SYNLETT
Spotlight 371

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

The Hieber Anion $[Fe(CO)_3(NO)]^-$

Compiled by Johannes E. M. N. Klein

Johannes Klein obtained his undergraduate degree in 2007 from the Dortmund University of Technology. He then moved to the University College Dublin where he worked on heterocyclic chemistry under the guidance of Dr. P. Evans and obtained his M.Sc. degree in 2009. He was a visiting scholar with Prof. T. Ritter at Harvard University and later with Prof. R. J. K. Taylor at the University of York. He is currently working in the laboratory of Prof. B. Plietker at the University of Stuttgart and investigates iron-catalyzed reactions.

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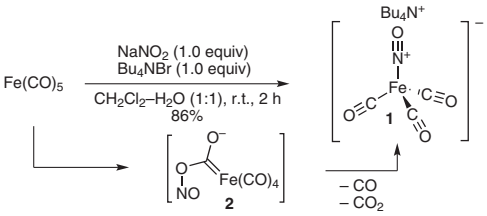
Introduction

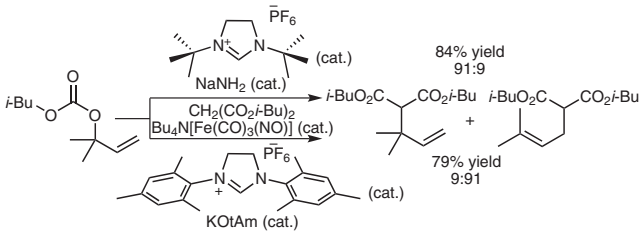
Transition metals are a cornerstone in organic chemistry and their application both as stoichiometric reagents and catalysts has gained much attention. Increased efforts towards economically and ecologically benign processes have put the spotlight on readily available and non-toxic metals, such as iron. Among these is the iron complex $[Fe(CO)_3(NO)]^-$, also referred to as a Hieber anion.[1] The Bu_4N salt may be easily prepared from $Fe(CO)_5$, $NaNO_2$, and Bu_4NBr (Scheme 1).[2] Nucleophilic attack of the nitrite onto a CO ligand forms putative intermediate **2** which results in **1** upon extrusion of CO and CO_2 causing a reduction of the iron center.



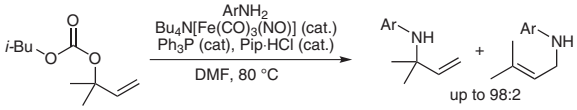
Scheme 1 Preparation of $Bu_4N[Fe(CO)_3(NO)]$

Abstracts

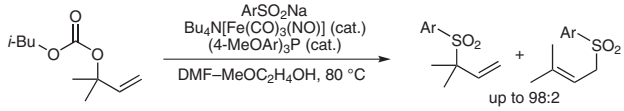
(A) *Allylic Substitutions with C-Nucleophiles*:
Building on early work by Roustan et al.[3a] and Xu et al.[3b] an efficient allylic substitution using carbon-centered nucleophiles was developed. In a first account the beneficial effects of Ph_3P were shown. *ipso* Substitution was observed and a σ-allyl-iron 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]



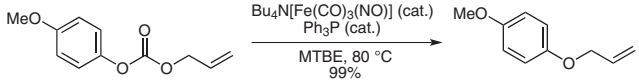
(B) *Allylic Substitutions with N-Nucleophiles:*
The allylic amination of allyl carbonates could be carried out by using catalytic amounts of $Bu_4N[Fe(CO)_3(NO)]$. The addition of piperidine·HCl proved to be crucial for the reaction to take place when less substituted carbonates were used. *ipso* Substitution 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 $Bu_4N[Fe(CO)_3(NO)]$ and sodium sulfinates 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 Ph_3P and $Bu_4N[Fe(CO)_3(NO)]$ 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]



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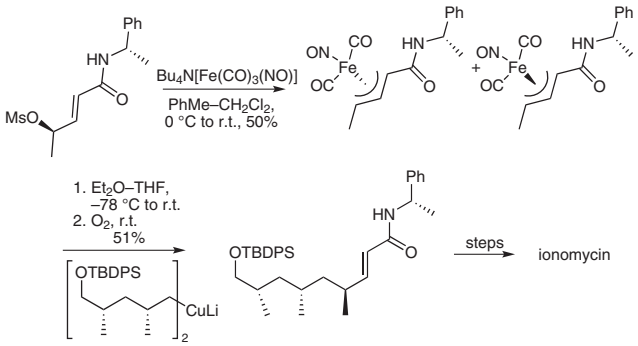
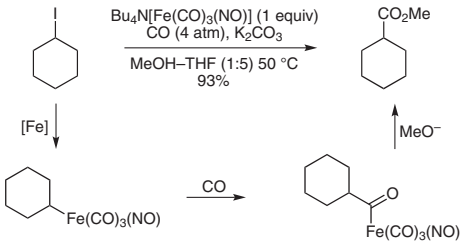
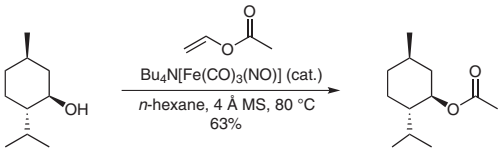
(E) *C1–C16 Fragment of Ionomycin:*
Kocienski and co-workers employed $Bu_4N[Fe(CO)_3(NO)]$ in the preparation of the C1–C16 fragment of the polyketide natural product ionomycin. In a stoichiometric reaction of the enantiopure mesylate with the Hieber anion a configurationally stable iron allyl complex 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]



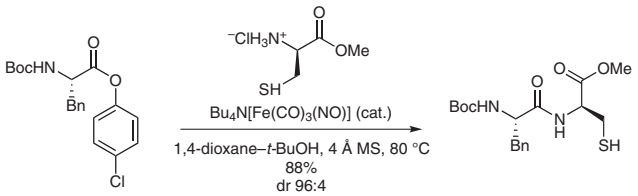
(F) *Carbonylation of Primary and Secondary Alkyl Halides*:
Davies et al. reported the carbonylation of alkyl halides with stoichiometric amounts of $Bu_4N[Fe(CO)_3(NO)]$ in the presence of a carbon monoxide atmosphere. Initial alkylation takes place at the iron nucleophile followed by CO insertion to 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.



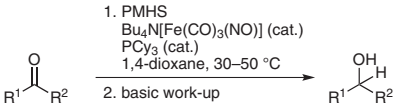
(G) *Transesterification:*
The $Bu_4N[Fe(CO)_3(NO)]$ catalyzed transesterification was recently reported. Alcohols were readily acylated using vinyl acetate in *n*-hexane at elevated temperature. Further, molecular sieves had to be employed as the reaction exhibited a severe sensitivity to towards moisture. 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 *p*-chlorophenyl esters in the presence of $Bu_4N[Fe(CO)_3(NO)]$. 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% $Bu_4N[Fe(CO)_3(NO)]$ results in excellent yields of the alcohols after basic workup. Inclusion of the phosphine ligand PCy_3 had a profound effect on the yield.[13]



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