

Synthesis of tricarbonylchromium(0) complexes of benzylic halides

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Addition of BX₃ (X = Br, I, Cl) to tricarbonylchromium(0) complexes of benzylic alcohols and ethers provides tricarbonylchromium(0) complexes of benzylic halides in excellent yield (90–99%).

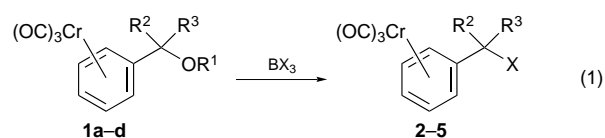
(Arene)tricarbonylchromium(0) complexes have been widely applied in organic, organometallic and materials synthesis over the last thirty years and as a result complexes containing most organic functional groups have been synthesised and characterised.¹ Against this background it is perhaps surprising to find that tricarbonylchromium(0) complexes of benzylic halides are rarely mentioned in the literature. For example, the tricarbonylchromium(0) complex of benzyl bromide is to date unreported, the benzyl iodide complex is mentioned in just one study,[‡] and the benzyl chloride complex is found in a mere handful of papers.³

The under-representation of benzylic halides in (arene)tricarbonylchromium(0) chemistry may be attributed to difficulties with their preparation. Reacting benzylic bromides, iodides and chlorides with even a labile source of tricarbonylchromium(0) such as [(CO)₃(NH₃)₃Cr⁰] under relatively mild conditions leads to insertion of the chromium(0) into the benzylic halide bonds, reductive coupling and the production of 1,2-diarylethanes rather than formation of η⁶-arene complexes.⁴ And whilst addition of HCl to (benzyl alcohol)tricarbonylchromium(0) gives (benzyl chloride)tricarbonylchromium(0) in acceptable yield (31–74%)³ and has thus enabled this complex to be used in both mechanistic studies^{3a} and in the synthesis of several heterobimetallic species,^{3b–d} the corresponding reactions with HBr and HI are unreported.[§]

In view of the under-utilisation to date of tricarbonylchromium(0) complexes of benzylic bromides and iodides due to the perceived difficulties associated with their preparation, we

report herein our recent discovery that tricarbonylchromium(0) complexes of benzylic halides are readily prepared in excellent yield by treatment of readily available tricarbonylchromium(0) complexes of either benzylic alcohols or benzylic ethers with the appropriate boron trihalide.

(Benzyl alcohol)tricarbonylchromium(0) **1a**⁵ was prepared from benzyl alcohol and hexacarbonylchromium(0) (69%). Addition of two equivalents of BBr₃ to a suspension of **1a** in CH₂Cl₂ at –78 °C gave a brown–yellow solution which was stirred for 1 h at –78 °C and then quenched with aqueous NaHCO₃ [eqn. (1)]. Subsequent work-up gave a yellow solid



which was identified as the novel tricarbonylchromium(0) complex of benzyl bromide **2** on the basis of its spectroscopic and microanalytical data (Table 1, entry 1).¶ Encouraged by the excellent yield obtained for this reaction (99%), the reaction of the benzyl alcohol complex **1a** was performed under identical conditions with BI₃ and BCl₃. These gave, respectively, the novel benzyl iodide complex **3**¶ in 99% yield and the previously reported³ but as yet not fully characterised benzyl chloride complex **4**¶ also in 99% yield (Table 1, entries 2 and 3).

Tricarbonylchromium(0) complexes of benzylic ethers are easily synthesised and commonly used as intermediates in (arene)tricarbonylchromium(0) chemistry.⁶ In order to ascertain whether or not these complexes may be regarded as precursors to benzylic halide complexes, the methyl and ethyl ether complexes **1b**⁷ and **1c**⁷ were synthesised by treatment of the alcohol complex **1a** with MeOH and EtOH, respectively, in the presence of H₂SO₄ (83 and 89% yield, respectively). Reaction of the methyl ether complex **1b** with BBr₃, BI₃ and BCl₃ and the ethyl ether complex **1c** with BBr₃ gave the corresponding benzylic halide complexes **2–4** in excellent yields (99–99%) (Table 1, entries 4–7). [It is worthy of comment at this point that reaction of the methyl ether complex **1b** with BF₃ failed to produce the corresponding benzyl fluoride complex. A related transformation has been reported recently, however, using cyclic benzylic alcohol complexes and the powerful fluoride source diethylaminosulfur trifluoride (DAST).⁸]

In order to test the effect of substitution at the benzylic centre, the secondary and tertiary benzylic ether complexes **1d** and **1e** were synthesised by Bu^tLi-promoted deprotonation of the methyl ether complex **1b** followed by quenching with iodoethane to give **1d**⁹ (93%), and then Bu^tLi-promoted deprotonation of **1d** and quenching with iodoethane to give the novel complex **1e** (70%). Whilst treatment of **1d** with BBr₃ gave an excellent yield of the corresponding novel bromide **5** (99%) indicating that secondary benzylic halide complexes may be synthesised by this approach (Table 1, entry 8), reaction of **1e** with BBr₃ resulted in elimination and the production of an α,β-dimethylstyrene complex in significant yield (70%) (Table 1, entry 9).

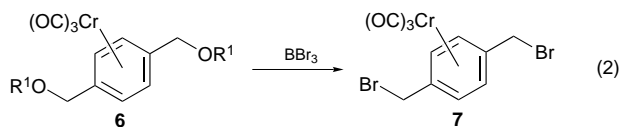
Finally, in order to test whether or not difunctionalised complexes may be accessed by boron trihalide treatment of alcohols and ethers, the novel dimethyl ether complex **6** was

Table 1 Reaction of benzylic alcohol and ether complexes **1a–e** and **6** with boron trihalides to give benzylic halide complexes **2–5** and **7**^a

Entry	Substrate	R ¹	R ²	R ³	BX ₃	Product	R ²	R ³	X	Yield (%)
1	1a	H	H	H	BBr ₃	2	H	H	Br	99
2	1a	H	H	H	BI ₃	3	H	H	I	99
3	1a	H	H	H	BCl ₃	4	H	H	Cl	99
4	1b	Me	H	H	BBr ₃	2	H	H	Br	95
5	1b	Me	H	H	BI ₃	3	H	H	I	99
6	1b	Me	H	H	BCl ₃	4	H	H	Cl	97
7	1c	Et	H	H	BBr ₃	2	H	H	Br	90
8	1d	Me	Me	H	BBr ₃	5	Me	H	Br	99
9	1e	Me	Me	Et	BBr ₃	—	—	—	—	^b
10	6	Me	—	—	BBr ₃	7	—	—	Br	95

^a The experimental procedure for the synthesis of **2** from **1a** is typical: BBr₃ (1 m in CH₂Cl₂, 2 cm³, 2 mmol) was added to a suspension of **1a** (0.244 g, 1.00 mmol) in CH₂Cl₂ (20 cm³) at –78 °C. The resulting brown–yellow solution was stirred at –78 °C for 1 h and then quenched with sat. aq. NaHCO₃ (10 cm³). The product mixture was allowed to warm to room temperature and then H₂O (10 cm³) was added before extracting the organic phase with diethyl ether (40 cm³ and 20 cm³). The organic phase was dried (MgSO₄), filtered through Celite and concentrated *in vacuo* to give complex **2** as a yellow solid (0.304 g, 99%). ^b Reaction of **1e** with BBr₃ resulted in elimination and the production of an α,β-dimethylstyrene complex (70%).

synthesised by methylation of 1,4-benzenedimethanol (NaH-MeI; 50%) and subsequent complexation $[(\text{CO})_6\text{Cr}^0]$; 85%]. Addition of BBr_3 to **6** [eqn. (2)] gave the novel dibromide



complex **7** in 95% yield (Table 1, entry 10).

Footnotes

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‡ Reaction of $[(\text{PhCH}_2)(\text{CO})_3\text{Cr}^0]_2\text{Hg}$, prepared in 65% yield from $(\text{PhCH}_2)_2\text{Hg}$ and $[(\text{CO})_3(\text{NH}_3)_3\text{Cr}^0]$, with iodine gave (benzyl iodide)-tricarbonylchromium(0) in 79% yield.²

§ In our hands, addition of HBr to (benzyl alcohol)tricarbonylchromium(0) gave a moderate yield (ca 60%) of an inseparable 1:3 mixture of benzyl bromide and its tricarbonylchromium(0) complex, whilst the corresponding reaction with HI led to a product mixture from which only benzyl iodide containing a trace (< 5%) of its tricarbonylchromium(0) complex could be extracted.

¶ Selected data for **2**: mp 73–5 °C; $\nu_{\text{max}}(\text{cyclohexane})/\text{cm}^{-1}$ 1983vs and 1920vs (C≡O); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.13 (2 H, s, CH₂) and 5.32–5.34 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 31.9 (CH₂), 91.6 (C_{para}), 92.3, 93.2 (C_{ortho,meta}), 105.5 (C_{ipso}) and 232.0 (C≡O); m/z (EI) 308/306 (M⁺, 15%), 227 (M – Br, 10), 224/222 (M – 3CO, 20), 199 (M – Br – CO, 15), 143 (M – Br – 3CO, 30), 91 (C₇H₇, 100) and 52 (Cr, 100). For **3**: mp 85–88 °C (decomp.); $\nu_{\text{max}}(\text{cyclohexane})/\text{cm}^{-1}$ 1982vs and 1920vs (C≡O); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.08 (2 H, s, CH₂) and 5.26–5.37 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 3.6 (CH₂), 91.2 (C_{para}), 92.6, 92.9 (C_{ortho,meta}), 107.6 (C_{ipso}) and 232.3 (C≡O); m/z (EI) 354 (M⁺, 50%), 298 (M – 2CO, 10), 270 (M – 3CO, 75), 227 (M – I, 25), 199 (M – I – CO, 50), 171 (M – I – 2CO, 15), 143 (M – I – 3CO, 65), 91 (C₇H₇,

100) and 52 (Cr, 70). For **4**: mp 59–61 °C; $\nu_{\text{max}}(\text{cyclohexane})/\text{cm}^{-1}$ 1984vs and 1920vs (C≡O); $\delta_{\text{H}}(\text{CDCl}_3)$ 4.25 (2 H, s, CH₂) and 5.34–5.36 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 45.1 (CH₂), 91.6 (C_{para}), 92.3, 92.8 (C_{ortho,meta}), 105.5 (C_{ipso}) and 231.9 (C≡O); m/z (EI) 262 (M⁺, 15%), 178 (M – 3CO, 30), 143 (M – Cl – 3CO, 10), 91 (C₇H₇, 100) and 52 (Cr, 35).

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