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Preliminary communication

RECOVERY OF CHROMIUM HEXACARBONYL AFTER NUCLEOPHILIC REACTIONS OF ARENECHROMIUM TRICARBONYL COMPLEXES

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Summary

The arenechromium tricarbonyl complexes $C_6H_4R_2Cr(CO)_3$, (R = H, $CHMe_2$), obtained from arenes $C_6H_4R_2$ and $Cr(CO)_6$, react with nucleophiles (Nu = $CH(CH_3)CN$, $CH(CH_3)CO_2$-t-Bu), to form adducts which give, after treatment with CF_3CO_2H under carbon monoxide, the substituted cyclohexadienes $C_6H_5R_2Nu$ (R = H, $CHMe_2$) and $Cr(CO)_6$ in good yield.

The reactivity of arenechromium tricarbonyl complexes towards nucleophilic reagents is well documented [1]. As a synthetic method, the nucleophilic reactions of these complexes suffer from the disadvantage that the necessary decomplexation from the metal (in order to give the product V) is always brought about by oxidative reactions, which lead to chromium(III) compounds [1b], unsuitable for complexing further molecules of the substrate arene [2]. We describe below a method in which the decomplexation from the metal produces chromium hexacarbonyl, suitable for complexing further molecules of the substrate [3].

When treated at −70°C with solutions of the lithium salts [1c] prepared from propionitrile or t-butyl propionate [4], substrates I led to solutions of adducts II (see Scheme 1), which were added at −70°C to an excess of trifluoroacetic acid [1c] under an atmosphere of carbon monoxide.

In the case of IIb, use of a 1 bar CO pressure directly gave a mixture of dienes IVb in 83% yield, whereas, in the case of IIa, the same reaction conditions led to isolation of intermediate IIIa [5,6]. Transformation of IIa into the mixture of dienes IVa was only possible (in 85% yield) at higher CO pressure (80 bars, room temperature). In both cases the diene mixtures [5] were separated by chromatography from the chromium hexacarbonyl, produced

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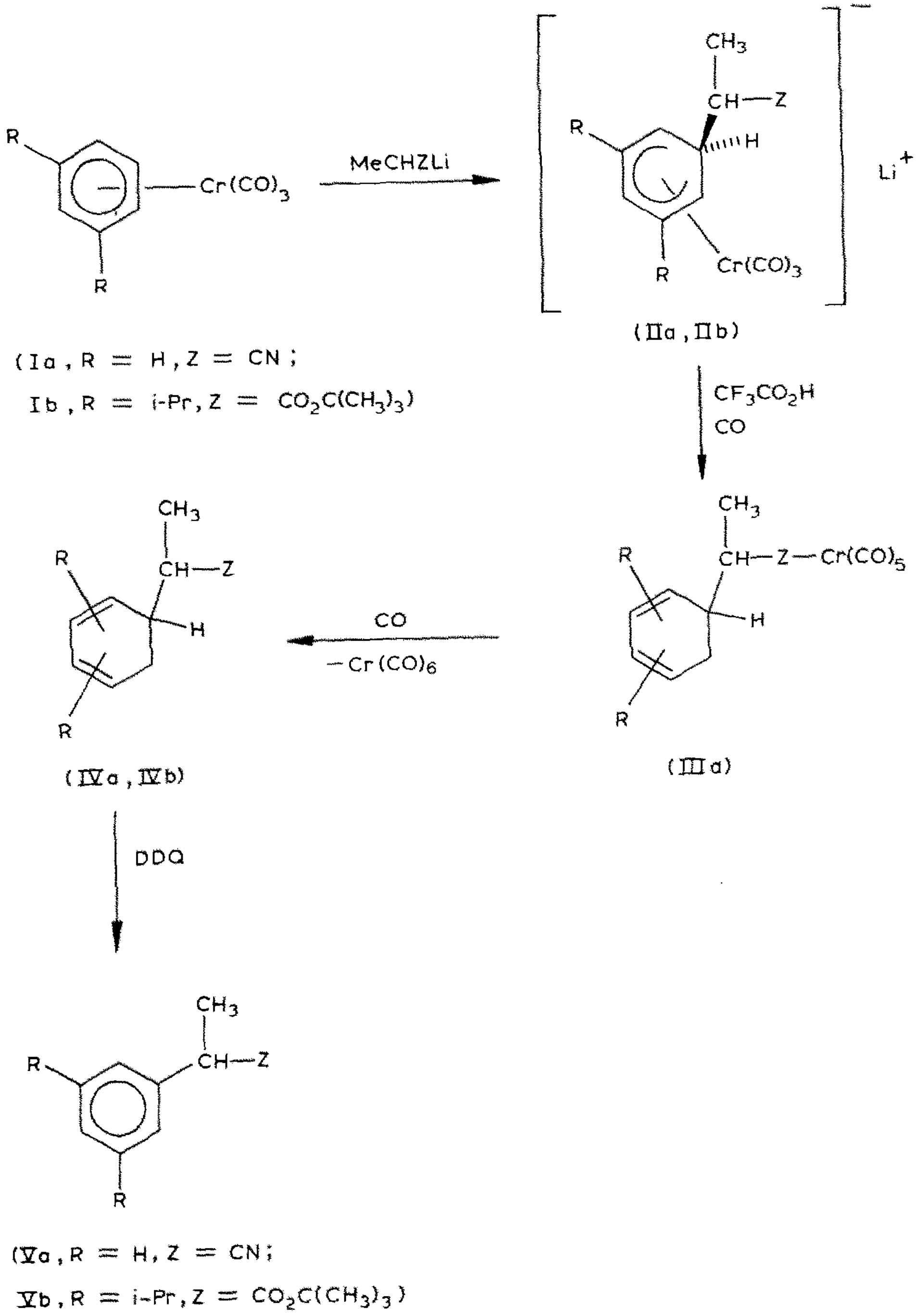

SCHEME 1

in 75% yield from Ia and 78% yield from Ib. Oxidation of the diene mixtures IVa and IVb by dicyanodichloro-*para*-benzoquinone (DDQ) [2a] gave the corresponding arenes Va and Vb in 90 and 70% yields, respectively [5].

The diene mixtures IVa and IVb could also be transformed into arenes Va and Vb simply by distillation at atmospheric pressure.

These examples clearly show that substrate arenes which react with chromium hexacarbonyl [3] to give arenechromium tricarbonyl complexes I, can be transformed in good yields into dienes IV or arenes V, with substantial recovery of chromium hexacarbonyl, thus allowing a cyclic, if not a catalytic process.

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2 This problem has been in the mind of several investigators, but no practical solution has previously been found; see for example: (a) M.F. Semmelhack, H.T. Hall, R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu and J. Clardy, J. Amer. Chem. Soc., 101 (1979) 3535; (b) G. Carganico, P. Del Buttero, S. Maiorana and G. Riccardi, J. Chem. Soc. Chem. Comm., (1978) 989.

3 C.A. Mahaffy and P.L. Pauson, Inorg. Synth., 19 (1979) 154.

4 Tetrahydrofuran solution for Ia tetrahydrofuran/hexamethylphosphotriamide (1/1) solution for Ib.

5 All the compounds give analyses and spectral data in agreement with the proposed structures.

6 Other nitrilechromium pentacarbonyl complexes have been obtained by other methods; see for example (a) L. Knoll and W. Wolff, Chem. Ber., 112 (1979) 2709; (b) M.F. Semmelhack, J.J. Harrison and Y. Thebtaranonth, J. Org. Chem., 44 (1979) 3275.