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## Catalytic Function of the Phenyl-lithium-treated Fe<sub>4</sub>S<sub>4</sub>Cl<sub>4</sub><sup>2-</sup> 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,<sup>1</sup> 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.<sup>2</sup> Recently it has been reported that Fe<sub>4</sub>S<sub>4</sub><sup>2-</sup>-attached silica gels exhibit no catalytic activity in the hydrogenation of unsaturated compounds.<sup>3</sup> We have studied the hydrogenating ability of the Fe<sub>4</sub>S<sub>4</sub> 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  $[Fe_4S_4Cl_4](Bun_4N)_2$  (1)<sup>4</sup> and phenyllithium 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<sub>4</sub>S<sub>4</sub>(SPh)<sub>4</sub>](Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub> (2) system exhibits no activity for such reactions, although the cluster (2) functions as an electron-transfer carrier in the reductions of carbonyl compounds.<sup> $\delta$ </sup>

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 <sup>a</sup>
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Molar ratio	% Yield of (4) <sup>b</sup>	
PhLi:(1):(3)	cis-( <b>3</b> )	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

<sup>a</sup> 0.14 mmol of (1) in 6—8 ml of ether was used. <sup>b</sup> 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.

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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 cisand 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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