

## Preliminary communication

### Isotopic hydrogen exchange in bisarenechromium complexes

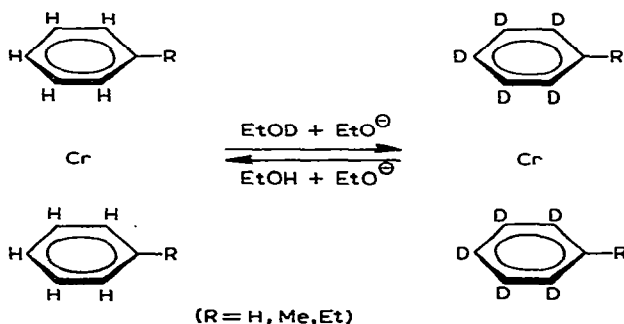
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Metalation is the only substitution reaction known for the  $\pi$ -aromatic ligands of bisarenechromium complexes<sup>1-3</sup>.

We have found that the hydrogen atoms of bisarenechromium complexes readily undergo isotopic hydrogen exchange under conditions of protophilic substitution, in the presence of bases. For example, isotopic equilibrium is reached after several hours in alcohol solutions in the presence of alkali metal alcoholates.



The kinetics of the hydrogen exchange were measured for dibenzenechromium in the alcohol/benzene medium in the presence of sodium alcoholate. The first order rate constant was found to be equal to  $8.35 (\pm 0.14) \times 10^{-5} \text{ sec}^{-1}$  at 45° (molar ratio of  $(\text{C}_6\text{H}_6)_2\text{Cr}/\text{EtOD}/\text{C}_6\text{H}_6/\text{EtONa} = 1/36/94/1.7$ ).

Under similar conditions, it was shown for ditoluenechromium and bis(ethylbenzene)chromium that both the  $\pi$ -aromatic ring hydrogens and those of the side chain may enter the hydrogen exchange reaction.

The cations of bisarenechromium complexes  $[(\text{Ar})_2\text{Cr}]^+\text{I}^-$  were found to undergo hydrogen exchange under even milder conditions; the reaction proceeds at an appreciable rate in aqueous alkali. The rate constant of hydrogen exchange in

bisarenechromium iodide in aqueous potassium hydroxide solution was found to be equal to  $\sim 0.6 \times 10^{-7} \text{ sec}^{-1}$  at  $50^\circ$  and the molar ratio of  $[(C_6H_6)_2Cr]^+I^-/D_2O/KOD = 1/599/6.8$ . For ditoluenechromium iodide under the same conditions, this value was  $\sim 0.3 \times 10^{-7} \text{ sec}^{-1}$ . It should be noted that this is the first example of a substitution in the  $\pi$ -aryl ligand part of the cations of bisarenechromium complexes.

It has been established that the rate of isotopic hydrogen exchange for both neutral chromium complexes  $[(Ar)_2Cr]^0$  and cations  $[(Ar)_2Cr]^+I^-$  increases in proportion to the concentration of base, while alkyl groups in the benzene ring reduce the rate of exchange. These results are in agreement with the protophilic mechanism described in which C-H bond cleavage in the  $\pi$ -aromatic ring is a rate-determining step of hydrogen exchange in reactions with bases.

It should be noted that under these conditions the aromatic hydrocarbons, benzene and its homologues, do not undergo hydrogen exchange. The exchange can only be achieved under more drastic conditions in liquid ammonia and in the presence of potassium amide<sup>4</sup>.

The isotopic hydrogen exchange reactions observed by us for arenechromium complexes  $[(Ar)_2Cr]^0$  and  $[(Ar)_2Cr]^+$  show that the  $\pi$ -aromatic ring hydrogen atoms in these complexes display an abnormally high acidity. This leads us to assume that base-catalysed substitution reactions are specific of bisarenechromium complexes.

#### REFERENCES

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