

Electron-transfer Reduction of Protons to Hydrogen mediated by a Phenyl-lithium-activated Fe_4S_4 Cluster

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A synthetic Fe_4S_4 cluster mediates the transfer of electrons from phenyl-lithium to protons from benzenethiol, in a homogeneous system, resulting in the generation of hydrogen.

The design of hydrogen-generating systems which incorporate a synthetic iron-sulphur cluster is of importance in connection with hydrogenase reactions. Recent studies have disclosed the reduction of acetylene to ethylene by the $\text{Fe}_4\text{S}_4(\text{SPh})_4^{3-}$ -acetic acid-acetic anhydride system in *N*-methylpyrrolidin-2-one¹ and by electrochemically reduced $\text{Fe}_4\text{S}_4(\text{SPh})_4^{2-}$ in

methanol/tetrahydrofuran, accompanied by the evolution of hydrogen,² and the reduction of protons from benzenethiol to hydrogen with $\text{Fe}_4\text{S}_4(\text{SPh})_4^{3-}$ in *N,N*-dimethylacetamide (though in low yield).³ We now report a novel hydrogen-generating system using a phenyl-lithium-activated cluster, $\text{Fe}_4\text{S}_4(\text{SPh})_4(\text{Bu}^n_4\text{N})_2$ (1), which transfers electrons from

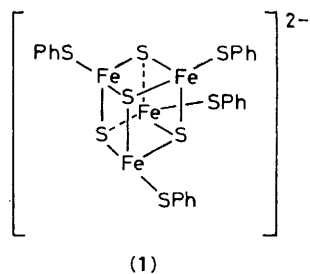
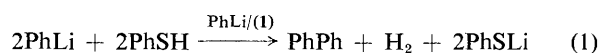


Table 1. Catalytic generation of H₂ using an iron-sulphur cluster.^a

PhLi:(1)	Solvent	mol/Fe ₄ S ₄ ^b		
		H ₂	9,9'-Bi-acridan	PhPh
4:1	Et ₂ O	0.4	0.4	0.9
8:1	Et ₂ O	1.0	0.8	1.9
8:1	Et ₂ O-HMPT	1.6	0.8	2.4
10:1	Et ₂ O	1.5	0.7	2.4
10:1	Et ₂ O-HMPT	2.2	0.8	2.9
12:1	Et ₂ O	1.8	0.7	2.6
16:1	Et ₂ O	1.1	0.7	1.9

^a (1), 0.2 mmol in Et₂O (8.8–11.2 ml) or Et₂O (7 ml)-HMPT (5 ml), PhSH:PhLi = 10:1; 0 °C, Ar. Time = 1 h (Et₂O) and 3 h (Et₂O-HMPT). ^b *i.e.* mol of product per Fe₄S₄ unit.

phenyl-lithium to protons to give *ca.* equimolar amounts of biphenyl and hydrogen [equation (1)].



The reactions were carried out as follows, using similar procedures to those used previously.⁴ The cluster (1) was added to a frozen solution of phenyl-lithium in degassed diethyl ether. The mixture, after melting, was stirred under argon at 0 °C for 30 min. To the resulting solution, a solution containing an excess of benzenethiol in degassed diethyl ether or hexamethylphosphoric triamide (HMPT) was added with stirring at 0 °C. Spontaneous hydrogen evolution was observed after the addition of the benzenethiol and the reaction went nearly to completion after 1 h (Et₂O) or 3 h (Et₂O-HMPT). In the former solvent the iron-sulphur cluster precipitated during the reaction; in the latter solvent the reaction system was homogeneous. As Table 1 shows, the amount

of hydrogen, measured by a volumetric technique, increased with increasing amounts of phenyl-lithium up to a molar ratio, PhLi:(1), of 12:1 and decreased above this molar ratio. The use of HMPT raised the efficiency of the hydrogen generation. The use of acetic acid and methanol instead of benzenethiol [AcOH or MeOH: PhLi:(1) = 20 or 30:10:1 in ether] also resulted in the generation of hydrogen (1.7 or 1.1 mol per Fe₄S₄ unit, respectively).

To investigate the oxidation state of the iron-sulphur cluster after the reaction, acridine was added to the mixture after 1 h (Et₂O) or 3 h (Et₂O-HMPT) and the amount of 9,9'-biacridan produced was determined [acridine is not reduced by (1)]. Acridan was not produced in this reaction. The cluster (1) was regenerated by treatment with acridine. As Table 1 shows, the iron-sulphur cluster is reduced after the generation of hydrogen and can supply 1 or 2 electrons to acridine. Furthermore, after the acridine was added, the amount of biphenyl produced was measured by g.l.c. As Table 1 shows, the amount of biphenyl produced coincides reasonably with the total amount of hydrogen and 9,9'-biacridan produced, indicating that the reduced cluster mediates the transfer of electrons between phenyl-lithium and protons to give biphenyl and hydrogen. In addition, we found that the hydrogen-generating system consisting of phenyl-lithium, (1), and benzenethiol (12:1:24 molar ratio) in diethyl ether reduces diphenylacetylene to *cis*- and *trans*-stilbenes (0.08 and 0.15 mol/Fe₄S₄, respectively) with concomitant generation of hydrogen (1.4 mol/Fe₄S₄).

The above results provide evidence that a phenyl-lithium-activated iron-sulphur cluster exhibits catalytic activity for the generation of hydrogen by transferring electrons from phenyl-lithium to protons.

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