

A Phenyl-lithium Activated Fe_4S_4 Cluster as a Hydride Transfer Agent in the Hydrogenation of Carbonyl Compounds

Hiroo Inoue,* Yoshiharu Nagao, and Eiichi Haruki

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

A phenyl-lithium activated Fe_4S_4 cluster acts as a hydride transfer agent in the hydrogenation of carbonyl compounds with hydrogen gas to give alcohols and exhibits substrate selectivity in the hydrogenation.

Recently we have reported that a synthetic Fe_4S_4 cluster, a model compound for the active centre of hydrogenase, catalyses the hydrogenation of olefins with hydrogen gas in the presence of phenyl-lithium.¹ However, the function of the activated Fe_4S_4 cluster in this system is not known. We now report that phenyl-lithium treated $[\text{Fe}_4\text{S}_4\text{Cl}_4][\text{Bu}^n\text{N}]_2$ (**1**) acts as a hydride transfer agent for the selective hydrogenation of carbonyl compounds using hydrogen gas.

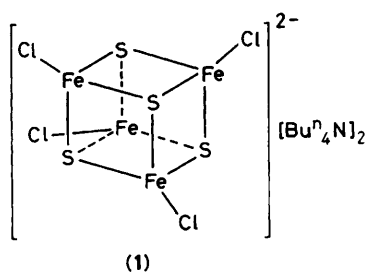
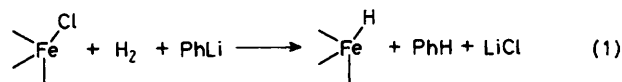
A solution of the cluster (**1**) and phenyl-lithium in degassed diethyl ether was stirred under hydrogen (1 atm) at 0 °C for 1 h, using procedures similar to those described previously.¹ The absorption of hydrogen began immediately and was completed in *ca.* 30 min. During this reaction, no precipitation occurred. The resulting black solution was treated with 1,2-dibromoethane (two moles per mole of phenyl-lithium) at room temperature for 2 h and subsequently with oxygen gas (atmospheric pressure) for 12 h. Analysis by g.l.c. showed that benzene is produced in quantities close to that of hydrogen absorbed (Table 1), thus indicating that molecular hydrogen is cleaved to form benzene. Biphenyl was produced by the oxidation of phenyl-lithium (Table 1). Furthermore, it was found that, when $\text{Fe}_4\text{S}_4(\text{SPh})_4^{2-}$ was used instead of (**1**), the amount of hydrogen absorbed, with $\text{PhLi}:\text{Fe}_4\text{S}_4$ molar ratios of (8 and 10):1, was 0.1 and 0.2 mol/ Fe_4S_4 unit respectively,

much less than in the case of (**1**). This observation indicates that an exchangeable ligand such as Cl^- serves to form a reactive site on the Fe_4S_4 cluster which activates hydrogen. From these results, it is postulated that the cluster (**1**) and phenyl-lithium react *via* the cleavage of a hydrogen molecule to form Fe_4S_4 cluster hydride species with an oxidation state² $[4\text{Fe}^{\text{II}}]$ (reaction 1). This hydride species is then active in the hydrogenation of carbonyl compounds; results are shown in Table 2. The reactions were carried out as follows. After complete absorption of hydrogen by the (**1**)-PhLi-diethyl ether solution, the carbonyl compound or a mixture of compounds was added and stirred under hydrogen at room temperature for 20 h. The aliphatic carbonyl compounds were hydrogenated to the corresponding alcohols in amounts equivalent to that of the hydrogen absorbed (Table 2). The hydrogenation of acetophenone and benzaldehyde preceded electron transfer reduction³ to the respective pinacols. When the PhLi-(**1**) molar ratio was 10:1, however, the amounts of alcohol and pinacol products produced from acetophenone and benzaldehyde were 0.5 and 1.3, and 0.7 and 1.3 mol/ Fe_4S_4 unit respectively, thus resulting in a lowering of the hydride-transfer efficiency. This indicates that the hydrogenation and the electron-transfer reduction are controlled by the amount of phenyl-lithium used. Furthermore, it was found that the

Table 1. Absorption of hydrogen and production of benzene and biphenyl.^a

Molar ratio PhLi : (1)	H ₂ ^b	mol/Fe ₄ S ₄ unit PhH	Ph-Ph
8 : 1	0.6	0.7	3.1
10 : 1	1.2	1.4	4.2
12 : 1	2.4	2.7	4.6

^a Conditions: 0.2 mmol (1) in Et₂O (6–8 ml) under H₂, 0 °C, 1 h. PhH and Ph-Ph were analysed by g.l.c. after dilute hydrochloric acid was added to the reaction mixture. The quantities of the products were corrected by subtracting those produced in the absence of (1). ^b Ref. 1.



hydride species exhibits substrate selectivity in the hydrogenation of ketone *vs.* ester, aldehyde *vs.* ester, and aldehyde *vs.* ketone (Table 2). The selective hydrogenation is considered to be governed by the ease of co-ordination of the carbonyl compound to the Fe₄S₄ cluster.

Table 2. The hydrogenation of carbonyl compounds by the PhLi-(1)-H₂ system.^a

Carbonyl compound	Reduction product ^b (mol/Fe ₄ S ₄ unit)
PhCOMe ^c	{ PhCH(OH)Me (2.7) Ph(Me)CH(OH)CH-(OH)(Me)Ph (0.2)
C ₉ H ₁₉ COMe	C ₉ H ₁₉ CH(OH)Me (3.2)
PhCHO ^c	{ PhCH ₂ OH (1.6) PhCH(OH)CH(OH)Ph (0.9)
C ₇ H ₁₅ CHO	C ₈ H ₁₇ OH (2.2)
C ₇ H ₁₅ CO ₂ Me	{ C ₇ H ₁₅ CO ₂ C ₈ H ₁₇ (1.4) C ₈ H ₁₇ OH (0.2)
C ₉ H ₁₉ COMe/C ₇ H ₁₅ CO ₂ Me	{ C ₇ H ₁₅ CO ₂ CH(OH)C ₉ H ₁₉ (2.0) C ₉ H ₁₉ CH(OH)Me (0.3)
C ₉ H ₁₉ CHO/C ₇ H ₁₅ CO ₂ Me	{ C ₇ H ₁₅ CO ₂ C ₁₀ H ₂₁ (2.8) C ₁₀ H ₂₁ OH (0.3)
C ₉ H ₁₉ COMe/C ₇ H ₁₅ CHO	C ₈ H ₁₇ OH (0.9)

^a Conditions: 0.2 mmol (1) in Et₂O (7–8 ml) under H₂, room temperature, 20 h. PhLi : (1) : carbonyl compound = 12 : 1 : 10 and in the case of a mixture, 12 : 1 : (10 + 10). Product analysis was by g.l.c.

^b The remainder is mainly aldol condensation products. ^c Carbonyl compound : (1) = 4 : 1.

These results provide evidence for mediation by a phenyl-lithium activated Fe₄S₄ cluster in the cleavage of hydrogen for subsequent transfer of a hydride to a carbonyl compound.

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