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WATER SOLUBLE σ-BONDED ORGANOCHROMIUM COMPOUNDS; UNSUBSTIT UTEDAND SUBSTITUTED DICHLOROTRIS(PYRIDINE)BENZYLCHROMIUM(III) COMPLEXES

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Anet and Leblanc reported the first preparation of water soluble organochromium compounds of the type $RCr(H_2O)_5^{2+}$, where R = $PhCH_2$[1] and $CHCl_2$[2]. The penta-aquobenzylchromium(III) cation was prepared by the action of chromous perchlorate, in aqueous or methanolic perchloric acid, on benzyl chloride in the appropriate stoichiometric ratios, eqn. (1). The same penta-aquobenzylchromium(III) cation was later prepared from chromous sulphate and 1,1-dimethyl-2-phenethylhydroperoxide[3] and from chromous perchlorate and bis(phenylacetyl) peroxide[4]. From a detailed investigation Kochi *et al.* deduced that benzyl halides react, at 0 to 20°, with chromous salts[5,6,7] in a two stage process (eqns. 2 and 3) giving the benzylchromium(III) cation and an equivalent amount of chromium(III) salts. Ion exchange chromatography subsequently furnishes dilute aqueous solutions of the penta-aquobenzylchromium(III) cation; however, all the attempts to isolate crystalline salts of this organochromium compound have been unsuccessful. The present work was undertaken with the objectives of extending the Grignard synthesis of organochromium compounds[8] to the preparation of the benzylchromium(III) cation and of a stable, crystalline monobenzylchromium complex.

$$PhCH_2Cl + 2\ Cr(ClO_4)_2 \xrightarrow[HClO_4]{H_2O} PhCH_2Cr(H_2O)_5(ClO_4)_2 + CrCl(H_2O)_5(ClO_4)_2 \qquad (1)$$

$$PhCH_2X + Cr^{2+} \xrightarrow{slow} PhCH_2^{\bullet} + CrX^{2+} \qquad (2)$$

$$PhCH_2^{\bullet} + Cr^{2+} \xrightarrow{fast} PhCH_2Cr^{2+} \qquad (3)$$

Penta-aquobenzylchromium(III) cation

It had been shown earlier[9] that the reaction between equimolar ratios of benzylmagnesium chloride and $CrCl_3(THF)_3$ is strikingly influenced by temperature. It was postulated that the reaction proceeded to give an intermediate: solvated monobenzylchromium dichloride; and this on warming (20°), underwent homolysis to the observed

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final products, bibenzyl and chromous chloride (see also ref. 10) eqn. (4). Reinvestigation indicated that this reaction proceeded in tetrahydrofuran at −20 to −10°, to give a stable homogeneous solution of monobenzylchromium dichloride. Treatment

$$PhCH_2MgCl + CrCl_3(THF)_3 \xrightarrow[\text{temp.}]{\text{low}} PhCH_2CrCl_2(THF)_n \xrightarrow{20^\circ} \tfrac{1}{2}\,PhCH_2CH_2Ph + CrCl_2(THF)_x \quad (4)$$

of this solution with a large excess of pre-cooled oxygen-free water at low temperatures did not bring about the hydrolysis of the organochromium compound; instead a homogeneous brown solution was obtained. The latter is stable over prolonged periods (2 months) if stored at −10°, and has all the properties associated with the penta-aquobenzylchromium(III) cation[1].

Aqueous solutions of this cation* can also be prepared by (*i*) the interaction of equimolar ratios of benzyl-Grignard and $CrCl_3(THF)_3$ in diethyl ether and subsequent extraction with pre-cooled oxygen-free water; (*ii*) the interaction of solvated tribenzylchromium and $CrCl_3(THF)_3$, ratio 1:2 in tetrahydrofuran, and subsequent dilution with pre-cooled oxygen-free water; (*iii*) the interaction of dichlorobis(pyridine)-chromium(II)[11,12] and benzyl chloride, ratio 2:1, in aqueous methanol, eqns. (5), (6) and (7). Attempts to isolate the cation either as its dichloride or as the salt with more

$$PhCH_2MgCl + CrCl_3(THF)_3 \xrightarrow[Et_2O]{THF} PhCH_2CrCl_2(THF)_n \xrightarrow[H_2O]{<5^\circ} PhCH_2Cr(H_2O)_5^{2+} \quad (5)$$

$$(PhCH_2)_3Cr(THF)_n + 2\,CrCl_3(THF)_3 \xrightarrow{THF} 3\,PhCH_2CrCl_2(THF)_n \xrightarrow[H_2O]{<5^\circ} 3\,PhCH_2Cr(H_2O)_5^{2+} \quad (6)$$

$$PhCH_2Cl + 2\,CrCl_2(py)_2 \xrightarrow[CH_3OH]{H_2O} PhCH_2Cr(H_2O)_5^{2+} \quad (7)$$

complex anions (BPh_4^-; BF_4^-; $B(OCH_3)_4^-$; PF_6^-) were unsuccessful. The present results together with earlier data[9] establish the course of the reaction between equimolar ratios of benzyl-Grignard and $CrCl_3(THF)_3$ in the temperature range −70 to +20°, eqns. (8), (9), (10). The initial product at −70° is a solvated tribenzylchromium,

$$3\,PhCH_2MgCl + 3\,CrCl_3(THF)_3 \xrightarrow[THF]{-70^\circ} (PhCH_2)_3Cr(THF)_x + 2\,CrCl_3(THF)_3 \quad (8)$$

$$(PhCH_2)_3Cr(THF)_x + 2\,CrCl_3(THF)_3 \xrightarrow[THF]{-70 \text{ to } -10^\circ} 3\,PhCH_2CrCl_2(THF)_x \quad (9)$$

$$3\,PhCH_2CrCl_2(THF)_x \xrightarrow[THF]{-10 \text{ to } +20^\circ} \tfrac{3}{2}\,PhCH_2CH_2Ph + 3\,Cr(II)Cl_2(THF)_y \quad (10)$$

eqn. (8). On warming to −10° this reacts with unchanged $CrCl_3(THF)_3$ to give a solvated monobenzylchromium dichloride. The latter is stable at this temperature and with excess water it gives the penta-aquobenzylchromium(III) cation, eqn. (5), which in turn undergoes slow hydrolysis at 0° to toluene. At higher temperatures the

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* It was subsequently confirmed by Kochi and Buchanan[2] that the benzylchromium cation is accessible by the Grignard route.

solvated monobenzylchromium dichloride homolyzes to bibenzyl and chromous chloride, eqn. (10).

*Dichlorotris(pyridine)benzylchromium(III)**

The isolation of a pure σ-bonded organochromium compound involves: (*i*) the preparation of a thermally stable complex by the introduction of suitable ligands bound to chromium, and (*ii*) the separation of the organochromium compound from accompanying reaction products (chromic salt in the case of the Cr^{2+} route and magnesium salt in the case of the Grignard route). Pyridine is known to stabilize σ-bonded organochromium(III) compounds[13], therefore dichlorobis(pyridine)chromium(II) was reacted with benzyl chloride, ratio 2:1, in pyridine at 0–20°. The chromic salt was precipitated quantitatively, as $CrCl_3(py)_3$, by the addition of benzene. Crystalline dichlorotris(pyridine)benzylchromium(III) was isolated in excellent yield from the mother liquor by precipitation with hexane.

The same crystalline organochromium compound was also isolated from tetrahydrofuran solutions of solvated monobenzylchromium dichloride (prepared by the benzyl-Grignard route) by treatment with pyridine, removal of the insoluble $MgCl_2(py)_4$, and subsequent concentration of the deep, red-brown solution.

Properties of dichlorotris(pyridine)benzylchromium(III)

The visible spectrum of the organochromium compound shows a single maximum at 379 mμ (in pyridine), 355 mμ (in methanol) and 358 mμ (in perchloric acid). Furthermore the UV and visible spectra of dichlorotris(pyridine)benzylchromium in perchloric acid (see Experimental) are the same as that reported for the pentaaquobenzylchromium(III) cation[1,6]. This solvent dependence is best explained by the replacement[15] of the original pyridine ligands by methanol and water respectively. In perchloric acid the original organochromium complex is quantitatively converted to the penta-aquate, eqn. (11).

$$PhCH_2CrCl_2(py)_3 \xrightarrow[H_2O]{HClO_4} PhCH_2Cr(H_2O)_5^{2+} \qquad (11)$$

A comparison of the infra-red spectra of $CrCl_3(py)_3$, $PhCH_2HgCl$ and the organochromium compound (see Fig. 1) reveal that the latter has bands associated with pyridine coordinated to chromium(III) and with the benzyl group. The compound is therefore best formulated as a monobenzylchromium chloride–pyridine complex.

In pyridine solution the compound is paramagnetic to the extent of 3.93 B.M., indicating a chromium(III) species. In aqueous solution the compound reacts with mercuric chloride to give benzylmercuric chloride and $Cr(H_2O)_6^{3+}$.

The above, together with the analytical data and molecular weight (see Experimental) indicate that this crystalline benzylchromium compound is one or a mixture of the isomeric σ-bonded dichlorotris(pyridine)benzylchromium(III) compounds, (I), (II), (III), assuming it to be an octahedral complex.

Dichlorotris(pyridine)benzylchromium(III) is stable for months when stored under dry nitrogen at 5 to —10°. In aqueous or methanolic solution it undergoes slow

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* In a preliminary communication[14] this compound was named tris(pyridine)benzylchromium(III) chloride. However, since we subsequently established that the chlorine atoms are not present as ions (see Experimental) the present name is perhaps more appropriate.

hydrolysis at 0–20° to toluene and chromic salts. At higher temperatures (40–60°), in benzene or pyridine it undergoes smooth homolysis to bibenzyl and chromous salts.

The products formed in the reaction of the pure organochromium compound with ferric chloride depend upon the reaction medium: in hydrochloric acid equimolar ratios of benzyl chloride and bibenzyl are formed, whilst in perchloric acid only benzyl chloride is formed. Care should therefore be exercised in using this reaction for the estimation of penta-aquobenzylchromium(III) cation[5] concentrations.

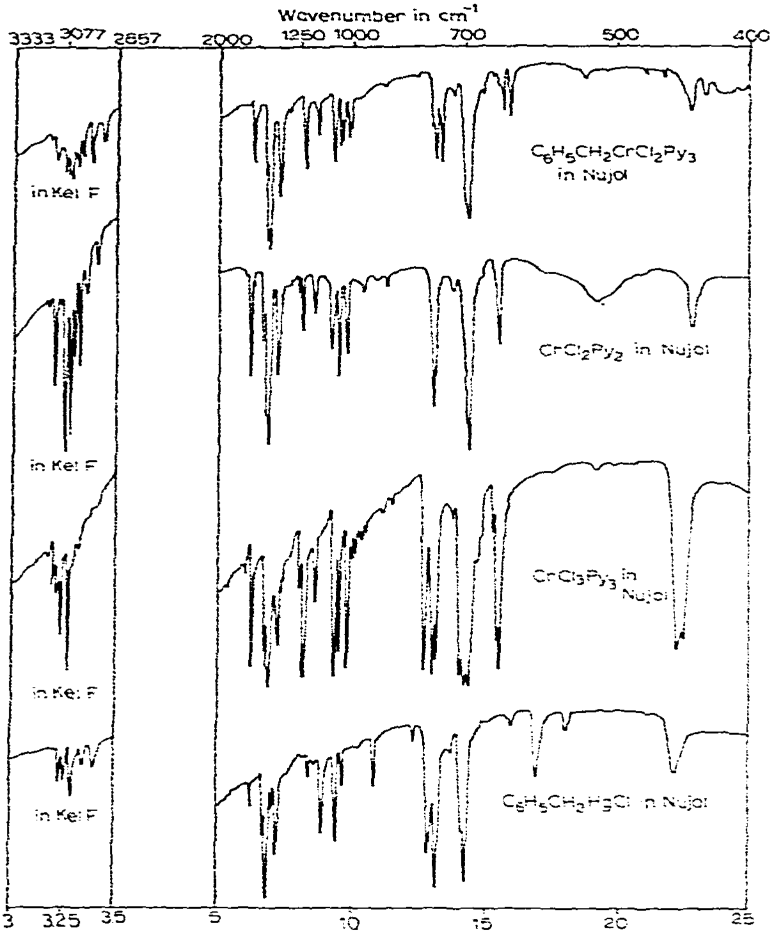
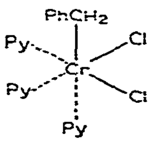
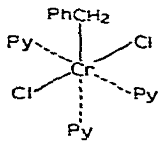


Fig. 1



I



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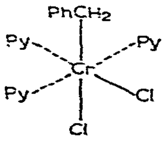

III

The pure organochromium compound on treatment with either 1,3- or 1,4-cyclohexadiene gives as final organic products, benzene, toluene and bibenzyl, indicating the occurrence of hydrogen abstraction reactions.

The observed properties of dichlorotris(pyridine)benzylchromium(III) and of the penta-aquobenzylchromium(III) cation[16] can be attributed to the fact that these compounds act as sources of benzyl anions and of benzyl radicals. The thermal instability of the monobenzylchromium species accounts for the erratic results obtained by Slaugh and Raley[17] in their "reduction of organic halides by metal salts".

Kochi and Davis[6] showed qualitatively that substituted monobenzylchromium-(III) complexes are accessible by the action of chromous salts on substituted benzyl halides. In the present work it has been shown that crystalline dichlorotris(pyridine)-(*o*-chlorobenzyl)chromium(III) (λ_{max} 377 mμ in pyridine) and dichlorotris(pyridine)-(*p*-chlorobenzyl)chromium(III) (λ_{max} 378 mμ in pyridine) are accessible by the action of dichlorobis(pyridine)chromium(II) on the appropriate benzyl halides, ratio 2:1, in pyridine solution.

The chromous route is not applicable, however, to the preparation of monoaryl- or monoalkylchromium(III) complexes[18]. In contrast the Grignard route may be used for the preparation of solvated σ-bonded monoalkyl- and monoarylchromium(III) compounds[19, 10].

EXPERIMENTAL

(with A. ANDERES, G. HÄUSERMANN and P. RÜESCH)

For general reaction conditions and gas chromatographic techniques see earlier papers[9, 20]. Spectrophotometric measurements were made on a Beckman DK 2 spectrophotometer equipped with a special quartz cell which could be flushed with nitrogen. Infrared spectra were obtained using a Grubb–Parsons "Spectromaster". Oxygen-free solvents and reagents were used in all reactions involving organochromium compounds.

Penta-aquobenzylchromium(III) cation

(*a*) *Benzyl-Grignard, $CrCl_3(THF)_3$, ratio 1:1 in THF, at −20 to −10°.* Benzylmagnesium chloride (20 ml, 13 mmoles) in tetrahydrofuran reacted rapidly with a briskly stirred suspension of $CrCl_3(THF)_3$[9, 20] also in tetrahydrofuran (100 ml), at −20 to −10°, to give a homogeneous, red-brown solution which was divided. One portion (50 ml) was treated with pre-cooled water (200 ml), at 0°, and filtered. The resulting homogeneous aqueous solution had all the properties associated with the penta-aquobenzylchromium(III) cation[1]. The remainder of the tetrahydrofuran solution was treated at −20° with pre-cooled (−10°) hexane (100 ml), and the whole chilled rapidly (−70°). The resulting precipitate, removed by filtration (−40°) under nitrogen and dried in h.v. at −40°, was isolated finally as an air-sensitive yellow-brown powder. It contained very little magnesium salts and was soluble in tetrahydrofuran, ethanol and water; λ_{max} (aqueous solution) 248, 275, 298 and 355 mμ (sh 400 mμ). It was not possible to obtain a crystalline specimen of this material.

(*b*) *Benzyl-Grignard, $CrCl_3(THF)_3$, ratio 1:1 in diethyl ether, at −70 to −20°.* Ethereal benzylmagnesium chloride (20 ml, 13.5 mmoles) was added to a briskly stirred suspension of $CrCl_3(THF)_3$ (5 g, 13.5 mmoles) also in diethyl ether (50 ml) at

—70°. Half an hour later the suspension was allowed to warm to —20° (Gilman color test No. 1, negative) and after three hours continuous stirring a heterogeneous brown solution was obtained. The latter was treated with pre-cooled (5°) water (50 ml). All the color passed into the aqueous layer, and the latter yellow-brown aqueous solution had all the properties associated with the penta-aquobenzylchromium(III) cation[1].

(*c*) *Solvated tribenzylchromium, $CrCl_3(THF)_3$ ratio 1:2, in THF.* Chromium trichloride tristetrahydrofuranate (9 g, 24 mmoles) was added to a briskly stirred solution of tribenzylchromium[19] [from $PhCH_2MgCl$ (55 ml, 36 mmoles) and $CrCl_3(THF)_3$ (4.5 g, 12 mmoles)] in tetrahydrofuran at —70°. After half an hour the reaction mixture was allowed to warm to —10°, giving finally a homogeneous yellow-brown solution. An aliquot (20 ml) was diluted at 0° with a tenfold excess of water, and the resulting aqueous solution had all the properties associated with the penta-aquobenzylchromium(III) cation[1]. The remainder of the solution on warming to 30° went colorless, and a copious white precipitate ($CrCl_2$ solvated with THF) was formed. The whole was subsequently treated with water, and the organic products, isolated with the aid of ether, consisted entirely of bibenzyl.

(*d*) *Dichlorobis(pyridine)chromium(II), benzyl chloride, ratio 2:1, in water/methanol.* Benzyl chloride (358 mg, 2.825 mmoles) was added to a briskly stirred suspension of dichlorobis(pyridine)chromium(II)[11,12] in water (10 ml) and methanol (20 ml) mixture at 0 to 5°. The course of the reaction was followed spectrophotometrically, and after 3 h the absorption at λ_{max} 355 mμ (characteristic of the penta-aquobenzylchromium(III) cation[1]) had reached its maximum. The resulting clear yellow-brown solution was divided. One portion was heated to 40° and the color of the solution changed to green, indicating that the organochromium compound was thermally unstable. A second portion was concentrated, in h.v. at 0°, however, it was not possible to isolate a crystalline organochromium compound from the resulting viscous green residue. A third portion, on treatment with excess aqueous mercuric chloride, gave immediately benzylmercuric chloride (m.p. and mixed m.p. 106–107°), 70 %, and $Cr(H_2O)_6^{3+}$ (λ_{max} 410 and 568 mμ).

Dichlorotris(pyridine)benzylchromium(III)

(*a*) *Dichlorobis(pyridine)chromium(II), benzyl chloride, ratio 2:1, in pyridine.* Benzyl chloride (1.043 ml, 9.4 mmoles) was added to a briskly stirred suspension of dichlorobis(pyridine)chromium(II) (5.081 g, 18.08 mmoles) in pyridine (35 ml) at 20°. After 2 h at 20° and 45 min at 0°, the homogeneous dark-brown reaction mixture was treated with pre-cooled benzene (140 ml) and the resulting green precipitate removed by filtration under nitrogen. The solid which was washed with benzene (30 ml) and dried in h.v. at 20° consisted of trichlorotris(pyridine)chromium(III) (3.37 g, 8.52 mmoles). (Found: C, 45.5; H, 3.8; Cl, 26.8; Cr, 13.0; N, 10.5. $C_{15}H_{15}Cl_3CrN_3$ calcd.: C, 45.5; H, 3.8; Cl, 26.9; Cr, 13.1; N, 10.6 %.)* Its infra-red spectrum was identical with that of an authentic specimen.

The combined *filtrate and washings* (205 ml) were added to pre-cooled (0°) hexane (600 ml) and the whole cooled to —20° for 3.5 h. The supernatant liquid was decanted and the crystalline residue (3.5 g, 7.75 mmoles, 82.5 %) washed thoroughly

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* Microanalyses by A. PEISKER, Brugg/AG, Switzerland.

with dry hexane and dried in h.v. at 0° for 2.5 h. A specimen was further purified from cold benzene/hexane mixture, washed with hexane and dried in h.v. at 0°, 4.5 h, in this way dichlorotris(pyridine)benzylchromium(III) was obtained as red-brown platelets (Found: C, 57.9; H, 4.6; Cl, 15.9; Cr, 11.9; N, 10.2; mol. wt.[*], 466.2. $C_{22}H_{22}Cl_2CrN_3$ calcd.: C, 58.5; H, 4.9; Cl, 15.7; Cr, 11.5; N, 9.3%; mol. wt., 451.3.): λ_{max}(pyridine) 379 mμ (sh 430 mμ), $\varepsilon_{max}^{molar}$ 2280; λ_{max} (H_2O and CH_3OH) 355 mμ; $\varepsilon_{max}^{molar}$ 2530; λ_{max} (1 M $HClO_4$) 247, 275, $\varepsilon_{max}^{molar}$ 8.200; 298, $\varepsilon_{max}^{molar}$ 7.800 and 358 mμ, $\varepsilon_{max}^{molar}$ 2.450 (sh 410 mμ). In pyridine solution the compound is paramagnetic[**] to the extent of 3.93 Bohr Magnetons (based on a molecular weight of 451.3). The pyridine solution of the compound is non-conducting.

(*b*) *Benzyl-Grignard, $CrCl_3(THF)_3$, ratio 1:1 in THF, at —20°, addition of pyridine.* A homogeneous solution of solvated monobenzylchromium dichloride in tetrahydrofuran [prepared from benzylmagnesium chloride (13 mmoles) and $CrCl_3$-$(THF)_3$ (13 mmoles), as under (*a*) above] was cooled to —50°, treated with pyridine (40 ml) and subsequently stored at —20° under nitrogen for 16 h. The resulting suspension was recooled to —50° and 2 h later was filtered at this temperature, the residue and filtrate being examined separately. The residue was washed with hexane, dried in h.v., and the resulting pale yellow solid (8 g)[***] was shown to consist essentially of $MgCl_2(py)_4$. (Found: Cl, 17.9; Mg, 5.4; pyridine, 72.5. $C_{20}H_{20}Cl_2MgN_4$ calcd.: Cl, 17.2; Mg, 5.9; pyridine, 76.8%.)

The *filtrate* was taken to dryness under h.v. at —20°, and the brown residue purified from benzene/hexane to give dichlorotris(pyridine)benzylchromium(III) (4 g, 8.9 mmoles) as red-brown crystals, identified by a direct comparison of the visible and infra-red spectra and X-ray powder photograph (in Nujol) with those prepared from $CrCl_2py_2$ and benzyl chloride in pyridine (see above).

Reactions of dichlorotris(pyridine)benzylchromium(III)

(*a*) *With mercuric chloride.* A solution of dichlorotris(pyridine)benzylchromium(III) (257 mg, 0.57 mmole) in a mixture of perchloric acid (20 ml of 1 M) and ethanol (10 ml) reacted immediately with excess aqueous mercuric chloride giving benzylmercuric chloride (129 mg, 0.39 mmole), m.p. and mixed m.p. 106–107°, and $Cr(H_2O)_6^{3+}$ (λ_{max} 410 and 575 mμ).

(*b*) *With ferric chloride.* (*i*) A solution of the organochromium compound (456 mg, 1.012 mmoles) in *pyridine* (10 ml) was added to a solution of ferric chloride (2.5 mmoles) in hydrochloric acid (15 ml of 5 M). The organic products, isolated with the aid of hexane, were shown by gas chromatography to consist of benzyl chloride and bibenzyl, ratio 1:1.

(*i*) A solution of the organochromium compound (185 mg, 0.41 mmole) in *perchloric acid* (5 ml of 2 M)/methanol (5 ml) mixture was added to aqueous ferric chloride (4 mmoles). The organic products, isolated with the aid of hexane, were shown by gas chromatography to consist only of benzyl chloride.

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[*] The molecular weight was kindly determined by Dr. J. J. DALY of MRSA Zürich, by an X-ray evaluation of the cell dimensions. The compound crystallizes in the monoclinic space group $P2_1$ or $P2_1/m$, with the cell constants a = 8.802, b = 13.383 Å, c* = 0.10439 Å^{-1}, V = abc* = 1128.3 Å (ρ = 1.372 g/ml).

[**] We thank Drs. G. and S. OLIVÉ of MRSA, Zürich, for this measurement.

[***] More $MgCl_2(py)_4$ is isolated than that expected from the reaction: $RMgCl + CrCl_3(THF)_3 \longrightarrow RCrCl_2 + MgCl_2$, since the original benzyl-Grignard solution contains $MgCl_2$.

(*c*) *With water.* A solution of the organochromium compound (384 mg, 0.85 mmole) in water (10 ml) on heating (60°) under nitrogen for 2 h gave toluene (0.6 mmole), bibenzyl (0.01 mmole) and $Cr(H_2O)_6^{3+}$ (λ_{max} 405 and 575 mμ).

(*d*) *With methanol.* A solution of the organochromium compound (1.764 g, 3.91 mmoles) in methanol (10 ml) was kept, under nitrogen, for 75 min at 20°. The green heterogeneous reaction mixture was acidified and the organic products, isolated with the aid of isopentane, consisted of toluene (2.8 mmoles) and bibenzyl (0.01 mmole).

(*e*) *Thermal stability.* (*i*) *In benzene.* A solution of the organochromium compound (339 mg, 0.75 mmole) in benzene (10 ml) on heating (60°) under nitrogen gave a solvated $CrCl_2$ and bibenzyl (0.26 mmole); no toluene or diphenylmethane were detected.

(*ii*) *In pyridine.* The homogeneous brown solution of the organochromium compound (1.817 g, 4.03 mmoles) in pyridine (30 ml) was heated (75°) under nitrogen for 3 h. The resulting green heterogeneous reaction mixture was filtered. The solid consisted of dichlorobis(pyridine)chromium(II). (Found: C, 42.0; H, 3.6; Cl, 24.9; Cr, 18.85; N, 10.4. $C_{10}H_{10}Cl_2CrN_2$ calcd.: C, 42.7; H, 3.6; Cl, 25.2; Cr, 18.5; N, 10.0 %.) The infra-red spectrum was identical with that of an authentic specimen. The filtrate was acidified and the organic products, isolated with the aid of isopentane, consisted of bibenzyl (0.98 mmole) together with some high-boiling basic material; no benzylpyridines could be detected.

(*f*) *With 1,4-cyclohexadiene.* Dichlorotris(pyridine)benzylchromium(III) (1.619 g, 3.59 mmoles) in pyridine (20 ml) at 0° was treated with 1,4-cyclohexadiene (288 mg, 3.59 mmoles) and the resulting solution kept for 4 days at 20°. The reaction mixture was then hydrolyzed and acidified with hydrochloric acid. The organic products were isolated with the aid of ether and were shown by gas chromatographic analysis to consist of: benzene (0.32 mmole), toluene (0.35 mmole), bibenzyl (0.26 mmole) and unchanged diene (2.45 mmoles).

(*g*) *With 1,3-cyclohexadiene.* In a similar experiment with the organochromium compound (1.025 g, 2.28 mmoles), pyridine (13 ml) and 1,3-cyclohexadiene (183 mg, 2.28 mmoles), the unreacted diene was destroyed by oxidation with potassium permanganate. The final organic products were benzene (0.35 mmole), toluene (0.15 mmole) and bibenzyl (0.15 mmole).

Dichlorotris(pyridine)(p-chlorobenzyl)chromium(III)

The reaction of *p*-chlorobenzyl chloride (1.533 g, 9.52 mmoles) with $CrCl_2py_2$ (5.35 g, 19.04 mmoles) in pyridine (40 ml) was carried out analogously to that described earlier for benzyl chloride. The products were $CrCl_3(py)_3$ (3.69 g, 9.35 mmoles) and dichlorotris(pyridine)(*p*-chlorobenzyl)chromium(III) (2.22 g, 4.58 mmoles, 48.5 %), obtained as red-brown platelets from benzene/hexane, λ_{max} (pyridine) 378 mμ (sh 440 mμ), $\varepsilon_{max}^{molar}$ 2475. (Found: C, 53.85; H, 4.2; Cl, 21.9; Cr, 11.2; N, 9.0. $C_{22}H_{21}Cl_3CrN_3$ calcd.: C, 54.4; H, 4.4; Cl, 21.9; Cr, 10.7; N, 8.65 %.)

Dichlorotris(pyridine)(o-chlorobenzyl)chromium(III)

o-Chlorobenzyl chloride (1.653 g, 10.27 mmoles) was allowed to react with $CrCl_2py_2$ (5.769 g, 20.54 mmoles) in pyridine (35 ml) analogously to that described earlier for benzyl chloride. The products were $CrCl_3(py)_3$ (3.8 g, 9.61 mmoles) and dichlorotris(pyridine)(*o*-chlorobenzyl)chromium(III) (3.6 g, 7.4 mmoles, 72 %), obtained as yellow-orange platelets from benzene/hexane, λ_{max} 377 mμ (sh 445 mμ),

$\varepsilon_{max}^{molar}$ 2115. (Found: C, 53.8; H, 4.25; Cl, 22.1; Cr, 11.75; N, 8.3. $C_{22}H_{21}Cl_3CrN_3$ calcd.: C, 54.4; H, 4.4; Cl, 21.9; Cr, 10.7; N, 8.65 %.)

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SUMMARY

The crystalline water-soluble, σ-bonded dichlorotris(pyridine)benzylchromium(III), dichlorotris(pyridine)(*o*-chlorobenzyl)chromium(III) and dichlorotris(pyridine)(*p*-chlorobenzyl)chromium(III) complexes have been isolated from the reaction of dichlorobis(pyridine)chromium(II) and the appropriate benzyl halides in pyridine solution. Solvated monobenzylchromium dichloride, prepared by the Grignard route, is converted with water to the penta-aquobenzylchromium(III) cation and with pyridine to the crystalline dichlorotris(pyridine)benzylchromium(II). The crystalline monobenzylchromium compound acts both as a source of benzyl anions and as a source of benzyl radicals.

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