formed. 2-Benzyltoluene was characterized by oxidation with alkaline potassium permanganate in aqueous–acetone solution to 2-benzoylbenzoic acid, m.p. and mixed m.p. 128–129°. Its NMR spectra at 60 Mc/sec showed $\tau(CH_2) = 6.11$ [bibenzyl has $\tau(CH_2) = 7.1$].

Ratio of 1:3 of chromium(III) chloride and benzylmagnesium chloride in diethyl ether

(*a*) *At 20°*. Ethereal benzylmagnesium chloride (50 ml, 53.2 mmoles) was added to a suspension of chromium trichloride tristetrahydrofuranate (5.55 g, 14.8 mmoles) in diethyl ether (50 ml) at —78°. After four hours at room temperature (Gilman test negative) the dark heterogeneous mixture was hydrolyzed with water (50 ml) in the presence of air, filtered, the residue being washed with hot acetone until the filtrate was colorless.

The organic layer contained toluene (34.2 mmoles) and a yellow oil (1.2 g). The latter on chromatography on silica gel gave an oil (0.6 g) which on vapor phase chromatography furnished pure 2-benzyltoluene (identified by a direct comparison), *trans*-stilbene (0.1 g), m.p. 117–120° (undepressed with an authentic specimen) and an unidentified yellow oil (0.1 g).

The acetone extract was concentrated by distillation under reduced pressure, and the residue combined with the aqueous phase. This clear solution was treated with excess sodium tetraphenylboron (7.6 g in 50 ml of water) thereby giving π-(2-benzyltoluene)-π-toluene-chromium(I) tetraphenylboron (0.995 g): yellow triclinic crystals from acetone, m.p. 189–190° (see below).

(*b*) *With intermediate reduction to chromium(II)*. In a similar experiment in which a total of 4.8 equivalents (41.1 mmoles) of Grignard reagent was added, removal of solvents after hydrolysis, left an oil (1.3 g) from which was isolated by micro-cup distillation (bath temp., 65–70°/0.02 mm) bibenzyl, 2-benzyltoluene and, in small yield, a dibenzyltoluene, m.p. 86–88°. (Found: C, 92.4; H, 7.5; Mol.wt. micro Rast, 261. $C_{21}H_{20}$ calcd.: C, 92.6; H, 7.4%; Mol.wt., 272.) An unidentified higher boiling oil (bath temp., 130–140°/0.03 mm) was also formed. The π-complex (0.7 g) was isolated also.

Examination for σ-benzylchromium cations and the isolation of the π-complex perchlorate

Benzylmagnesium chloride (11.3 mmoles) was added to a suspension of $CrCl_3(THF)_3$ (3.87 g, 10.3 mmoles) in ether (50 ml) at —78° and then warmed to room temperature for 30 min when a further 2.2 equivalents of the Grignard solution were added. After 30 min the mixture was cooled to —20° and hydrolyzed by the slow addition of 100 ml of air-free, aqueous perchloric acid (10%). Both the ether and aqueous layers were orange-brown with the yellow insoluble π-complex, [(2-benzyltoluene)(toluene)-Cr]ClO_4, at the interface. On exposure to air at 0° the color faded in the ether layer and the aqueous solution turned green. Filtration gave the yellow π-complex (0.3 g) which was explosive when dry and decomposed on standing in air overnight. The aqueous solution was rapidly and repeatedly extracted at 0° with ether to free it from soluble organic material. Portions of the final deep green aqueous solution gave no evidence of benzylchromium(III) species such as $[C_6H_5CH_2Cr(H_2O)_5]^{2+}$ since heating in air gave no benzaldehyde and heating in the absence of air gave no bibenzyl[7].

Isolation of π-(2-benzyltoluene)-π-toluene-chromium(I) tetraphenylboron

An experiment was carried out exactly as described above up to the hydrolysis stage when, in place of perchloric acid, a solution of sodium tetraphenylboron (8 g) in water (50 ml) was used. Filtration in air gave a mixture of π-complex and pale green chromium salts from which the π-complex was separated by extraction with hot acetone. Recrystallization from aqueous acetone gave 0.9 g of the yellow triclinic crystals of π-(2-benzyltoluene)-π-toluene-chromium(I) tetraphenylboron, m.p. 190° (dec.). (Found: C, 83.4; H, 6.8; B, 1.4; Cr, 8.2. $C_{45}H_{42}BCr$ calcd.: C, 83.7; H, 6.6; B, 1.7; Cr, 8.1%): λ_{max}/log ε, 342.1 mμ/3.8 and 211.5 mμ/4.8 in ethanol–acetone.

The complex was unaffected by boiling with 1 *M* sodium hydroxide or 1 *M* hydrochloric acid for 7 h and was stable to ultraviolet light both as solid and in acetone solution. Its magnetic moment measured in acetone solution was 1.72 Bohr magnetons.

Crystals of the π-complex are triclinic and probably of space group $P\bar{1}$, since the intensities exhibit the characteristics of a centro-symmetric crystal. Cell dimensions are $a = 10.40$ Å, $b = 11.19$ Å, $c = 15.88$ Å, $\alpha = 96.590°$, $\beta = 94.248°$ and $\gamma = 110.947°$, and its density = 1.243 g/ml. Assuming that in the cell there are two molecules which are related to one another by a center of symmetry, its molecular weight is calculated to be 637 (theory, 644)*.

The yield of π-complex was not increased by using a larger excess of the Grignard reagent (5:1 ratio) or by boiling the mixture prior to hydrolysis. It was also independent of the presence of sodium tetraphenylboron either during the hydrolysis or when added subsequently.

Decomposition of the π-complex with lithium aluminum hydride

The π-complex (0.5 g) in ether (1000 ml) was stirred at room temperature in a nitrogen atmosphere for 3 days with lithium aluminum hydride (3 g). Hydrolysis and normal work up gave back 0.26 g of unreacted π-complex. Toluene and an oil (0.2 g) containing 2-benzyltoluene were detected by vapor phase chromatography.

Pyrolysis of the π-complex

The π-complex (0.25 g) was heated at 10^{-3} mm, volatile products being collected in a cold trap. At 183° the color changed from orange to dark-brown and at 190° extensive decomposition occurred as the complex melted. Toluene and benzene were isolated from the cold trap. A yellow-green oil and some crystalline material which condensed just above the heated surface was shown by vapor phase chromatography to contain at least 10 components, all more volatile than bibenzyl. A colorless oil which condensed well above the heated surface was similarly shown to contain only 2-benzyltoluene by infrared and NMR characterization. The residue from the pyrolysis was red-brown. On exposure to air it fumed, became quite hot and turned black.

Ratio of 1:3 of chromium(III) chloride and benzylmagnesium chloride in diethyl ether–tetrahydrofuran mixtures

(*a*) *With intermediate reduction to chromium(II).* The complex, $CrCl_3(THF)_3$ (4.85 g, 13.0 mmoles) in *tetrahydrofuran suspension* (50 ml) was treated at —78° with ethereal benzylmagnesium chloride (10 ml, 13.0 mmoles). After one and three-quarter hours at room temperature the dark-brown mixture was recooled to —78° and benzylmagnesium chloride (20 ml, 26.0 mmoles) added. Methanolysis after 16 h at room temperature, was carried out with a methanol–tetrahydrofuran mixture. Filtration

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* The crystallographic data was obtained by Dr. J. J. DALY of these laboratories to whom we express best thanks.

after exposure to air gave all the chromium as a green solid. Toluene (25.4 mmoles) and crude bibenzyl (5.5 mmoles) were isolated as previously described. No π-complex was formed under these conditions. Refluxing the mixture for two and one half hours before hydrolysis gave only 40 mg of π-complex and a black amorphous solid, insoluble in dilute acetic acid.

(*b*) *At 20°*. Ethereal benzylmagnesium chloride (50 ml, 38.9 mmoles) was added to $CrCl_3(THF)_3$ (13 mmoles) and tetrahydrofuran (30 ml) at —78°. After 4 h at room temperature the dark orange-brown solution containing much dark suspended material was hydrolyzed with air-free aqueous tetrahydrofuran giving hydrogen (~ 7 mmole; characterized by combustion). The solution was filtered and the solid washed well with ether and acetone. Extraction with hexane removed a pale yellow oil (1.15 g) which was mainly 2-benzyltoluene containing a small amount of bibenzyl and tarry material. Addition of sodium tetraphenylboron to the yellow aqueous solution gave π-(2-benzyltoluene)-π-toluene-chromium(I) tetraphenylboron (0.4 g).

A similar experiment using benzylmagnesium chloride (33.9 mmoles) gave toluene (24.8 mmoles) and 2-benzyltoluene (0.7 g, 3.85 mmoles).

(*c*) *At —78°*. A similar reaction using benzylmagnesium chloride (42 mmoles) held at —78° for 18 h and then hydrolyzed with wet methanol without any intermediate warming, gave toluene (39.7 mmoles, 95 %) and impure 2-benzyltoluene (0.65 mmole). By contrast, if the reaction mixture was maintained at —60° for the same period, toluene (26.4 mmoles) and impure 2-benzyltoluene (5.8 mmoles) were isolated.

Trilithiohexaphenylchromium(III) etherate

This complex, prepared according to Hein and Herzog[16] formed orange-yellow crystals which were pumped at 10^{-3} mm for 2 h. The resulting compound, density 1.18 (0.1990 g) was hydrolyzed with a large excess of water in a vacuum apparatus, and the resulting ether–benzene–water mixture separated by repeated fractional condensation through a series of traps at —30, —65, —78 and —196°. Ether, vapor pressure of 183 mm at 0° (0.0694 g) was collected in the trap at —196°. Benzene, vapor pressure of 27 mm at 0° (0.1110 g) which collected in the traps at —65 and —78°, was further purified by condensation on lithium aluminum hydride. Both the ether and benzene obtained in this way were pure by vapor phase chromatographic analysis. [$Li_3Cr(C_6H_5)_6$]$\cdot 4(C_2H_5)_2O$ requires: C_6H_6, 56.3 %; $(C_2H_5)_2O$, 35.6 %. Found: C_6H_6, 55.7 %; $(C_2H_5)_2O$, 34.9 %]. This compound should have a molecular weight of 832.22. Based on this value the X-ray density is 1.200* which is in good agreement with the value of 1.18 obtained by the flotation method.

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SUMMARY

The reactions and reacting ratios of benzylmagnesium chloride and chromium(III) chloride have been examined in detail. The appearance or absence of the overall

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products after hydrolysis namely, hydrogen, bibenzyl, toluene, 2-benzyltoluene, π-(2-benzyltoluene)-π-toluene-chromium(I) and *trans*-stilbene depends critically on stoichiometry, temperature, mode of addition and solvent. Hydrogen transfer processes within organochromium complexes are uniquely involved in coordinative synthesis.

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