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HYDRO-DE-ALKOXYLATION OF ALKOXYBENZENETRICARBONYLCHROMIUM COMPLEXES

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***Abstract:** Hydro-de-alkoxy nucleophilic aromatic substitution by an hydride readily occurs at the position ipso to the alkoxy leaving group of alkoxybenzenetricarbonylchromium complexes*

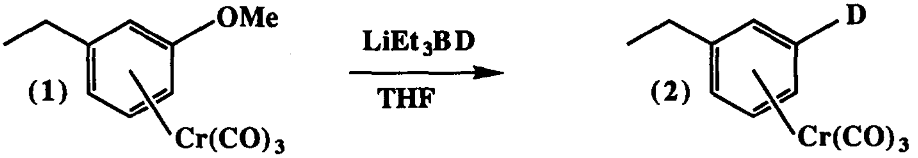
Hydride addition on the arene ring of cationic arenetricarbonylmanganese complexes [1], whose arene ring is substituted by an alkoxy group, yields only neutral η^5-methoxycyclohexadienyl complexes. In the case of the corresponding cationic arene-iron (II) complexes, the major product obtained after hydride addition is also a neutral η^5-methoxy-cyclohexadienyl complex and the minor products are demethoxy-cyclohexadienyl derivatives [2]. Hydride addition to neutral arenetricarbonylchromium complexes has never been reported in the literature [3]. In this communication, we describe the cleavage of an ether by the action of Et_3BHLi on neutral arenetricarbonylchromium complexes.

3-Ethyl-anisoletricarbonylchromium complex [4] (1) reacts with Et_3BDLi in refluxing THF for 2h giving quantitatively deutero-3 ethylbenzenetricarbonylchromium (2) in agreement with an *ipso* S_NAr [5]: no isomer which could be obtained via a *cine* S_NAr [6] is detected.

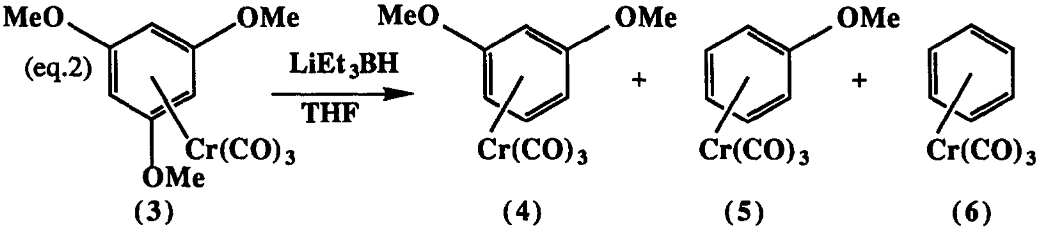
1, 3, 5 Trimethoxy-benzenetricarbonylchromium [4] (3) in solution in THF, treated with an excess of $LiEt_3BH$ (4 eq.) at 60°C for 2h gives quantitatively benzenetricarbonylchromium (6). Complex (3) treated with $LiEt_3BH$ (4.4 eq.) at 40°C for 20mn yields 1,3-dimethoxy-benzenetricarbonylchromium (4) (73% yield) and anisoletricarbonylchromium (5) (13% yield). This reaction, followed by ^1H NMR spectroscopy under anaerobic conditions, indicates the predominant formation of complex (4). 1,2,3-Trimethoxy-benzene tricarbonylchromium [4] reacts similarly with $LiEt_3BH$ to produce mainly the veratroletricarbonylchromium complex providing some information on the regioselectivity of this reaction : no complex (4) is formed which shows that the 2-position is less reactive to hydride addition. The same reaction takes place with oxygenated heterocycles (dibenzofuran, 9,9-dimethylxanthene, 1,4-benzodioxane and methyl-piperonyl-ether complexes) as will be described in a full paper.

In conclusion, our results show that an *ipso*-substitution occurs cleanly by treatment of alkoxyarenetricarbonylchromium complexes with $LiEt_3BH$. This reaction represents to our knowledge the first hydro-de-alkoxylation by $LiEt_3BH$ described in the literature in the case of alkoxyarenetricarbonylchromium complexes and could be used advantageously in organic synthesis. Indeed simple ethers are not normally cleaved by reducing agents in organic synthesis, although such cleavage has sometimes been reported with $LiAlH_4$-$AlCl_3$ [7], with a mixture of $LiAl(O\text{-}t\text{-}Bu)_3$ [8], with organo-alkali-metal compounds or with alkali metals [9-12].

(eq.1)



(eq.2)



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