Allylic Substitutions

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Preformed π-Allyl Iron Complexes as Potent, Well-Defined Catalysts for the Allylic Substitution**

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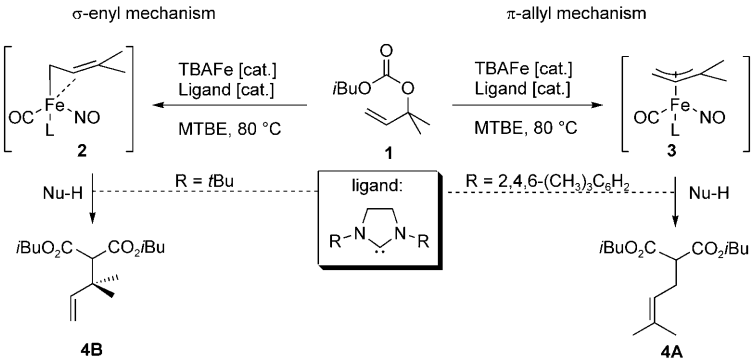
A key feature for the successful development of selective catalytic process is the use of defined catalysts. Knowledge of the electronic and steric properties at the active metal center offers the chance to optimize structure–reactivity relationships. Within the past few years, catalysts based on abundant, inexpensive first-row transition metals, for example, iron have attracted considerable interest.[1] For future elaboration of these reactions, detailed knowledge of the structure of the intermediate catalyst–substrate complexes is important. However, the high reactivity of the in-situ formed active iron complex often prohibits a deeper investigation of the mechanism. The gap between catalysis development[2] and mechanistic know-how might be reduced by the synthesis and characterization of postulated intermediates and comparison of their catalytic activities[3] against known systems. Herein we present structurally defined π-allyl iron complexes as novel, air and moisture stable precatalysts for the allylic substitution and demonstrate that the reactions in the presence of aryl-substituted N-heterocyclic carbene ligands (NHCs) follow a π-allyl mechanism.[4–9]

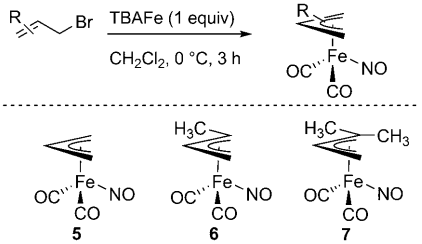


Scheme 1. Model for the mechanistic dichotomy. MTBE *tert*-butyl methyl ester, Nu–H = H–CH(CO_2*i*Bu)$_2$.

Based upon earlier reports by Roustan et al.[10] and Zhou et al.[11] we recently developed an efficient method for the iron-catalyzed allylic substitution using the [Fe(CO)$_5$]-derived ferrate complex [Bu$_4$N][Fe(CO)$_3$(NO)] (TBAFe). Whereas early investigations concentrated mainly on the use of PPh_3 as a ligand[12,13] a more efficient method was elaborated recently by employing NHC ligands instead.[14] Furthermore, depending on the N-substituent within the ligand core we observed a significant shift of the regioisomeric ratio for which, based upon empirical results, we postulated a ligand-dependant mechanistic dichotomy (Scheme 1).

Based upon the mechanistic hypothesis that π-allyl iron complexes, such as **3**, are intermediates in the catalytic cycle, we assumed that these compounds, although described to date as being catalytically inactive, could act as structurally defined precatalysts.[15] Furthermore we were hoping for a further proof of our proposed π-allyl mechanism through a direct comparison of the regioselective courses using preformed π-allyl iron complexes in either a stoichiometric or a catalytic allylation.[14]

Our investigations started with an analysis of the regioselective course of the allylation of diisobutyl malonate with stoichiometric amounts of the preformed π-allyl iron complexes **5**–**7**. These complexes are accessible in one step starting from the corresponding allyl halides (Scheme 2) and



Scheme 2. Preparation of defined π-allyl iron complexes.

can be purified by column chromatography.[16] Reaction of the complexes **5**–**7** with the malonate anion resulted in the formation of the corresponding allyl malonates **8**, **9**, and **4** (Table 1). Owing to the high vapor pressure of **5**–**7** the

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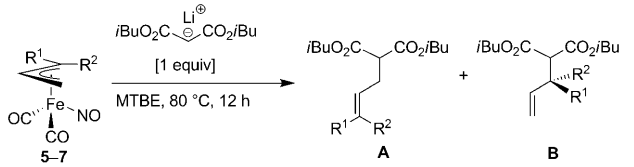
Table 1: Stoichiometric allylation reactions.[a]



Fe complex	R^1	R^2	Product	**A**:**B**[b]	Yield [%][b]
5	H	H	**8**	–	68
6	CH_3	H	**9**	79:21	59
7	CH_3	CH_3	**4**	96:4	65

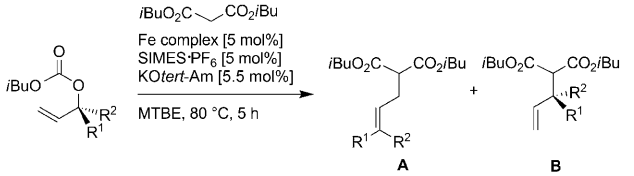
[a] All reactions were performed on a 1 mmol scale in MTBE (1 mL) under a N_2 atmosphere. [b] Determined by GC integration.

complexes were used as a stock solution in methyl *tert*-butyl ether (MTBE).

In analogy to the results reported by Nakanishi et al.[17] and Mattern and Eberhardt[18], a mixture of two regioisomers was obtained with the major isomer being formed by attack of the nucleophile at the sterically less-hindered carbon atom of the allyl ligand. The regioselectivities are not influenced by additional ligands. Only the reactivity and stability of the complexes is significantly altered. Hence, in the presence of PPh_3 the corresponding phosphane complex **5′** (see Scheme 4) was isolated as an air- and moisture-stable solid. Its corresponding NHC adduct on the other hand is thermally instable and can not be isolated and does not undergo stoichiometric reactions.

Knowing the regioselective course of the stoichiometric allylation reactions we subsequently wondered whether the preformed π-allyl iron complexes were catalytically active. Hence the corresponding allylic carbonates were treated with the respective allyl complex under our previously established conditions in the presence or absence of the aryl substituted NHC ligand SIMES (1,3-dimesitylimidazolin-2-ylidene; Table 2).

Table 2: π-Allyl iron complexes as catalysts.[a]

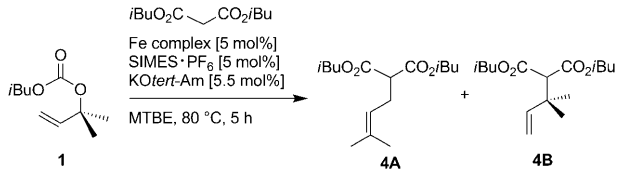


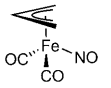
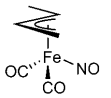
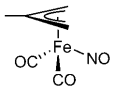
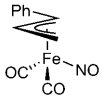
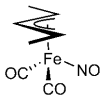
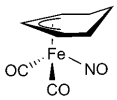
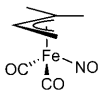
Entry	Carbonate	Cat.	Ligand	**A**:**B**[b]	Yield [%][c]
1	**10**	**5**	–	–	traces
2	(R^1=H, R^2=H)		SIMES	–	86
3	**11**	**6**	–	n.d.	<10
4	(R^1=CH_3, R^2=H)		SIMES	78:22	78
5	**1**	**7**	–		12
6	(R^1=R^2=CH_3)		SIMES	94:6	89

[a] All reactions were performed on a 1 mmol scale in MTBE (1 mL) under a N_2 atmosphere. KO*tert*-Am = $KOC(CH_3)_2CH_2CH_3$, potassium 2-methyl-2-butoxide. [b] Determined by GC integration; n.d. = not determined. [c] Yields of isolated product.

The preformed π-allyl iron complexes are transferred into potent catalysts for the allylic substitution upon addition of the SIMES ligand. The regioselectivities of the catalytic reactions are in good agreement with the selectivities observed in the stoichiometric reactions (compare Tables 1 and 2). Subsequently, a variety of differently substituted π-allyl iron complexes was prepared and evaluated with respect to their relative catalytic activities in the allylic substitution of carbonate **1** (Table 3).

Table 3: Relative activity of different π-allyl iron complexes.[a]

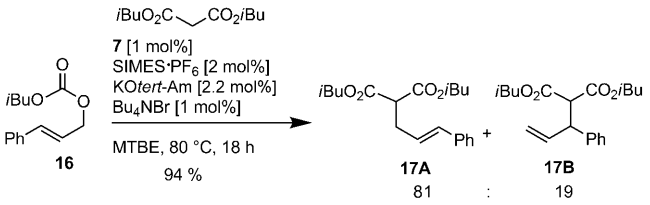


Entry	Catalyst		**4A**:**4B**[b]	Yield [%][b]
1		**5**	94:6	84
2		**6**	93:7	94
3		**12**	94:6	89
4		**13**	93:7	42
5		**14**	94:6	84
6		**15**	94:6	69
7		**7**	94:6	95

[a] All reactions were performed on a 1 mmol scale in MTBE (1 mL) under a N_2 atmosphere. [b] Determined by GC integration using *n*-dodecane as internal standard.

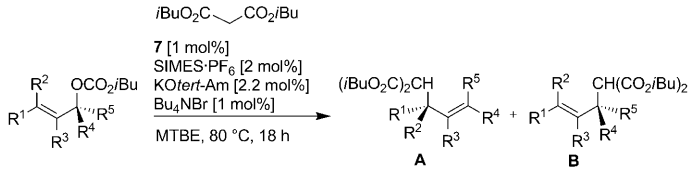
We were pleased to find that various π-allyl iron complexes acted as reactive precatalysts. After extensive optimizations we were finally able to catalyze the allylic substitution of the model compound **16** with a significantly reduced catalyst loading of only 1 mol% of complex **7** (Scheme 3).

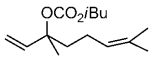
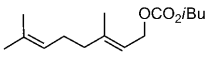
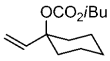
The optimized method is applicable to the alkylation of various allyl carbonates. Independent on the constitution of the starting material, identical regioselectivities are observed with the major isomer being formed by attack of the



Scheme 3. The allylic substitution catalyzed by **7** and SIMES.

Table 4: Alkylation of various allyl carbonates.[a]



Entry	Carbonate					Product(**A**:**B**)[b]	Yield [%][c]
	R^1	R^2	R^3	R^4	R^5		
1[d]	H	H	H	H	H	**8**	81
2[e]	H	H	H	CH_3	H	**9** (76:24)	93
3	CH_3	H	H	H	H	**9** (26:74)	82
4[e]	H	H	CH_3	H	H	**18**	94
5	H	H	H	Ph	H	**17** (80:20)	89
6	Ph	H	H	H	H	**17** (19:81)	84
7[d]	CH_3	H	H	CH_3	H	**19**	96
8	Ph	H	H	CH_3	H	**20** (6:94)	93
9	CH_3	H	H	Ph	H	**20** (95:5)	81
10	H	H	H	CH_3	CH_3	**4** (6:94)	95
11	CH_3	CH_3	H	H	H	**4** (96:4)	97
12						**21** (96:4)	77
13						**21** (96:4)	82
14						**22** (98:2)	94
15[d]	H	H	H	CH_2OBn	H	**23** (94:6)	85
16[d]	H	$BnOCH_2$	H	H	H	**23**[f] (4:96)	89

[a] All reactions were performed on a 1 mmol scale in MTBE (1 mL) under a N_2 atmosphere. [b] Determined by GC integration. [c] Yields of isolated product. [d] 2.5 mol% **7**, 5 mol% SIMES·PF_6, and 2.5 mol% Bu_4NBr. [e] 5 mol% **7**, 10 mol% SIMES·PF_6, and 5 mol% Bu_4NBr. [f] The *Z*-configured product was observed as the sole double-bond containing isomer.

nucleophile at the sterically less-hindered terminus of the allyl ligand (Table 4).

Thus for the first time we were able to show that 1) π-allyl iron complexes are catalytically active intermediates in the presence of NHC ligands, and that 2) the observed regioselective courses of the catalytic transformations in the presence of SIMES ligand are the direct consequence of a nucleophilic attack at a π-allyl iron complex.

Moreover a broad range of pronucleophiles is allylated in good to excellent yields using the conditions mentioned above (Table 5). Different functional groups are tolerated. Preliminary investigations indicated that apart from isobutylcarbonate, methyl carbonates and *tert*-butyl carbonates are also suitable leaving groups (Table 5, entries 8, 9, and 11). In particular *tert*-butyl carbonate is important to prevent undesired transesterification processes.[19] However, this suppression is at the expense of reactivity. Furthermore, the π-allyl iron complex **7**, because of its higher solubility and a smaller induction period, shows a better performance than with TBAFe after identical reaction times even at a catalyst concentration of only 1 mol% (Table 5, entries 1–3, 5, 6, 12–14). At a catalyst loading of 2.5 mol%, however both precatalysts are of equal activity in the allylation of problematic substrates (Table 5, entries 4, 7–9, 11).

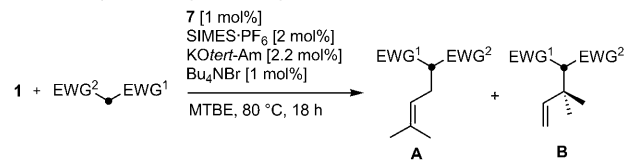
Although the monophosphane adduct **5′** proved to be catalytically inactive, it is a solid and hence shows some important advantages with regard to the overall operational simplicity of the process. We tried to reanimate the catalytic activity of this complex by adding SIMES as a ligand. We were pleased to find that this approach proved successful. Although the turnover numbers are somewhat lower than for the same reaction in the presence of complex **7**, the regioselective course of the reaction remained unchanged (Scheme 4).

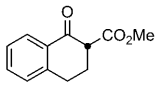
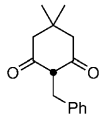
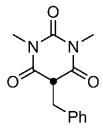
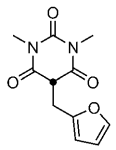
Herein we report, for the first time, the use of structurally defined preformed π-allyl iron complexes as stable precatalysts for allylic substitution reactions. Upon addition of the N-heterocyclic carbene ligand SIMES an activation of the inactive metal complexes occurred leading to a system that has improved catalytic activity compared to the previous TBAFe/SIMES system. The improvement is a result of the better solubility of the new system in organic solvents and the reduced induction period which lead to an overall reduction of the catalyst concentration required down to 1 mol%. Furthermore by direct comparison of the regioselectivities, both in stoichiometric and catalytic allylic substitutions, direct support for the π-allyl mechanism was obtained. These results build the base for the future development of an allylic substitution according to the principles of a dynamic-kinetic asymmetric transformation.

Experimental Section

Preparation of (π-allyl)dicarbonylnitrosyl iron complexes (general procedure): In a 100 mL Schlenk tube $[Bu_4N][Fe(CO)_3(NO)]$ (1.65 g, 4 mmol) was dissolved in methylene chloride (40 mL) under a

Table 5: Allylation of pronucleophiles.[a]



Entry	Nucleophile		Product (**A**:**B**)[b]	Yield [%][c,d]
	EWG^1	EWG^2		
1	CO_2iBu	CO_2iBu	**4** (94:6)	95 (81)
2	CO_2iBu	$COCH_3$	**24** (93:7)	78 (63)
3	CO_2iBu	COPh	**25** (96:4)	82 (74)
4[e]	CO_2iBu	SO_2Ph	**26** (96:4)	58 (53)
5	CO_2iBu	CN	**27** (64:36)	79 (74)
6	SO_2Ph	CN	**28** (82:18)	85 (83)
7[e]	CN	CN	**29** (7:93)	96 (92)
8[e,f]	CO_2Me	$N{=}CPh_2$	**30** (58:42)	67 (65)
9[e,g]	$(EtO)_2P{=}O$	CO_2Et	**31** (98:2)	91 (90)
10			**32** (82:18)	75 (64)
11[e,f]			**33** (97:3)	78 (81)
12			**34** (99:1)	70 (61)
13			**35** (95:5)	74 (56)
14			**36** (97:3)	78 (61)

[a] All reactions were performed on a 1 mmol scale in MTBE (1 mL) under a N_2 atmosphere. [b] Determined by GC integration. [c] Yields of isolated products. [d] Yields of isolated products from the corresponding reaction using TBAFe as the precatalyst are given in parenthesis. [e] 2.5 mol% **7**, 5 mol% SIMES·PF_6, and 2.5 mol% Bu_4NBr. [f] The methoxy carbonate $CH_2{=}CHC(CH_3)_2OCO_2CH_3$ was employed. [g] The *tert*-butoxy carbonate $CH_2{=}CHC(CH_3)_2OCO_2tBu$ was employed.

nitrogen atmosphere and cooled down to 0 °C. The corresponding allylic halide (4 mmol) was added dropwise and the mixture was stirred for 3 h at 0 °C. Subsequently the mixture was concentrated in vacuum and the crude product was purified under a nitrogen atmosphere by flash-chromatography using silica gel and methylene chloride/petroleum ether (1:1) as the eluent. After removal of the solvent the corresponding π-allyl iron complexes were obtained as deep red liquids.

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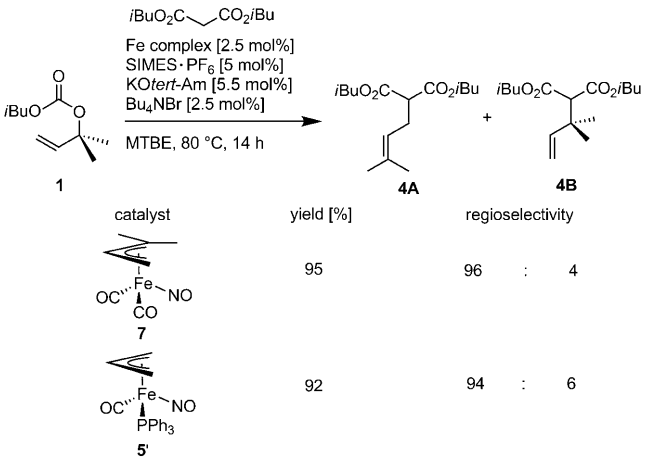

Scheme 4. "Reanimation" of catalytically inactive **5'**.

Keywords: allyl ligands · homogeneous catalysis · iron · nucleophiles · regioselectivity

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