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Convenient Preparation and Use of Potassium Tetracarbonylferrate, K₂[Fe(CO)₄], an Easy-to-Handle Analogue of the Collman Reagent

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CONVENIENT PREPARATION AND USE OF POTASSIUM TETRACARBONYLFERRATE, K₂[Fe(CO)₄], AN EASY-TO-HANDLE ANALOGUE OF THE COLLMAN REAGENT.

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<u>Abstract</u>: A convenient synthesis of $K_2[Fe(CO)_4]$ from $Fe(CO)_5$, KOH and tri(*n*-butyl)phosphine is described. This non-pyrophoric dianionic potassium ferrate displays the same reactivity as $Na_2[Fe(CO)_4]$, provided that the reactions are conducted in DMAC or THF-DMAC solvent mixtures.

Sodium tetracarbonylferrate, $Na_2[Fe(CO)_4]$, has been the subject of many studies and has many useful applications.¹ Although this reagent is sold commercially as a dioxane adduct, $Na_2[Fe(CO)_4](dioxane)_{1.5}$, its use in organic synthesis is hampered by its extreme sensitivity to moisture and its exceedingly pyrophoric character.² Accordingly, most reactions using this reagent must be conducted in a glove box. In contrast, $K_2Fe(CO)_4$ is not pyrophoric and much

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easier to handle. New applications of this reagent in organic synthesis have been reported recently.³⁻⁵

 $K_2[Fe(CO)_4]$ may be obtained by reduction of $Fe(CO)_5$ with either potassium metal ⁶ or $K(s-Bu)_3BH$,⁷ the latter giving flammable trialkylborane derivatives as undesirable by-products.⁷ As part of our study of the reactivity of $M^+[HFe(CO)_4]^-$,⁸ we recently observed that the reaction of KHFe(CO)₄ with phosphines in THF promotes the precipitation of the dianionic ferrate $K_2Fe(CO)_4$.⁹ We report here the use of this novel reaction for a convenient preparation of $K_2Fe(CO)_4$ on a 10 g scale and show that this reagent allows the same organic syntheses as $Na_2[Fe(CO)_4]$, although in different solvents, dimethylacetamide (DMAC) or DMAC-THF solvent mixtures.

The new preparation of $K_2[Fe(CO)_4]$ involves a two-step sequence: A methanolic solution of $KHFe(CO)_4$ is first prepared (eq 1) as previously described.⁹ The protic solvent is then replaced by anhydrous THF and the potassium bicarbonate is removed by filtration.

$$Fe(CO)_5 + 2 \text{ KOH} \xrightarrow{\text{MeOH}} \text{KHFe}(CO)_4 + \text{KHCO}_3 (1)$$

The second step involves the reaction of tri(*n*-butyl)phosphine (2 equiv) with the THF solution of $KHFe(CO)_4$. The reaction can be monitored by measuring the gas evolution (eq 2).

$$2 \text{ KHFe(CO)}_{4} \quad \frac{\text{THF, } P(n-\text{Bu})_{3}}{\text{reflux, 18 h}} \quad \text{K}_{2}\text{Fe(CO)}_{4} + \text{Fe(CO)}_{3}[P(n-\text{Bu})_{3}]_{2} + \text{CO} + \text{H}_{2} \quad (2)$$

At the end of the reaction, $K_2[Fe(CO)_4]$ precipitates as a white solid which is easily separated from the yellow solution, and washed with anhydrous THF. Triphenylphosphine promotes the same reaction, but the reaction time is longer (48 h) and subsequent decantations and washings are more time-consuming.

This new preparation of $K_2[Fe(CO)_4]$ can easily be conducted on a 10 g (40 mmol) scale (see experimental section). Pure $K_2[Fe(CO)_4]$ can be stored for months under argon. Since this ferrate is non-pyrophoric, it is easier-to-handle than the commercial Collman's reagent. Its possible use as a replacement for the Collman's reagent has been tested for three classical carbonylation reactions.

While carbonylation reactions with $Na_2[Fe(CO)_4]$ are generally conducted in a THF-NMP solvent mixture, $K_2[Fe(CO)_4]$ is insoluble in THF though is fairly soluble in DMAC. Thus, the reactions of $K_2[Fe(CO)_4]$ with 1-bromododecane were conducted in DMAC and three different reactions of the intermediate potassium dodecylferrate were carried out.

$$K_2Fe(CO)_4 + C_{12}H_{25}Br \xrightarrow{DMAC} C_{12}H_{25}Fe(CO)_4K$$

$$C_{12}H_{25}Fe(CO)_{4}K \xrightarrow{C_{2}H_{5}I} C_{12}H_{25}COC_{2}H_{5}I \\ C_{12}H_{25}Fe(CO)_{4}K \xrightarrow{C_{2}H_{5}I} C_{12}H_{25}COC_{2}H_{5} \\ 90\% \\ CH_{2}=CH_{2} \\ DMAC-THF \\ 83\% \\ Scheme$$

As shown in the scheme, high yields of isolated carbonylation products were obtained in each case.

This very easy preparation of $K_2[Fe(CO)_4]$ thus provides an alternative reagent for the carbonylation reactions discovered by Collman *et al.*.¹

EXPERIMENTAL SECTION

General procedures.

Iron pentacarbonyl was purchased from Aldrich, stored under argon, and used without further purification. Potassium hydroxide (Prolabo RP Normapur, 86%), methanol (Carlo Erba, ERB quality), 1-bromododecane (Janssen, 98%), and iodoethane (Fluka, 99%) were used as received. Tetrahydrofuran and diethyl ether (SDS) were distilled over sodium-benzophenone under argon before use. N,Ndimethylacetamide (Riedel de Haën) and tri(*n*-butyl)phosphine (Aldrich) were distilled under reduced pressure under argon and stored under argon. Oxygen C and ethylene N35 (L'Air Liquide) were used.

All reactions were conducted under an argon atmosphere.

Preparation of methanolic and THF solutions of KHFe(CO)₄ (88 mmol scale)

A methanolic solution of potassium tetracarbonylhydridoferrate is prepared in a 250 mL Schlenk tube by adaptation of the general procedure described in *Inorganic Syntheses* ¹⁰ using Fe(CO)₅ (12 mL) and two equivalents of KOH (12 g) in methanol (55 mL). The solution is stirred for 0.5 h, at which point methanol is slowly evaporated under reduced pressure to leave a pale pink solid. Freshlydistilled THF (30 mL) is added, the mixture is stirred for a few min and THF is then evaporated. This procedure is repeated twice. More THF (60 mL) is then added and the resulting suspension is filtered through a sintered glass into a 250 mL Schlenk tube. The residue (KHCO₃) is then rinsed with THF (2x30 mL) and the filtrates are collected. The combined washings are then used for the preparation of K₂Fe(CO)₄.

Preparation of K₂Fe(CO)₄ (10 g, 40 mmol scale)

Freshly distilled $P(n-Bu)_3$ (44 mL) is added to a THF solution of KHFe(CO)₄ and the Schlenk tube equipped with a reflux condenser. (The argon flow is maintained at the top of the condenser through an adaptator which is directly connected to an oil bubbler). The reaction medium is then stirred at reflux for 18 h in a oil bath, at which point no more gas evolution is observed. A white suspension forms in the yellow solution. After the mixture cools to room temperature, the supernatant liquid is carefully removed by syringe and the remaining solid is washed repeatedly with diethyl ether until the decanted solution is clear (4x60 mL). The white solid is then dried to constant weight under reduced pressure (10⁻² torr) (10.8 g, 99% of the theoretical yield).

This reagent is easily transferred from one Schlenk tube to another, and weighed, under argon. It is insoluble in THF, diethyl ether and hexane but fairly soluble in N,N-dimethylacetamide.

If the above product $(K_2Fe(CO)_4)$ becomes pink because of an adventitious introduction of moisture, it can be washed with dry THF, under argon, to remove the soluble hydrolysis product, KHFe(CO)₄.

Synthesis of tridecanoic acid from 1-bromododecane.

A solution of 1-bromododecane (1.794 g, 7.2 mmol) in DMAC (20 mL) is degassed and added to $K_2Fe(CO)_4$ (2.042 g, 8.29 mmol) in a 250 mL Schlenk tube equipped with a septum cap. The mixture is stirred for 2 hours at room temperature. Oxygen is then bubbled into the stirred reaction mixture through a needle for 1 hour (some foaming occurs during that operation).

An aqueous, 0.5 M solution of sodium hydroxide (100 mL) is then added and the mixture is stirred until precipitation of the red oxidized iron species occurs (2 h). After removal of the iron species by filtration, the aqueous phase is washed with diethyl ether (2x100 mL) and then acidified with dilute hydrochloric acid to pH 1. The product is extracted with diethyl ether (3x200 mL), dried (overnight) over Na_2SO_4 and is obtained as a white solid (1.643 g) after evaporation of the solvent. Recrystallisation of this solid from hexane (20 mL) affords 1.405 g of tridecanoic acid. Concentration of the mother liquor to 10 mL and cooling to -20°C in the refrigerator allow the recovery of a further 0.133 g of tridecanoic acid. Total yield: 1.51 g, 98%.

mp = 42°C, (lit 11 : 44°C).

Anal. Calcd for C₁₃H₂₆O₂: C, 72.85; H, 12.23. Found: C, 72.99; H, 12.38.

Synthesis of 3-pentadecanone from 1-bromododecane and iodoethane.

A solution of 1-bromododecane (3.520 g, 14.12 mmol) in DMAC (20 mL) is degassed and added to $K_2Fe(CO)_4$ (3.685 g, 14.98 mmol) in a 100 mL Schlenk tube equipped with a septum cap. The mixture is stirred for 2 h at room temperature. Next, a solution of iodoethane (6.40 g, 41 mmol) in DMAC (10 mL) is degassed and added by syringe the reaction mixture, which is then stirred for 24 h at 50°C. The reaction medium is poured into water (100 mL) and is stirred in air until precipitation of the red oxidized iron species (24 h). Extraction of the product using diethyl ether (3x200 mL), followed by drying over Na₂SO₄ (overnight) and evaporation of the solvents under reduced pressure afford a white solid (3.178 g). Recrystallisation from hexane yields 3-pentadecanone (2.9g, 90%).

mp = 36-37°C (lit ¹²: 38°C)

Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.81; H, 13.58. IR (CH₂Cl₂) $\nu_{(CO)} = 1712 \text{ cm}^{-1}$ Mass spectrometry (70eV, EI): m/z: 226 (2%), 197 (61%), 72 (90%), 57 (100%), 43 (62%) Semicarbazone (from methanol) m.p. = 90°C, (lit ¹²: 90.5°C)

Synthesis of 3-pentadecanone from 1-bromododecane and ethylene.

A solution of 1-bromododecane (1.34 g, 5.38 mmol) in DMAC (10 mL) is degassed and added to $K_2Fe(CO)_4$ (1.4 g, 5.69 mmol) in a 200 mL Schlenk tube equipped with a septum cap, and the mixture is stirred for 2 h at room temperature. Freshly distilled THF (40 mL) is added and the argon atmosphere is replaced by ethylene. The reaction medium is then stirred for 24 h at 50°C under ethylene (1 atm). After addition of acetic acid (0.8 mL) in THF (10 mL), the reaction medium is stirred for 5 min, poured into water (100 mL) and stirred in air until precipitation of red oxidized, iron species. Work-up as above affords 3-pentadecanone (1.01 g , 83%).

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