## Double Nucleophilic Addition to Fluoroarenetricarbonylchromium Complexes

Françoise Rose-Munch\*, Laurent Mignon and Jean Paul Souchez

Laboratoire de Chimie Organique associé au CNRS, Université P. et M.Curie, Tour 44-45, 4 Place Jussieu, 75252 Paris Cedex 05, France

Key words: fluoroarenetricarbonylchromium complexes, nucleophilic aromatic substitution

Abstract: Double addition of carbanions to fluoroarenetricarbonylchromium complexes readily occurs giving disubstituted cyclohexadienes

The addition of two nucleophiles to a coordinated  $\pi$ -hydrocarbon is a synthetically important goal. A convenient route to trans difunctionalized 1,3-cyclohexadienes involves sequential nucleophile and electrophile addition on an arenetricarbonylchromium complex <sup>1</sup>, but the reaction is severely limited as to the range of nucleophiles and electrophiles. Another procedure involves a manganese-mediated route in order to obtain disubstituted 1,3-cyclohexadienes via the sequence: nucleophilic addition on the cationic manganese complex, reactivation of the neutral cyclohexadienyl derivative, and a second nucleophilic addition of the new cationic cyclohexadienyl manganese derivative <sup>2</sup>. In this communication, we report a "one pot" synthesis of 1,3-disubstituted cyclohexadienes involving a double nucleophilic addition to fluoroarenetricarbonylchromium complexes.

p-Fluorotoluenetricarbonylchromium complex 1 reacts with 2 equivalents of 2-lithio 2-methyl propionitrile in solution in THF to give, after 5 days at -30°C and acidic treatment under a CO atmosphere, the cyclohexadiene 5\* (47% yield) and traces of complex 2\* (7% yield). Compound 5 is obtained with a 75% yield if the reaction mixture is left several weeks instead of 5 days.

Similarly, 2,6-dimethylfluorobenzenetricarbonylchromium complex 6 reacts with 2-lithio 2-methyl propionitrile using the same experimental conditions to afford after 5 days the cyclohexadiene 7 (32% yield) and complex 8\* (13% yield, eq.2).

Formation of the cyclohexadienes 5 and 7 can be easily explained. For example, in the case of complex 1, the first equivalent of carbanion adds regioselectively on the carbon bearing the fluoro leaving group (*ipso* nucleophilic aromatic substitution  $S_NAr$ ), yielding a new complex 2. The second equivalent adds also regioselectively to this complex in order to give an anion 3 which reacts with H<sup>+</sup> and CO to yield the observed cyclohexadiene 5 via a chromium hydride <sup>3</sup> 4. Of course, complex 2 reacts with one equivalent of LiCMe<sub>2</sub>CN to

give after CF3CO2H treatment the cyclohexadiene 5 in the presence of CO. The precise stucture of cyclohexadiene 5 has been unambigously determined by the NOE effect between the C-7 methyl group and the H-5 hydrogen, definitively proving that the second carbanion adds to the position *ortho* to the methyl group.



In conclusion, our results describe the first double nucleophilic addition of the same carbanion to fluoroarenetricarbonylchromium complexes, to give rise to a direct synthesis of difunctionalized cyclohexadienes.

\*Satisfactory spectral and analytical data have been obtained for all new compounds.<sup>1</sup>H NMR (CDCl<sub>3</sub>), 200MHz, Bruker AC.2: 5.61 (2H, H-2 and H-6, d, J=6.8); 5.09 (2H, H-3 and H-5, d, J=6.8); 2.20 (3H, Ar-Me, s); 1.68 (6H, CMe<sub>2</sub>, s). 5: 5.98 (1H, dd, H-3, J=5.6 and 1.4); 5.88 (1H, H-2, d, J=5.6); 2.56 (2H, H-6, d, J=4.9); 2.29 (1H, H-5, t, J=4.9); 2.01 (Me, s br); 1.47 (6H, CMe<sub>2</sub>, d, J=1.4); 1.36 (6H, CMe<sub>2</sub>, d, J=2.7). 8: 5.51 (1H, t, H-4, J=6.3); 4.97 (2H, d, H-3 and H-5, J=6.3); 2.50 (3H, s, Ar-Me); 1.93 (6H, s, CMe<sub>2</sub>). We thank Prof.N.Platzer and O.Convert for NMR assistance, UNICA for financial support (J.P.S.).

- 1 a) E.P.Kündig, Pure and Appl. Chem., 1985, 57, 1855.
  - b) E.P.Kündig, A.F.Cunningham, P.Paglia, D.P.Simmons, G.Bernardinelli, Helv.Chim.Acta, 1990, 73, 386.
- 2 R.D.Pike, D.A.Sweigart, Synlet., 1990, 10, 565.
- 3 J.C.Boutonnet, F.Rose-Munch, E.Rose, A.Semra, Bull.Soc.Chim.Fr., 1987, 640.

(Received in France 22 July 1991)