Catalytic Function of the Phenyl-lithium-treated $Fe_4S_4Cl_4^{2-}$ Cluster in the Hydrogenation of *cis*- and *trans*-Stilbenes

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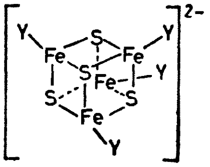
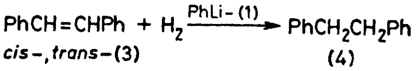
Summary The phenyl-lithium/iron–sulphur cluster (**1**) system exhibits catalytic activity in the hydrogenation of *cis*- and *trans*-stilbenes with molecular hydrogen under mild conditions.

The catalytic ability of the synthetic Fe_4S_4 cluster, which is a model compound for the active site of the bacterial enzyme hydrogenase,[1] in the hydrogenations of unsaturated compounds with molecular hydrogen has not yet been studied, although the cluster has been shown to act as an electron-transfer cocatalyst in the reduction of acetylene with a molybdenum catalyst.[2] Recently it has been reported that $Fe_4S_4^{2-}$-attached silica gels exhibit no catalytic activity in the hydrogenation of unsaturated compounds.[3] We have studied the hydrogenating ability of the Fe_4S_4 cluster with a labile terminal ligand which we thought might enhance cluster reactivity, and now report the first example of a hydrogenating system {prepared under hydrogen from $[Fe_4S_4Cl_4](Bu^n{}_4N)_2$ (**1**)[4] and phenyl-lithium in ether} which exhibits catalytic activity for the hydrogenation of *cis*- and *trans*-stilbenes (**3**) under mild conditions. Furthermore, we report that the phenyl-lithium/$[Fe_4S_4(SPh)_4](Bu^n{}_4N)_2$ (**2**) system exhibits no activity for such reactions, although the cluster (**2**) functions as an electron-transfer carrier in the reductions of carbonyl compounds.[5]



(1) Y = Cl

(2) Y = SPh



$$\underset{cis\text{-},trans\text{-}(3)}{PhCH{=}CHPh} + H_2 \xrightarrow{PhLi\text{-}(1)} \underset{(4)}{PhCH_2CH_2Ph}$$

The reactions were carried out as follows. The cluster (**1**) was added to a frozen solution of phenyl-lithium in degassed ether. The mixture, after melting, was stirred under atmospheric pressure of hydrogen at 0 °C for 30 min. In this process, biphenyl was produced by the reduction of the cluster (**1**) with phenyl-lithium, and absorption of hydrogen was observed. Furthermore, it was confirmed that the addition of a mixture of benzenethiol and diphenyl disulphide to the resulting solution leads to the formation of the cluster (**2**) in 90% yield. The black solution prepared was frozen again and *cis*- or *trans*-(**3**) was added under hydrogen. The mixture, after melting, was stirred vigorously under atmospheric pressure of hydrogen at room temperature for 3 h. The reactions were stopped by adding dilute hydrochloric acid. The product, 1,2-diphenylethane (**4**), was analysed by g.l.c. and the results are summarized in the Table. The yield was found to be

Table[a]

Molar ratio PhLi : (1) : (3)	% Yield of (4)[b] *cis*-(3)	 *trans*-(3)
8 : 1 : 4	0(20)	18
10 : 1 : 4	23(40)	29
12 : 1 : 4	86(2)	89
12 : 1 : 16	92(8)	38
16 : 1 : 4	94(0)	33

[a] 0·14 mmol of (**1**) in 6—8 ml of ether was used. [b] The yield of (**4**) is based on *cis*- and *trans*-(**3**). In the case of *cis*-(**3**), the yield of *trans*-(**3**) is shown in parentheses. The remainder was the unchanged substrate.

strongly dependent on the molar ratio of phenyl-lithium to (**1**) When the molar ratio was 4:1, no reaction occurred but the starting materials [*cis*- and *trans*-(**3**)] were recovered unchanged The optimal molar ratio to form (**4**) in high yield was 12.1 (Table) In addition, the (12.1) system exhibited catalytic activity in the hydrogenation of *cis*- and *trans*-(**3**) In the catalytic system, the yield of (**4**) from *cis*-(**3**) became higher than that from *trans*-(**3**) In the system giving (**4**) in low yield, the hydrogenation of *cis*-(**3**) was accompanied by isomerisation to form *trans*-(**3**) The hydrogenation of diphenylacetylene by the (12:1) system was compared with that of (**3**) Diphenylacetylene was also hydrogenated affording (**4**) in 77% yield together with *trans*-(**3**) in 3% yield [diphenylacetylene (**1**) = 4.1]

The phenyl-lithium/(**2**) system exhibited no activity for the hydrogenations of *cis*- and *trans*-(**3**), however, under similar conditions [PhLi:(**2**):(**3**) = 12 1 4], although diphenylacetylene was hydrogenated to *cis*- and *trans*-(**3**) in 6 and 8% yields, respectively The significant difference in activity between (**1**) and (**2**) indicates that the activity of the Fe_4S_4 cluster responsible for hydrogenations is induced by the labile terminal ligand

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[1] R H Holm, *Acc Chem Res* , 1977, **10**, 427

[2] G N Schrauzer G W Kiefer, K Tano, and D A Doemeny, *J Am Chem Soc* , 1974, **96** 641

[3] R G Bowman and R L Burwell, Jr , *J Am Chem Soc* , 1979, **101**, 2877

[4] G B Wong, M A Bobrik, and R H Holm, *Inorg Chem* , 1978, **17**, 578, R W Johnson and R H Holm, *J Am Chem Soc* , 1978, **100**, 5338

[5] H Inoue, N Fujimoto, and E Imoto, *J Chem Soc* , *Chem Commun* , 1977, 412, H Inoue, M Suzuki, and N Fujimoto, *J Org Chem* , 1979, **44**, 1722