

# SYNLETT Spotlight 137

## Tetracarbonylhydridoferrate Salts: NaHFe(CO)<sub>4</sub> and KHFe(CO)<sub>4</sub>

Compiled by Jiří Pospíšil



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

Jiří Pospíšil was born in Třebíč (Czech republic) in 1979. He completed his M.Sc. (2002) in chemistry at Masaryk University in Brno, Czech republic, under the supervision of Prof. M. Potáček. He is currently working towards his Ph.D. in organic chemistry under the supervision of Prof. I. E. Markó at the Université catholique de Louvain, Louvain-la-Neuve, Belgium. His research interests include the total synthesis of natural products and the development of new methodologies.

Université catholique de Louvain, Département de Chimie,  
Bâtiment Lavoisier, Place Louis Pasteur 1, 1348 Louvain-la-Neuve,  
Belgium  
E-mail: [pospasil@chim.ucl.ac.be](mailto:pospasil@chim.ucl.ac.be)

### Introduction

The HFe(CO)<sub>4</sub> anion was first prepared by Feigl and Krumholtz in 1932<sup>1</sup> in its sodium form and the structure was unambiguously established by X-ray diffraction analysis of an appropriate bis(triphenylphosphoranylidene)ammonium salt nearly 50 years later.<sup>2</sup> This monohydride iron complex is a source of hydride anion that behaves as an extremely soft reducing reagent. Therefore, this hydride complex is highly suitable for the reduction of, for example, unactivated olefins in the presence of a wide variety of other functional groups. Moreover, all the reactions mediated by NaHFe(CO)<sub>4</sub> or KHFe(CO)<sub>4</sub> proceed under extremely mild and essentially neutral conditions.

The second main property of NaHFe(CO)<sub>4</sub> or KHFe(CO)<sub>4</sub> is their high affinity for alkynes, with which they form various iron complexes. These complexes are not only interesting for their structure, but also for their chemical reactivity.

### Preparation

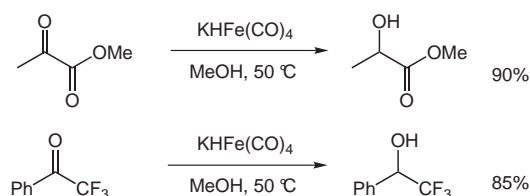
The preparation of NaHFe(CO)<sub>4</sub> and KHFe(CO)<sub>4</sub> is easy and efficient, but the reagents cannot be stored for a long period of time, and they are light sensitive (formation of nonreactive dimer).

KHFe(CO)<sub>4</sub> is generally prepared in situ, prior to the reaction, from Fe(CO)<sub>5</sub> (1 equiv) and KOH (3 equiv) in MeOH, under an inert atmosphere.<sup>3</sup> THF solutions of NaHFe(CO)<sub>4</sub> can be prepared from sodium amalgam and Fe(CO)<sub>5</sub> in anhydrous THF.

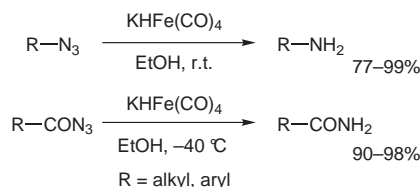
NaHFe(CO)<sub>4</sub> or KHFe(CO)<sub>4</sub> can be also generated by careful acidification of Na<sub>2</sub>Fe(CO)<sub>4</sub> or K<sub>2</sub>Fe(CO)<sub>4</sub>.<sup>4</sup>

### Abstracts

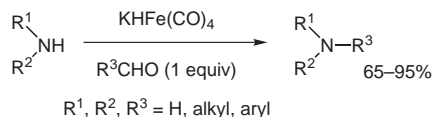
(A) Brunet and co-workers showed that KHFe(CO)<sub>4</sub> is a selective reducing agent for the reduction of electron deficient ketones as well as a highly selective reducing agent for the mono-reduction of the keto group in  $\alpha$ -ketocarbonyl compounds. Ester, amide and nitrile groups, as well as other unactivated carbonyl functions, remain intact under the reaction conditions.<sup>5</sup>



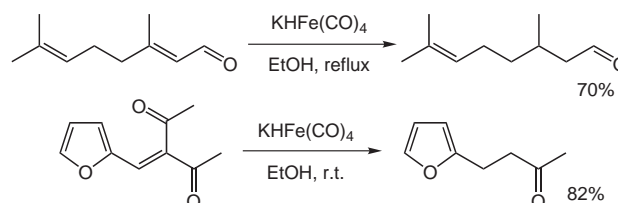
(B) In the presence of  $\text{NaHFe}(\text{CO})_4$  or  $\text{KHFe}(\text{CO})_4$ , azides or acyl azides can be converted into the corresponding primary amines or amides.<sup>6</sup>



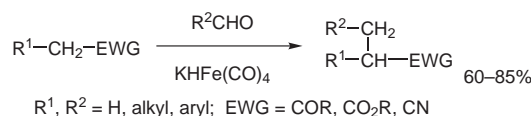
(C)  $\text{HFe}(\text{CO})_4$  salts are convenient and general hydride sources for reductive amination reactions.<sup>7</sup> This method can be applied to aromatic as well as aliphatic amines and aldehydes. When dialdehydes are employed, cyclic amines are obtained.<sup>8</sup>



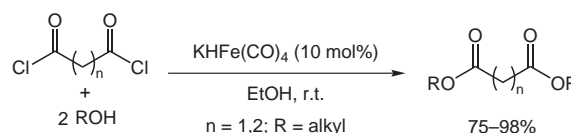
(D) Selective reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds is another typical reaction of  $\text{NaHFe}(\text{CO})_4$  or  $\text{KHFe}(\text{CO})_4$ . Under these conditions, a wide variety of functional groups such as ketones, esters, nitriles, amides, etc. are tolerated and the reaction can be performed in the presence of other olefins.<sup>3</sup> One exception are  $\alpha,\beta$ -unsaturated diketones that undergo deacylative reduction under the reaction conditions, affording saturated monoketones.<sup>9</sup>



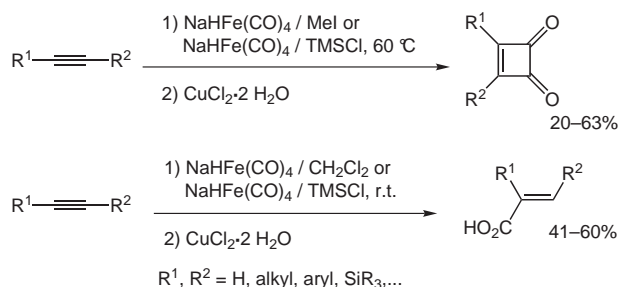
(E) Umani-Ronchi and co-workers described a formal ' $\alpha$ -alkylation' of carbonyl compounds (aldol reaction/elimination/reduction) with aldehydes, in the presence of  $\text{KHFe}(\text{CO})_4$ . The yields depend upon the steric requirements of the aldehyde.<sup>10</sup>



(F) Shin and co-workers used  $\text{KHFe}(\text{CO})_4$  to convert carboxylic acid chlorides into the corresponding esters under mild and neutral conditions.<sup>11</sup>



(G) The reagent, formed by combining in situ  $\text{NaHFe}(\text{CO})_4$  and MeI, reacts with alkynes. After  $\text{CuCl}_2$  oxidation, cyclobutenediones can be obtained in moderate yields.<sup>4,12</sup> Similarly, the reagent generated in situ from  $\text{NaHFe}(\text{CO})_4/\text{CH}_2\text{Cl}_2$  reacts with alkynes and, after  $\text{CuCl}_2$  oxidation, leads to  $\alpha,\beta$ -unsaturated acids.<sup>13</sup> The reaction using  $\text{NaHFe}(\text{CO})_4/\text{TMSCl}$  system gives the corresponding  $\alpha,\beta$ -unsaturated carboxylic acids at room temperature and the corresponding cyclobutenediones at 60 °C.



## References

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