The Hieber Anion [Fe(CO)₃(NO)]⁻

Compiled by Johannes E. M. N. Klein

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Abstracts

(A) Allylic Substitutions with C-Nucleophiles:
Building on early work by Roustan et al.³a and Xu et al.³b an efficient allylic substitution using carbon-centered nucleophiles was developed. In a first account the beneficial effects of Ph₃P were shown. ipso Substitution was observed and a α-allyl-iron intermediate was suggested.⁴a A second-generation protocol allowed for the selective formation of either linear or branched products based on the choice of ligand. The t-Bu-substituted NHC ligand gave access to branched selectively, whereas the aryl-substituted NHC ligand gave access to the linear product preferentially.⁴b

(B) Allylic Substitutions with N-Nucleophiles:
The allylic amination of allyl carbonates could be carried out using catalytic amounts of Bu₄N[Fe(CO)₃(NO)]. The addition of piperidine·HCl proved to be crucial for the reaction to take place when less substituted carbonates were used. ipso Substitution and retention of the stereochemistry was observed in all cases.⁵

(C) Allylic Substitutions with S-Nucleophiles:
The allylic sulfonation of allyl carbonates was reported using catalytic amounts of Bu₄N[Fe(CO)₃(NO)] and sodium sulfinites as nucleophiles. Consistent with previous observations ipso substitution and retention of the stereochemistry was observed.⁶ Recently an allylic sulfenylation has been reported.⁷

(D) Allylic Substitutions with O-Nucleophiles:
The O-allylation of phenols was reported using allyl carbonates, which upon treatment with catalytic amounts of Ph₃P and Bu₄N[Fe(CO)₃(NO)] forms allyl phenyl ethers. Interestingly, this reaction was suggested to proceed via a π-allyl mechanism, based on the regiochemical outcome of this reaction.⁸
(E) C1–C16 Fragment of Ionomycin:
Kocienski and co-workers employed Bu4N[Fe(CO)3(NO)] in the preparation of the C1–C16 fragment of the polyketide natural product ionomycin. In a stoichiometric reaction of the enantiopure mesylate with the Hieber anion a configurationally stable iron allyl complex is formed as a 4:1 mixture of diastereoisomers. Separation via crystallization and subsequent reaction with an organocuprate gives rise to the desired advanced intermediate with retention of the stereochemistry based on the mesylate.9

(F) Carbonylation of Primary and Secondary Alkyl Halides:
Davies et al. reported the carbonylation of alkyl halides with stoichiometric amounts of Bu4N[Fe(CO)3(NO)] in the presence of a carbon monoxide atmosphere. Initial alkylation takes place at the iron nucleophile followed by CO insertion to give an iron acyl species which upon substitution by methoxide gives the product.10 It has to be noted that potential β-hydride elimination does not take place. When MeOH was replaced by the hydride source NaHB(OMe)3 the corresponding alcohols were obtained.

(G) Transesterification:
The Bu4N[Fe(CO)3(NO)] catalyzed transesterification was recently reported. Alcohols were readily acylated using vinyl acetate in n-hexane at elevated temperature. Further, molecular sieves had to be employed as the reaction exhibited a severe sensitivity to moisture. Phenyl esters or activated methyl esters also proved to be good acyl donors in this reaction. Mechanistically the reaction proceeds via a putative iron acyl intermediate.11

(H) Thioesterification:
The transesterification was developed into a protocol for the preparation of thioesters from ρ-chlorophenyl esters in the presence of Bu4N[Fe(CO)3(NO)]. In the course of this study this reaction was applied to a native chemical ligation affording dipeptides via intermediate thioesters.12

(I) Hydrosilylation of Aldehydes and Ketones:
Treatment of the appropriate carbonyl compounds with polymethylhydrosiloxane (PMHS), a hydride source, in the presence of as little as 1 mol% Bu4N[Fe(CO)3(NO)] results in excellent yields of the alcohols after basic workup. Inclusion of the phosphine ligand PCy3 had a profound effect on the yield.13

References