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Protodeboronation of arylboronic acids and triarylboroxines in Bu₂O/THF

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Abstract

The arylboron compounds Ph₃B₃N₃Me₃, Ar₃B₃O₃, or ArB(OH)₂ (Ar = Ph, *p*-BrC₆H₄, *p*-MeC₆H₄, *m*-NH₂C₆H₄) react with [Cr(CO)₆] in refluxing Bu₂O/THF (9:1) to afford the (η⁶-arene)tricarbonyl-chromium(0) complexes of the protodeboronated substrates in yields of up to 55%. The proposed mechanism involves protodeboronation of the arylboron compound followed by complexation of the free arene by the chromium carbonyl moiety.

1. Introduction

In the context of the co-ordination chemistry of triarylboroxines, we thought it of interest to determine whether a [Cr(CO)₃] fragment would prefer to be bonded to the heterocyclic or an aryl ring. Both co-ordination modes have been found in related arylborazine chemistry [1,2], whereas only the former is known in triarylborthiin systems [3]. To date, only one (poorly characterized) complex of a triarylboroxine, [(Ph₃B₃O₃)(Cr(CO)₃)₃], has been reported [4]. In this paper, we report the results of reactions of triarylboroxines and arylboronic acids with [Cr(CO)₆] in refluxing Bu₂O/THF. These reactions lead unexpectedly to chromium tricarbonyl complexes of the protodeboronated arenes. The mechanism of this reaction has been studied.

2. Results and discussion

Triarylboroxines, Ar₃B₃O₃ (Ar = Ph, *m*-NH₂C₆H₄, *p*-BrC₆H₄, *p*-MeC₆H₄), or the B', B'', B'''-triarylborazine, Ph₃B₃N₃Me₃, when treated with 3 equiv. of [Cr(CO)₆] in refluxing (dried) Bu₂O/THF (9:1) produced (η⁶-arene)tricarbonylchromium(0) complexes of the protodeboronated arenes, [(η⁶-ArH)Cr(CO)₃], in

low yields (Table 1). The related arylboronic acids, ArB(OH)₂, when treated with 1 equiv. of [Cr(CO)₆] under identical conditions, gave the same complexes but in higher yields. With neat dry Bu₂O as solvent, Ph₃B₃O₃ and Ph₃B₃N₃Me₃ gave negligible amounts of [(η⁶-C₆H₆)Cr(CO)₃]. The reaction of [Cr(CO)₆] and PhB(OH)₂ in boiling diglyme/octane was investigated by Razuvaev and co-workers, who obtained a mixture of reaction products including [(Ph₃B₃O₃)(Cr(CO)₃)₃] and [(η⁶-PhB(OH)₂)Cr(CO)₃] [4]. However, the only isolable products from our reactions in Bu₂O or Bu₂O/THF were the non-boron-containing (η⁶-arene)tricarbonylchromium(0) complexes. Thus, the overall reaction between [Cr(CO)₆] and arylboronic acids or triarylboroxines in Bu₂O/THF is that of protodeboronation/complexation of the arylboron compound. Protodeboronation of aromatic C–B bonds under hydrolytic conditions is well documented, and is catalysed by concentrated sodium hydroxide, concentrated hydrochloric acid, and some transition metal salts [5–9]. The reactions reported here are unusual in that non-hydrolytic conditions are employed. The mechanism of formation of these protodeboronated complexes was therefore investigated.

Thermolysis of [(η⁶-PhB(OH)₂)Cr(CO)₃] (prepared according to [4]) in refluxing Bu₂O/THF did not give any significant amounts of [(η⁶-C₆H₆)Cr(CO)₃], implying that protodeboronation occurs before complexation. Phenylboronic acids are known [10,11] to be de-

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TABLE 1. Reactions of $[\text{Cr}(\text{CO})_6]$ with arylboron compounds

	Boron substrate	Molar ratio (Ar:Cr)	Reflux time (h)	Solvent	Yield ^a (%) $[(\eta^6\text{-ArH})\text{Cr}(\text{CO})_3]$
1	$\text{Ph}_3\text{B}_3\text{O}_3$	1:1	24	$\text{Bu}_2\text{O}/\text{THF}$	26
2	$(p\text{-BrC}_6\text{H}_4)_3\text{B}_3\text{O}_3$	1:1	24	$\text{Bu}_2\text{O}/\text{THF}$	5
3	$(p\text{-MeC}_6\text{H}_4)_3\text{B}_3\text{O}_3$	1:1	24	$\text{Bu}_2\text{O}/\text{THF}$	11
4	$(m\text{-NH}_2\text{C}_6\text{H}_4)_3\text{B}_3\text{O}_3$	1:1	24	$\text{Bu}_2\text{O}/\text{THF}$	10
5	$\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$	1:1	67	$\text{Bu}_2\text{O}/\text{THF}$	41
6	$\text{PhB}(\text{OH})_2$	1:1	48	$\text{Bu}_2\text{O}/\text{THF}$	55
7	$m\text{-NH}_2\text{C}_6\text{H}_4\text{B}(\text{OH})_2 \cdot \text{H}_2\text{O}$	1:1	48	$\text{Bu}_2\text{O}/\text{THF}$	42
8	$p\text{-BrC}_6\text{H}_4\text{B}(\text{OH})_2$	1:1	48	$\text{Bu}_2\text{O}/\text{THF}$	33
9	$p\text{-MeC}_6\text{H}_4\text{B}(\text{OH})_2$	1:1	48	$\text{Bu}_2\text{O}/\text{THF}$	54
10	$\text{Ph}_3\text{B}_3\text{O}_3$	1:1	24	Bu_2O	2
11	$\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$	1:1	70	Bu_2O	2
12	$\text{PhB}(\text{OH})_2$	1:1	24	Bu_2O	36
13	$\text{Ph}_3\text{B}_3\text{O}_3$	30:1	118	$\text{Bu}_2\text{O}/\text{THF}$	21
14	$\text{Ph}_3\text{B}_3\text{O}_3$	3:1	100	$\text{Bu}_2\text{O}/\text{THF}$	31
15	$\text{Ph}_3\text{B}_3\text{O}_3$	1:1	100	$\text{Bu}_2\text{O}/\text{THF}$	52
16	$\text{Ph}_3\text{B}_3\text{O}_3$	1:1	24	$\text{Bu}_2\text{O}/d_8\text{-THF}$	38

^a Yields based on $[\text{Cr}(\text{CO})_6]$.

phenylated quantitatively to give the related arene and metaboric acid at elevated temperatures. Consistent with this, benzene was detected by GLC analysis in 26% yield in a previously refluxed (24 h) $\text{Bu}_2\text{O}/\text{THF}$ solution of $\text{PhB}(\text{OH})_2$. Metaboric acid and $\text{PhB}(\text{OH})_2$ were also detected by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy after removal of solvent and dissolution of the residue in CDCl_3 . Triarylboroxines and triarylborazines are reported to be thermally more stable than arylboronic acids [6]. Surprisingly therefore, GLC analysis of a refluxed (24 h) $\text{Bu}_2\text{O}/\text{THF}$ solution of $\text{Ph}_3\text{B}_3\text{O}_3$ revealed a 46% conversion of the phenyl groups to the benzene. The possibility that despite its low concentration, this liberated benzene could react with $[\text{Cr}(\text{CO})_6]$ to form the product was investigated. The yield of $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ from C_6H_6 and $[\text{Cr}(\text{CO})_6]$ under similar reaction quantities/conditions (24 h reflux) to those in Table 1 was 44%. These results are consistent with the view that the likely reaction pathway involves protodeboronation of the arylboron compound to yield the free arene which is then complexed by the chromium carbonyl moiety (Fig. 1). The presence of THF considerably speeds up this protodeboronation/complexation reaction for $\text{Ph}_3\text{B}_3\text{O}_3$ and $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$. The possibility that THF was acting as a hydrogen atom source was investigated by an experiment using $\text{Bu}_2\text{O}/d_8\text{-THF}$ as solvent. The mass spectrum of the product showed a normal isotopic distribution around its molecular ion peaks demonstrating that deuterium had not been incorporated into the product. The source of hydrogen atoms in this protodeboronation reaction must therefore be either the Bu_2O , the arylboron compound itself, or possibly traces of water or other

proton sources remaining in the "dry" solvents. The catalytic role of THF in these reactions is probably related to the greater donor ability of THF compared with that of Bu_2O and to the formation of labile complexes such as $[\text{Cr}(\text{CO})_{6-n}(\text{THF})_n]$ ($n = 1, 2, 3$) in the mixed $\text{Bu}_2\text{O}/\text{THF}$ system [12].

3. Experimental details

3.1. General

Reactions were carried out by use of standard Schlenk technique under N_2 and all solvents were dried and distilled before use. $[\text{Cr}(\text{CO})_6]$ and the aryl-

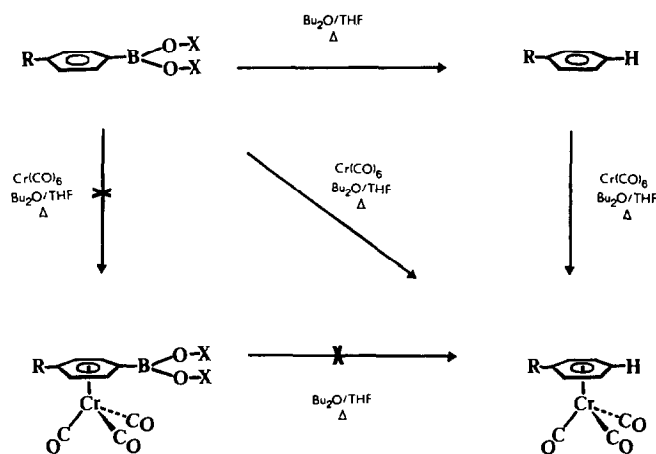


Fig. 1. Proposed reaction scheme for protodeboronation reactions in $\text{Bu}_2\text{O}/\text{THF}$. ($\text{X} = \text{H}$ for arylboronic acids and $\text{X} =$ remainder of the heterocyclic B_3O_3 system in arylboroxines; $\text{R} = \text{H}, \text{Me}, \text{Br}$).

boronic acids PhB(OH)_2 , $p\text{-MeC}_6\text{H}_4\text{B(OH)}_2$, $p\text{-BrC}_6\text{H}_4\text{B(OH)}_2$, and $m\text{-NH}_2\text{C}_6\text{H}_4\text{B(OH)}_2$, were obtained from commercial sources. Triarylboroxines were prepared from the arylboronic acids by dehydration at 100°C for several hours *in vacuo* [13]. $\text{Ph}_3\text{B}_3\text{N}_3\text{Me}_3$ and $[(\eta^6\text{-C}_6\text{H}_5\text{B(OH)}_2)\text{Cr(CO)}_3]$ were prepared as described previously [4,14]. Solution IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrophotometer using standard liquid cells with NaCl windows. Melting points were determined on an Electrothermal Melting Point apparatus. Mass spectra were recorded on Finnigan 1020 GC mass spectrometer. GLC analyses were performed on a Perkin-Elmer 8410 GC fitted with a Rtx-1701 crossbonded capillary column. Multi-element NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer operating at 250 MHz for ^1H and 80.25 MHz for ^{11}B . Chemical shifts (δ) are given in ppm with positive values towards high frequency (downfield) from SiMe_4 and from $\text{BF}_3 \cdot \text{OEt}_2$ for ^{11}B . NMR spectra were obtained on samples dissolved in CDCl_3 .

3.2. Interaction of arylboron compounds with $[\text{Cr(CO)}_6]$ in $\text{Bu}_2\text{O}/\text{THF}$ (9:1)

The general procedure for the interaction of aryl/boron compounds with $[\text{Cr(CO)}_6]$ in refluxing $\text{Bu}_2\text{O}/\text{THF}$ (9:1) is given below for $\text{Ph}_3\text{B}_3\text{O}_3$ (entry 1, Table 1). Similar conditions were employed for entries 2–16 in Table 1, (6 mmol of $[\text{Cr(CO)}_6]$ and 40 cm^3 of solvent) except entry 16 which was run on 1/2 scale. The $(\eta^6\text{-arene})\text{tricarboxylchromium(0)}$ products were identified by comparison of melting points and IR spectra (cyclohexane or CH_2Cl_2) with literature data [12,15–18] and by mass spectrometry.

3.3. Interaction of $[\text{Cr(CO)}_6]$ with $\text{Ph}_3\text{B}_3\text{O}_3$

$[\text{Cr(CO)}_6]$ (1.32 g, 6.0 mmol) and $\text{Ph}_3\text{B}_3\text{O}_3$ (0.63 g, 2.0 mmol) were refluxed in 9:1 $\text{Bu}_2\text{O}/\text{THF}$ (40 cm^3) for 24 h under nitrogen. Removal of solvent and unchanged $[\text{Cr(CO)}_6]$ under vacuum (5 mmHg, 50°C) left a yellow/green solid residue, which when sublimed under vacuum (0.5 mmHg, 100°C) gave $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3]$ (0.34 g, 1.6 mmol 26%) as yellow crystals; m.p. 161°C . IR: $\nu(\text{CO})$ 1982, 1914 cm^{-1} , MS: 216, $(\text{M}+2)^+$, (0.8%); 215, $(\text{M}+1)^+$, (3.7%); 214, M^+ , $[\text{C}_9\text{H}_6\text{Cr}^{16}\text{O}_3]$, (18%); 212, $(\text{M}-2)^+$, (0.8%); 130, $[(\text{M}-3\text{CO})^+]$, (35%); 52, (100%), $[\text{Cr}^+]$. (Lit. [12] m.p. $161\text{--}163^\circ\text{C}$. IR: $\nu(\text{CO})$ 1982, 1915 cm^{-1}).

3.4. Thermal decomposition of arylboron compounds

The thermolysis of the arylboron compounds $\text{Ph}_3\text{B}_3\text{O}_3$ and PhB(OH)_2 was studied in refluxing Bu_2O or $\text{Bu}_2\text{O}/\text{THF}$ (9:1) solution. In duplicate experiments, reaction mixtures were analysed by GLC by comparison of peak area for benzene with that from a standard solution. Yields are based on available phenyl groups. $\text{Ph}_3\text{B}_3\text{O}_3$, $\text{Bu}_2\text{O}/\text{THF}$, 18 h, 43%, 24 h, 44% and 46%; $\text{Ph}_3\text{B}_3\text{O}_3$, Bu_2O , 24 h, 8% and 11%; PhB(OH)_2 , $\text{Bu}_2\text{O}/\text{THF}$, 24 h, 22% and 26%; PhB(OH)_2 , Bu_2O , 24 h, 3% and 6%, 42 h, 8%. $^{11}\text{B}\text{-}\{^1\text{H}\}$ NMR spectra in CDCl_3 solution of the residues obtained after removal of volatiles showed absorption peaks at +28.0 (major component) and +19.0 ppm. $[(\eta^6\text{-C}_6\text{H}_5\text{B(OH)}_2)\text{Cr(CO)}_3]$ (0.576 g; 2.23 mmol) was thermolysed in $\text{Bu}_2\text{O}/\text{THF}$ (40 cm^3 ; 9:1) for 24 h; work up as above resulted in a small amount of $[(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3]$ (0.014 g, 3%).

Acknowledgements

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