

## One-pot synthesis of transition metal-substituted carboxylic acids

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### Abstract

Transition metal-substituted carboxylic acids,  $\text{MRCOOH}$  ( $\text{R} = \text{CH}_2, \text{CH}_2\text{CH}_2$ ), are prepared by the reactions of metal anions with trimethylsilyl halocarboxylates,  $\text{XRCOOSiMe}_3$ , followed by treatment with silica gel. The carboxylic acid moiety is readily transformed into various acyl derivatives  $\text{MRCONu}$  such as esters and amides via an acyl chloride intermediate,  $\text{MRCOCl}$ .

Of the transition metal-substituted carboxylic acid derivatives  $\text{MRCONu}$ , metal enolates (**1**) ( $\text{R} = \text{CH}_2$ ) have attracted much attention, because they can undergo condensations not only with polar substrates such as aldehydes and ketones but also with less polar substrates such as acetylenes and olefins [1]. The compounds **1** have been prepared by the usual alkylation of metal anions with chloroacetic acid derivatives  $\text{ClCH}_2\text{CONu}$  ( $\text{Nu} = \text{OR}, \text{NR}_2$  etc.) by route I. Recently, we [2] and Bergman's group [1a] have shown independently that the parent carboxylic acid  $\text{MCH}_2\text{COOH}$  (**2**) serves as a useful precursor for various  $\eta^1$ -(*C*)-enolato complexes  $\text{MCH}_2\text{CONu}$  (**1**) via the acyl chloride intermediate (**3**) (Scheme 1). However, **2** has been hitherto prepared by acidic hydrolysis of **1** (route I) [1a,3]. Here we describe the direct, one-pot synthesis of a variety of transition metal-substituted carboxylic acids including **2** (route II).

### Results and discussion

The reaction of  $\text{NaFp}$  [ $\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ ] with trimethylsilyl chloroacetate (**4**), which was readily prepared by condensation of chlorotrimethylsilane with chloroacetic acid, gave a deep yellow oil.  $^1\text{H}$  NMR spectroscopy revealed that the only product was  $\text{FpCH}_2\text{COOSiMe}_3$  (**5a**) [ $\delta(\text{CDCl}_3)$  0.30 ( $\text{SiMe}_3$ ), 1.48 ( $\text{CH}_2$ ), 4.41 (*Cp*)]. Deprotection of the silyl group was readily accomplished during separation by column chromatography on silica gel to give an iron-substituted acetic acid,  $\text{FpCH}_2\text{COOH}$  (**2a**), in 70% yield. The action of the bromoacetic acid ester in place





gel column made up in hexane. The dimetallic complex M–M was eluted first with hexane-CH<sub>2</sub>Cl<sub>2</sub> = 5–3 : 1. Elution with polar solvent (acetone for **2a**, **2b**, **2d**; CH<sub>2</sub>Cl<sub>2</sub> for **2c**, **2e**) gave a yellow to orange band, from which **2** was isolated as yellow to orange microcrystals after recrystallization.

The structures of **2a**, **2b**, **2d**, **2e** were determined by comparison of spectral data with those of authentic samples reported by Green [3]. **2c**: yellow microcrystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.14 (C<sub>5</sub>Me<sub>5</sub>), 1.75 (CH<sub>2</sub>). IR (KBr) ν(O–H) 2800–2200, ν(C≡O) 1993, 1938, ν(C=O) 1648, ν(C–O) 1281 cm<sup>-1</sup>. Found: C, 53.62; H, 6.08. C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>Fe calcd.: C, 53.19; H, 5.93%.

#### Reactions of **2a**–**2e** with nucleophiles

Oxalyl chloride (1.52 g, 12 mmol) was added dropwise to a solution or suspension (10 ml) of the carboxylic acid (**2**) (10 mmol) in THF (10 ml). After cessation of the vigorous gas evolution, the mixture was cooled at –78 °C, and MeOH (2 ml) and Et<sub>3</sub>N (2 ml) were simultaneously added dropwise to the solution, which was then stirred at room temperature for 1 h. Evaporation of the volatiles, extraction with ether and filtration through an alumina plug followed by recrystallization from ether-hexane yielded the methyl ester as yellow [**6a** (84%), **6b** (83%), **6c** (96%), **6d** (75%)] or white crystals [**6e** (79%)].

The structures were confirmed by comparison of spectral data with those of authentic samples. **6c**: yellow crystals. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.33 (C<sub>5</sub>Me<sub>5</sub>), 1.39 (CH<sub>2</sub>), 3.60 (OMe). IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(C≡O) 1996, 1947, ν(C=O) 1677 cm<sup>-1</sup>. Found: C, 56.58; H, 6.42. C<sub>15</sub>H<sub>20</sub>O<sub>5</sub>Fe calcd.: C, 56.27; H, 6.30%.

Reactions of **2a** with NH<sub>3</sub> [3] and **7** with MeOH were carried out in the manner as described above. If an excess amount of nucleophile is not available, the excess oxalyl chloride and the dissolved HCl should be removed in vacuo before nucleophile is added. FpCH<sub>2</sub>CH<sub>2</sub>COOMe: yellow crystals. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.40–1.77 (Fp-CH<sub>2</sub>), 2.21–2.61 (CH<sub>2</sub>COOMe), 3.62 (OMe), 4.69 (C<sub>5</sub>H<sub>5</sub>). Found: C, 50.62; H, 5.06. C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>Fe calcd.: C, 50.03; H, 4.58%.

The preparation of **7** and the diiron complexes bridged by μ-CH<sub>2</sub>CO and μ-CH<sub>2</sub>CH<sub>2</sub>CO ligands was published previously [2b].

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