Substrate Selectivity of the Phenyl-lithium Activated $Fe_4S_4Cl_4^{2-}$ Cluster as a Catalyst in the Hydrogenation of Octenes with Hydrogen Gas

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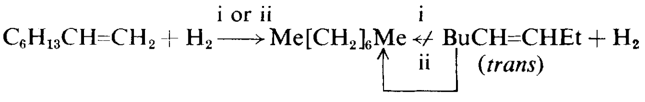
The phenyl-lithium activated $Fe_4S_4Cl_4^{2-}$ cluster exhibits catalytic activity and substrate selectivity in the hydrogenation of octenes with hydrogen gas.

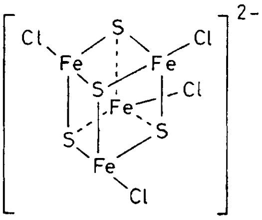
The synthetic Fe_4S_4 cluster is of interest as a model compound for the active site of bacterial hydrogenase. Recently we have shown that the phenyl-lithium/$Fe_4S_4Cl_4(Bu^n_4N)_2$ (**1**) system exhibits catalytic activity in the hydrogenation of *cis*- and *trans*-stilbenes with hydrogen gas.[1] However, further details of the function of the Fe_4S_4 cluster as a hydrogenation catalyst are not known. We now report that the phenyl-lithium activated cluster (**1**) exhibits remarkable substrate selectivity in the hydrogenation of terminal *vs.* internal double bonds when the amount of phenyl-lithium used is controlled or hexamethylphosphoric triamide (HMPT) is used as a cosolvent (Scheme 1).



$$C_6H_{13}CH{=}CH_2 + H_2 \xrightarrow{\text{i or ii}} Me[CH_2]_6Me \underset{\xleftarrow[\text{ii}]{}}{\overset{\text{i}}{\not\leftarrow}} \underset{(trans)}{BuCH{=}CHEt} + H_2$$

Scheme 1. i, (4:1)PhLi/(**1**) or PhLi/(**1**)/HMPT; ii, (8:1)PhLi/(**1**).

The reactions were carried out as follows, using procedures similar to those described previously.[1] The cluster (**1**)[2] was added to a frozen solution of phenyl-lithium in degassed diethyl ether. The mixture, after melting, was stirred under atmospheric pressure of hydrogen at 0 °C for 30 min. During this time, the absorption of hydrogen was observed: 0.6, 1.2, and 2.3 mol/Fe_4S_4 unit with PhLi:Fe_4S_4 molar ratios of 8:1, 10:1, and 12:1, respectively. The resulting black solution was



(**1**)

Table 1. Catalytic hydrogenation of octenes using the phenyl-lithium/(**1**)/H_2 system.[a]

Octenes	PhLi:(**1**)	Yield, %[b]		
		Octane	Oct-2-ene[c]	Other octenes
trans-Oct-1-ene	4:1	49	15	35
	6:1	79	15	6
	8:1	92	0	Trace
	12:1	81	6	11
	16:1	55	28	17
trans-Oct-2-ene	4:1	3	91	0
	8:1	52	27	17
trans-Oct-3-ene	4:1	0	0	95
	6:1	11	0	82
	8:1	78	5	15
trans-Oct-4-ene	8:1	71	3	17

[a] (**1**), 0.2 mmol in Et_2O (8.8—9.6 ml), octene:(**1**) = 50:1; room temp., 20 h. [b] Based on octenes. [c] A mixture of *cis*- and *trans*-oct-2-enes.

Table 2. Substrate selectivity of the PhLi/(**1**)/HMPT system in the hydrogenation of octenes with H_2.[a]

	Yield, %[b]		
Octenes	Octane	Oct-2-ene	Other octenes
trans-Oct-1-ene	85	5	3
trans-Oct-2-ene	3	93	0
trans-Oct-3-ene	1	0	93
trans-Oct-4-ene	0	0	100

[a] (**1**), 0.2 mmol in Et_2O (7.4 ml)–HMPT (5 ml), PhLi : (**1**) : octenes = 12 : 1 : 50; room temp., 20 h. [b] Based on octenes.

frozen again and a solution containing octenes (50 mol/Fe_4S_4 unit) in degassed diethyl ether or HMPT was added under hydrogen. The mixture, after melting, was stirred vigorously under atmospheric pressure of hydrogen at room temperature for 20 h. The reactions were stopped by adding dilute hydrochloric acid. The products were analysed by g.l.c. and the results are summarized in Tables 1 and 2.

The hydrogenation efficiency in the formation of octane was found to be strongly dependent on the molar ratio of phenyl-lithium to (**1**). The yield of octane increased with increasing amounts of phenyl-lithium up to a molar ratio of 8—12 : 1 and decreased above this. In the system giving octane in low yield, hydrogenation was accompanied by isomerisation. At the optimal molar ratio of 8 : 1, all octenes were hydrogenated efficiently to octane (Table 1). Furthermore, it was confirmed that the cluster is converted into $Fe_4S_4(SPh)_4^{2-}$ after the reaction by treatment with benzenethiol and diphenyl disulphide. When the PhLi : (**1**) molar ratio was 4 : 1, the catalytic system exhibited selectivity by hydrogenating oct-1-ene much more readily than oct-2-ene and oct-3-ene, thus limiting substrates to the least-hindered olefins. In addition, the 5 : 1 PhLi/(**1**) system exhibited substrate selectivity in the competitive hydrogenation of an equimolar mixture of dec-1-ene and oct-3-ene (50 mol/Fe_4S_4 unit) to give decane in 53% yield without the formation of octane, although the isomerisation of dec-1-ene occurred. Furthermore, when HMPT was used as the cosolvent, it was found that with a PhLi : (**1**) molar ratio of 12 : 1, oct-1-ene is hydrogenated to octane in a high yield, but the hydrogenations of oct-2-, -3-, and -4-enes are retarded significantly (Table 2). This function of the PhLi/(**1**) (12 : 1)/HMPT system was demonstrated by the hydrogenation of oct-4-yne (50 mol/Fe_4S_4 unit) which resulted in *cis*- and *trans*-oct-4-enes only in 29% yield after 20 h without the formation of octane. In contrast with the function of cluster (**1**), a mononuclear complex consisting of phenyl-lithium and iron(III) chloride (2—4 : 1 molar ratio) in diethyl ether–HMPT did not exhibit selectivity toward oct-1-ene *vs.* oct-3-ene.

The above results provide evidence that the catalytic activity of the phenyl-lithium activated cluster (**1**) is controlled selectively by phenyl-lithium and HMPT favouring hydrogenation of the terminal double bond of unsaturated systems.

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