The Preparation and Isolation of Tris(pyridine)benzylchromium(III) Chloride

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ANET and LEBLANC[1,2] have reported that chromium(II) perchlorate reacted directly, in aqueous methanol, with certain organic halides to give organochromium cations. In the case of benzyl chloride the reaction (Equation 1) was believed to proceed to give the "penta-aquobenzylchromium" cation (I). Subsequent investigators[3,4] studied this reaction in detail but were unsuccessful in isolating crystalline salts of this water-soluble σ-bonded organochromium cation.

$$PhCH_2Cl + 2\ Cr^{2+} \rightarrow \underset{(I)}{PhCH_2Cr(H_2O)_5{}^{2+}} + CrCl(H_2O)_5{}^{2+} \qquad (1)$$

Preliminary work has now shown that solutions of solvated monobenzylchromium dichloride (prepared by the action of $PhCH_2MgCl$ on $CrCl_3(THF)_3$ in THF at less than −10°) give this "penta-aquobenzylchromium" cation on treatment with excess of oxygen-free water at +5°.* However all our attempts to isolate the "penta-aquobenzylchromium" cation either as the perchlorate, the dichloride, or as the salt with more complex anions ($BPh_4{}^-$; $BF_4{}^-$; $B(OMe)_4{}^-$; $PF_6{}^-$ were also unsuccessful. Therefore attention was turned to replacing the co-ordinated water molecules by other ligands which would confer greater stability to the organochromium compound.

It is found that $Cr^{II}py_2Cl_2$[5] reacts smoothly with benzyl chloride in pyridine solution in the ratio 2 : 1 at 0° and gives a separable mixture of tris(pyridine)chromium(III) chloride and a red-brown *crystalline benzylchromium compound.* The *same crystalline organochromium* compound can also be 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, provided the temperature throughout is kept at less than −10°.

The crystalline benzylchromium compound, mol. wt.,** 466·2, has λ_{max} (pyridine) 378 (sh 430) mμ; ϵ_{max} 2·280; ν_{max} (nujol) 1595, 1484, 1460, 1218; 1149; 1073; 1044, 1036; 1010, 1003; 766; 759; 749; 694; 637; 626; 533; 437 cm.$^{-1}$ ν_{max} (Kel F.) 3106; 3058; 3049; 3012; 2954; 2908 cm.$^{-1}$ [H of aromatic rings (phenyl and pyridine) and CH_2]. The substance was shown to be paramagnetic to the extent of 3·93 B.M., in agreement with a chromium valency of three.† The crystalline compound reduces Fe^{III} salts, and reacts with oxygen-free

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* Kochi and Buchanan[4] subsequently confirmed this observation.

** Kindly determined by Dr. J. J. Daly of MRSA Zurich, by *X*-Ray evaluation of the cell constants and based on a measured density of 1·372 g./cm.^{3}

† Kindly determined by Drs. G. and S. Olivé of MRSA Zürich, for a pyridine solution, and based on a molecular weight of 451·34.

[1] F. A. L. Anet and E. Leblanc, *J. Amer. Chem. Soc.*, 1957, **79**, 2649.

[2] F. A. L. Anet, *Canad. J. Chem.*, 1959, **37**, 58.

[3] J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 5264.

[4] J. K. Kochi and D. Buchanan. *J. Amer. Chem. Soc.*, 1965, **87**, 853.

[5] H. Lux, L. Eberle, and D. Sarre, *Chem. Ber.*, 1964, **97**, 503.

solutions of mercuric chloride to give benzylmercuric chloride (70% yield) m.p. and mixed m.p. 106—107°. All the above data indicate that the crystalline benzylchromium compound is probably one or a mixture of the isomeric σ-bonded tris(pyridine)benzylchromium(III) chlorides, $PhCH_2Crpy_3Cl_2$.

The compound is stable in the solid state under nitrogen at 0°. At higher temperatures it undergoes homolysis to yield ultimately bibenzyl and solvated chromium(II) chloride. It dissolves in oxygen-free aqueous perchloric acid to give a homogeneous solution at 0° whose properties (*i.e.* visible spectrum and behaviour towards Fe^{III} salts, $HgCl_2$ solution, and oxygen) are identical with those associated with the "penta-aquobenzylchromium" cation.[1]

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