Preparation and Characterization of Chromium(II) Tetrahydroborate–Tetrahydrofuran (1/2)

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Summary A convenient synthesis has been developed for the light blue adduct $Cr(BH_4)_2$.2tetrahydrofuran by the reaction of $Cr(OBu^t)_4$ with diborane in tetrahydrofuran; the BH_4 groups are covalently attached to chromium by double hydrogen bridges.

ONLY a few solvent-free transition-metal tetrahydroborates are known[1] and very few of the ether or tetrahydrofuran (THF) adducts have been characterized. This is especially true with regard to the number of co-ordinated THF molecules; in particular the chromium(II) tetrahydroborate $Cr(BH_4)_2 \cdot n$THF has been described as being green[2] or blue[3] in colour.

Attempts to prepare this compound from $Cr(OMe)_3$ and diborane in THF according to the procedures described by Klejnot[2] or by Mirviss *et al.*[3] gave erratic results. Either a black amorphous material or a green solution were formed slowly and in low yield. Evaporation of the green solutions gave small quantities of a material containing chromium and BH_4 groups. We have found that the homogeneous reaction of $Cr(OBu^t)_4$ with diborane in THF yielded light blue crystals of $Cr(BH_4)_2 \cdot 2THF$, (**1**). The reduction of Cr^{IV} by diborane commenced at *ca.* −40 °C and was complete at −20 °C. H_2 evolution (95—104% of theory) clearly indicated direct reduction of Cr^{IV} to Cr^{II}, this being accompanied by the development of a red coloration. Subsequent warming to −15 °C led to a green solution and, finally, at room temperature, to a light blue solution from which (**1**) crystallized readily. Crystals of (**1**) separated from the green solutions at −20 °C, and at −70 °C green crystals were also obtained which may be analogous to the green product from $Cr(OMe)_3$.

Compound (**1**) is stable at −20 °C but decomposes readily at room temperature. Hydrolysis in 50% acetic acid proceeds according to the equation (**1**) $+ 6\,H_2O \rightarrow Cr + 2\,B(OH)_3 + 7\,H_2 + 2\,THF$. Addition of degassed hydrochloric acid dissolves the metal with evolution of 1 mole of H_2 per mole of Cr. This, in addition to the analytical data, confirms the formula $Cr(BH_4)_2 \cdot 2THF$ for (**1**).

The i.r. spectrum of (**1**) shows bands at 2380, 2350, 2120, and 2015 cm^{-1} for terminal and bridging hydrogen atoms, indicating covalently bonded double-hydrogen-bridged BH_4 groups. Thus the co-ordination number for chromium in (**1**) is effectively 6. Since the difference in band positions between terminal and bridging B–H is small (230 cm^{-1} for the 2nd and 3rd band) in comparison *e.g.* to $(C_5H_5)_2VBH_4$ (*ca.* 750 cm^{-1}) the bonding of the BH_4 group must have a substantial polar character, which is not unexpected for Cr^{II}.

Compound (**1**) is paramagnetic. Its ^{11}B n.m.r. signal at +96·5 p.p.m. (upfield from $BF_3 \cdot OEt_2$) is rather broad (half width *ca.* 375 Hz) and no BH coupling could be observed. The position of the signal is due to the paramagnetism.

The co-ordinated THF may be displaced by pyridine or ethylenediamine. Moreover, (**1**) readily loses THF *in vacuo* indicating the possibility of obtaining solvent-free $Cr(BH_4)_2$ which could have inherent catalytic potential similar to the recently described $(C_5H_5)Cr(BH_4)_2$.[4]

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