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Tetrahedron Letters 48 (2007) 4539–4541

Tetrahedron Letters

Fe-Catalyzed reactions of 2-chloro-1,7-dienes and allylmalonates

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Received 23 February 2007; revised 19 April 2007; accepted 27 April 2007
Available online 3 May 2007

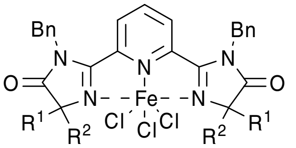
Abstract—Fe(III)(BIAP)Cl_3 complex catalyzes alkylative cyclization of 2-chloro-1,7-heptadiene in the presence of triethylaluminum. It also catalyzes deallylation of certain 2-allyl-2-substituted malonates under the same reaction conditions.

Although iron is one of the most abundant metals found in nature, the use of its compounds as catalysts for the formation of C–C bonds in organic synthesis is rather limited, especially in comparison with other transition metals (Ni, Pd, Rh, etc.). Problems associated with the use of the iron compounds as the catalysts often stem from the fact that the catalytically active species are sensitive to reaction conditions used and often lack generality with respect to the structure of reactants. On the other hand, iron compounds are able to catalyze a plethora of interesting transformations,[1] and are thus attractive targets for further research. In iron-catalyzed cross-coupling reactions, for example, after pioneering work by Kochi in the early 1970s,[2] iron catalyzed processes made a comeback in the work of Fürstner and Knochel, who showed its generality.[3,4]

We have recently reported a new process: an alkylative cyclization of 2-chloro-1,7-dienes in the presence of a catalytic amount of a Fe-phosphine complex and trialkylaluminums. The main feature of this reaction was an unprecedented iron-catalyzed alkyl group (Et, Me) transfer from the trialkylaluminum to the cyclized products.[5] In addition we observed that under the same reaction conditions certain allylmalonate substrates underwent deallylation. The latter process was later shown to proceed also under Ni-[6] and Rh-[7] catalyses.

Because of our interest in the development of new Fe-catalyzed reactions, we decided to search for a better iron-based catalytic system, especially because Fe-phosphine complexes lack generality with respect to the substrate. We envisioned that a change of the phosphorus-based ligand for a nitrogen-based one (BIAP = bis-(imidazolonyl)pyridine) could result in the formation of more powerful catalysts. This assumption was based on the results obtained during Rh-catalyzed deallylations, in which it was clearly demonstrated that the BIAP ligated complexes are more catalytically active then those with phosphines.[7]

At the outset, the starting Fe(III)(BIAP)Cl_3 **1a–e** complexes were prepared according to the previously reported procedure (Fig. 1).[8] As a test reaction we chose alkylative cyclization of 9-allyl-9-(2-choroallyl)-9*H*-fluorene **2**. The reaction was carried out under standard conditions.[9] The results obtained are presented in Table 1. In all cases the reaction was almost complete within 1 h and prolonging the reaction time to 24 h did not result in substantial improvement in the yield of the cyclized product **3**. This is in sharp contrast with



1a, $R^1 = CH(CH_3)_2$, $R^2 = Me$
1b, $R^1 = Ph$, $R^2 = Me$
1c, $R^1 = CH_2CH(CH_3)_2$, $R^2 = Me$
1d, $R^1 = C(CH_3)_3$, $R^2 = Me$
1e, $R^1 = R^2 = Me$

Figure 1. Fe(III)(BIAP)Cl_3 complexes **1a–e**.

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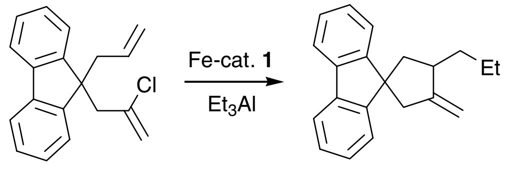
doi:10.1016/j.tetlet.2007.04.143

Table 1. Alkylative cyclization catalyzed by **1a**–**e**[a]



2 **3**

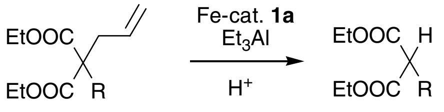
Catalyst **1**	*t* (h)	**3**, Yield[b] (%)
1a	1	35 (53)[c]
	24	48 (61)[c]
1b	1	11
	24	27
1c	1	26
	24	38
1d	1	30
	24	38
1e	1	26
	24	36

[a] 5 mol % of the catalyst.

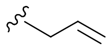
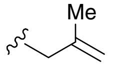
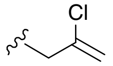
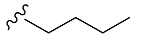
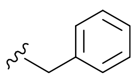
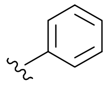
[b] GC yields.

[c] 15 mol % of the catalyst.

Table 2. Deallylation catalyzed by Fe(III)(BIAP)Cl$_3$ complex **1a**[a]



4 **5**

Malonate **4**	R	**5**, Yield[b] (%)
4a		**5a**, 13
4b		**5b**, 26
4c		**5c**, 83 (48)[c]
4d		**5d**, 59 (45)[c]
4e		**5e**, 38
4f		**5f**, 91

[a] 5 mol %; Et$_3$Al, 200 mol %, 20 °C, 24 h.

[b] ^{1}H NMR yields.

[c] 1 h.

Fe-phosphine catalysts, where the yield gradually increased with the reaction time. As for the catalytic activity, the best yield of **3** was obtained with catalyst **1a**. It was slightly higher when 15 mol % of **1a** was used (see Table 2).

Next we turned our attention to the deallylation reaction, because in our previous experiments the Fe-phosphine complex catalyzed the reaction only with allyl(chloroallyl)malonate **4c**.[5] Catalyst **1a** was used because it had proved to be the most active catalyst in the alkylative cyclization, and reactions were carried out under standard conditions.[10] The deallylation of diallylmalonate **4a** proceeded with low conversion giving only a low yield (13%) of allylmalonate **5a** together with recovered starting material. Similarly allyl(methallyl)malonate **4b** was deallylated and also in low yield giving only 26% of methallylmalonate **5b**. On the other hand, the deallylation of allyl(chloroallyl)malonate **4c** gave rise to the deallylated product, (chloroallyl)malonate **5c**, in high 83% yield (48% after 1 h). Also, the deallylation of butyl(allyl)malonate **4d** proceeded to a reasonable extent: butylmalonate **5d** was formed in 59% yield (45% in 1 h). The efficiency of deallylation fell again in the case of allylbenzylmalonate **4e**, which gave only 38% of **5e**. Surprisingly, almost quantative deallylation was observed for allylphenylmalonate **4f**: 91% of **5f**. Attempts to deallylate diallylcoumaranone failed completely, the starting material remaining intact.

In summary, we have shown that Fe(III)-BIAP complexes **1** can catalyzed alkylative cyclization, the catalytic activity of **1a** being close to that of Fe-phosphine complexes.[5] As for the deallylation, the reactions carried out in the presence of **1a** gave better results than Fe-phosphine complexes. Nonetheless, the results again showed that the course of the reaction is highly dependent on the structure of substrates and is rather unpredictable. The scope of the reaction with respect to other substrates as well as further elaboration of the ligand structure is under investigation. Spectral characteristics (^{1}H and ^{13}C NMR) of all formed compounds were in agreement with the previously published data.[6,7]

Acknowledgements

We gratefully acknowledge financial support by the Ministry of Education of the Czech Republic to the Center for Structural and Synthetic Application of Transition Metal Complexes (Project No. LC06070), the Project MSM 002 162 7501, and the Project MSM 002 162 0857.

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9. A typical experimental procedure for alkylative cyclization. To a solution of **2** (0.5 mmol, 140 mg) and Fe-BIAP complex **1a** (0.025 mmol, 18 mg) in dry toluene (3 ml) under argon was added Et_3Al solution in toluene (2 M, 1 mmol, 0.5 ml). The reaction mixture was stirred under argon for 24 h at 20 °C. After that it was quenched with water (1 ml) followed by 3 M solution of HCl (3 ml). The organic layer was separated and dried ($MgSO_4$). Then the reaction mixture was analyzed by ^1H NMR.
10. A typical experimental procedure for deallylation reaction. To a solution of **4** (0.5 mmol, 140 mg) and Fe-BIAP complex **1a** (0.025 mmol, 18 mg) in dry toluene (3 ml) under argon was added Et_3Al solution in toluene (2 M, 1 mmol, 0.5 ml). The reaction mixture was stirred under argon for 24 h at 20 °C. After that it was quenched with water (1 ml) followed by 3 M solution of HCl (3 ml). The organic layer was separated and dried ($MgSO_4$). Then the reaction mixture was analyzed by ^1H NMR.