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A Convenient One-Flask Preparation of Pure Potassium Cyclopentadienyldicarbonylferrate, K[(η^5-C_5H_5)Fe(CO)$_2$]

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Recently, various metal carbonyl complexes were utilized in organic and inorganic synthetic reactions as a catalyst or quantitative reagent.[1-3] In particular, iron carbonyl complexes are very useful because of their low cost compared with other metal carbonyl complexes. Among them, several authors have demonstrated that MCpFe(CO)$_2$ (M = Na, K) (1) are valuable reagents for various synthetic reactions. Rosemblum et al. reported useful reactions which proceeded via (η^1-allyl)Fp complex or (η^5-alkenyl)Fp complex as a intermediate.[4] (η^5-C_5H_5)Fe(CO)(PPh$_3$)COCH$_3$ has been utilized in various asymmetric syntheses.[5] More recently, Hossain et al. reported that 1 serves as a precursor for the electrophilic iron–carbene complex by the reaction with aldehyde.[6] But, the preparation of 1 has been rather tedious. So, it is of interest to develop a convenient method for the preparation of 1.

Here, we report a novel and convenient one-flask synthesis of analytically pure 1 (M = K). In a typical procedure, 1 equiv of [CpFe(CO)$_2$]$_2$ was added to 2.1–2.5 equiv of commercially available K(s-C_4H_9)$_3$BH at room temperature. The reaction mixture was refluxed for 3–4 h and cooled. After washing with benzene and drying by blowing argon through the flask, pure 1 (M = K) is obtained as a yellow-orange powdery solid in 75–80% yield. The infrared spectrum and elemental analysis of 1 (M = K) isolated in this report are in good agreement with the values in the literature.[7]

Usually, for the preparation of 1 (M = K), it is necessary to use hazardous and cumbersome reducing agents such as sodium amalgam[8,9] or sodium potassium alloy.[7a] Potassium benzophenone ketyl is also used to reduce [CpFe(CO)$_2$]$_2$ in THF to afford 1,[10] but this procedure is experimentally more elaborate than ours.

Potassium hydride[11] and certain trialkylborohydrides[12] also efficiently reduce [CpFe(CO)$_2$]$_2$ to 1, but sluggish reaction rates are encountered unless a highly coordinating cosolvent such as hexamethylphosphoramide is used with THF.

In conclusion, K(s-C_4H_9)$_3$BH was found to be a good reducing agent of [CpFe(CO)$_2$]$_2$ to 1 (M = K) in good yield. This novel method gave analytically pure 1 (M = K) without any hazardous, troublesome reducing reagents, long reaction time, and complicating operations.

Experimental Section

All operations were performed under argon atmosphere. Tetrahydrofuran (THF) was dried and distilled under an argon atmosphere from potassium–benzophenone just before use. Benzene was distilled from calcium hydride. Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer. Potassium tri-s-butylhydroborate was purchased from Aldrich Chemical Co. as a 1.0 M THF solution under the trade name K-selectride. [CpFe(CO)$_2$]$_2$ was a commercial product and used without further purification.

[CpFe(CO)$_2$]$_2$ (1.06 g, 3 mmol) was added to the THF solution (6.5 mL) of 1.0 M K-selectride in a reactor. The reaction mixture was refluxed for 4 h. After cooling, the resultant yellow-orange precipitate was washed with benzene in the reaction flask, and was dried by blowing argon through the flask.

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