The Selective Reduction of Benzene to Cyclohexene

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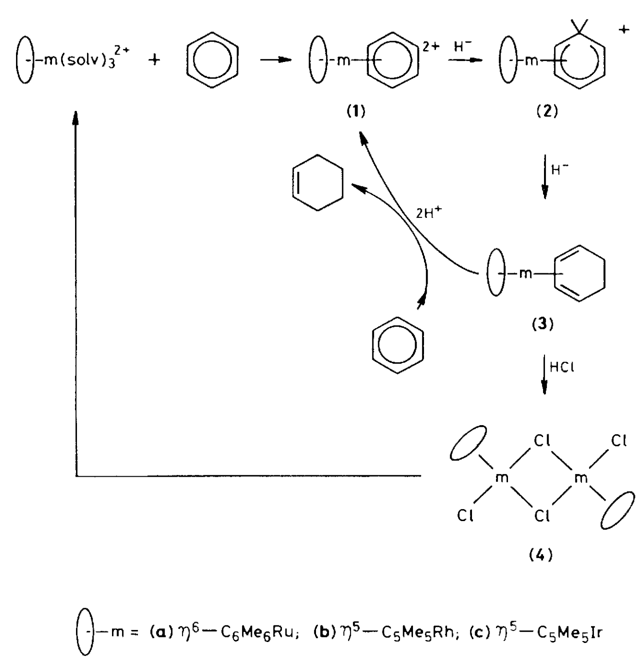
Hydride attack on a dicationic η^6-benzene complex gives the η^4-cyclohexadiene, which with acid yields cyclohexene; in the presence of benzene the initial η^6-benzene complex can be regenerated and a cycle established.

There are now a number of catalyst systems, heterogeneous,[1] homogeneous,[2] and mixed,[3] for the complete hydrogenation of benzene to cyclohexane. Synthetically and industrially, however, it would be of much greater interest to reduce partially benzene to cyclohexene. Unfortunately ΔG° (298 K) for benzene to cyclohexene (-23 kJ mol^{-1})[4] is substantially smaller than for the through reaction, benzene to cyclohexane (-98 kJ mol^{-1}).[4] Hence there is a strong tendency for



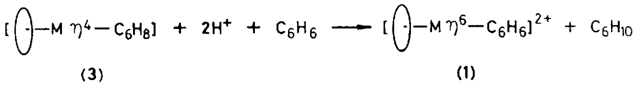
Scheme 1

the reaction, once it is initiated, to proceed all the way to cyclohexane. Nevertheless, heterogeneous catalysts promoting the hydrogenation to cyclohexene have been reported,[5] but the selectivity achieved was low (<20%).[6]

We describe here an alternative approach which yields cyclohexene with high selectivity and uses the strategy outlined in Scheme 1.

The formation of the η^6-benzene complexes (**1a**—**c**) and their reduction to the η^5-cyclohexadienyl complexes (**2a**—**c**) are well documented.[7] For example, (**2a**) is obtained in 86% yield by NaBH$_4$ reduction of (**1a**) (in H$_2$O at 0 °C), and (**2c**) is obtained similarly (76% yield).

We now find that a further hydride can be added to (**2**) under more forcing conditions[8] {*e.g.* Na[AlH$_2$(OCH$_2$CH$_2$OMe)$_2$] in toluene} to give the cyclohexadiene complexes (**3**) in good yield [*e.g.* 70% for (**3a**), 56% for (**3b**),[9] and 83% for (**3c**)]. Reaction of the cyclohexadiene complexes (**3**) with HCl



Scheme 2

liberates cyclohexene (≥92% yield) with 100% selectivity. The other product is (**4**), which can be easily reconverted into (**1**).[7]

Alternatively, the cyclohexadiene complex (**3**) can be treated with BF$_3$.2H$_2$O in benzene; this again gives only cyclohexene and directly regenerates the η^6-benzene dicationic complex (**1**), for example, (**1a**), 60%; (**1c**), 94% (Scheme 2). This reaction therefore completes the cycle where first two hydrides and then two protons are added to η^6-complexed benzene to give cyclohexene; this can be further developed into a process catalytic in the platinum metal complex.

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