Hydrodeamination of *N,N*-Dimethylaminoarenetricarbonylchromium Complexes *via cine* and *tele-meta* Nucleophilic Aromatic Substitutions

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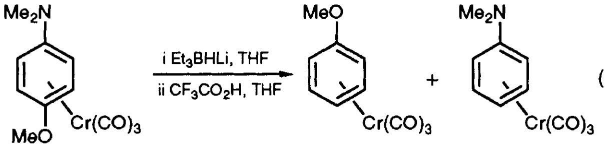
Treatment of *N,N*-dimethylaminoarenetricarbonylchromium complexes with Et_3BDLi gives after CF_3CO_2H treatment arenetricarbonylchromium complexes *via cine* and *tele-meta* nucleophilic aromatic substitutions which correspond to an unprecedented aromatic carbon–tertiary amine nitrogen cleavage.

We recently described[1] that hydrides such as Et_3BHLi or $LiAlH_4$ can cleave the carbon–oxygen bond of arylethertricarbonylchromium complexes *via* an *ipso*[2] aromatic substitution. Such a cleavage of an aryl–oxygen bond is well documented in organic chemistry.[3] In extending this reaction to the case of *p*-methoxy-*N,N*-dimethylanilinetricarbonylchromium complex, we obtained not only the cleavage of this C–O bond but unexpectively also the rupture of the C–N bond. We now report this unprecedented cleavage of an aryl–nitrogen bond of aminoarenetricarbonylchromium complexes by Et_3BDLi and some data relating to the mechanism of this hydrodeamination reaction. Herein we describe the results obtained with Et_3BDLi as nucleophile but analogous products are formed in the case of Et_3BHLi.

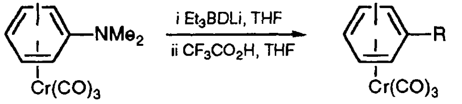
p-Methoxy-*N,N*-dimethylanilinetricarbonylchromium complex **1** [eqn. (1)] gives a mixture of the anisole (34% yield) and aniline (23% yield) derivatives **2** and **3** (ratio 60 : 40) after treatment with Et_3BHLi (5 equiv., 3 h, room temperature) and CF_3CO_2H [eqn. (1)].†



(1)

1 **2** **3**

Addition of Et_3BDLi to a tetrahydrofuran (THF) solution of *N,N*-dimethylanilinetricarbonylchromium complex **4a** yields monodeuteriobenzenetricarbonylchromium **5a** (23% yield), after CF_3CO_2H treatment [eqn. (2), R = H] and the starting substrate **4a**. In order to shed light on the regioselectivity of this substitution, we tried the same reaction with *o*-trimethylsilyl-*N,N*-dimethylanilinetricarbonylchromium complex **4b**‡ in order to obtain deuteriated trimethylsilyltricarbonylchromium: the ^1H NMR spectrum of which being known to be first order resolved,[4] should give the answer. In fact, addition of Et_3BDLi to a THF solution of complex **4b** [eqn. (2), R = *o*-$SiMe_3$] leads to the formation of complexes **5b** and **6b**‡ (ratio 20 : 80, 55% yield) both resulting from *tele-meta* nucleophilic aromatic substitution, a reaction for which we have previously discovered the mechanism in the case of phenoxyarenetricarbonylchromium complexes.[5]



(2)

4a; R = H
4b; R = *o*-$SiMe_3$
4c; R = *m*-$SiMe_3$

5a; R = H
5b; R = $SiMe_3$, *p*-D **6b**; R = $SiMe_3$, *o*-D

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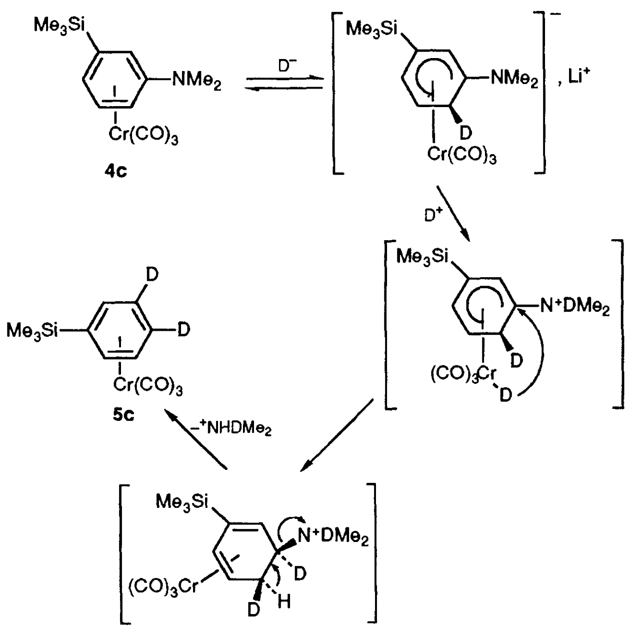
† *Typical reaction procedure*: To an anhydrous THF solution of a substituted *N,N*-dimethylaminoarenetricarbonylchromium complex is added a known excess of Et_3BDLi (1 mol dm^{-3} in THF, Aldrich, 1 to 5 equiv.) at room temperature. The reaction mixture is stirred for several hours under dry nitrogen and added dropwise to a THF solution of CF_3CO_2H in excess. After extraction, neutralization and separation by silica gel flash chromatography of the crude mixture the deuteriodeamination product is obtained and recrystallized in a mixture of acetone and light petroleum.

‡ Satisfactory spectral and analytical data have been obtained for all new compounds. ^1H NMR ($CDCl_3$), 200 MHz, Bruker AC for **4b**: δ 0.36 ($SiMe_3$, 9H, s), 2.63 (NMe_2, 6H, s), 4.91 (H-5, t, ^3J 6 Hz), 4.94 (H-3, d, ^3J 6 Hz), 5.49 (H-6, dd, ^3J 6 and ^4J 1 Hz), 5.60 (H-4, td, ^3J 6 and ^4J 1 Hz); for **4c**: 0.30 ($SiMe_3$, 9H, s), 2.87 (NMe_2, 6H, s), 4.72 (H-2, s), 4.81 (H-6, d, ^3J 7 Hz), 4.95 (H-4, dd, ^3J 7 and ^4J 2 Hz), 5.55 (H-5, t, ^3J 7 Hz); for **5b**: 0.28 ($SiMe_3$, 9H, s), 5.17 (H-3,5, d, ^3J 6 Hz), 5.41 (H2-6, 2H, d, ^3J 6 Hz); for **6b**: 0.28 ($SiMe_3$, 9H, s), 5.17 (H-3,5, dt, ^3J 6 Hz), 5.41 (H-6, d, ^3J 6 Hz), 5.49 (H-4, t, ^3J 6 Hz).



The same experiment carried out with the *meta* isomer **4c**‡ affords complex **5b**‡ [38% yield, eqn. (2), R = *p*-SiMe$_3$]. If CF$_3$CO$_2$D is used, complex **5c** is obtained which results from the incorporation of a second deuterium at the *meta* position relative to the SiMe$_3$ group. These data demonstrate clearly that a *cine* S$_N$Ar[6] reaction occurred and allow us to suggest the following speculative mechanism for the formation of the dideuteriated complex **5c** (Scheme 1).

In conclusion, our preliminary results clearly show that the cleavage of an aryl–nitrogen bond is possible if aminoarenetricarbonylchromium complexes are treated with Et$_3$BHLi. Using Et$_3$BDLi, it was possible to ascertain that these unexpected deuteriodeamination reactions proceed *via cine* and *tele-meta* nucleophilic aromatic substitutions. These unprecedented substitutions, even if the yields are not yet impressive, represent the first cleavage of the bond between an aromatic carbon and the nitrogen of a tertiary amine in chemistry.

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