

## $(\eta^5\text{-C}_5\text{R}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$ (R = H, CH<sub>3</sub>): A CONVENIENT ONE-POT SYNTHESIS USING CHLOROMETHYL PIVALATE

MICHAEL E. WRIGHT and GREGORY O. NELSON \*

*Department of Chemistry, University of Arizona, Tucson, AZ 85721 (U.S.A.)*

(Received September 16th, 1983)

### Summary

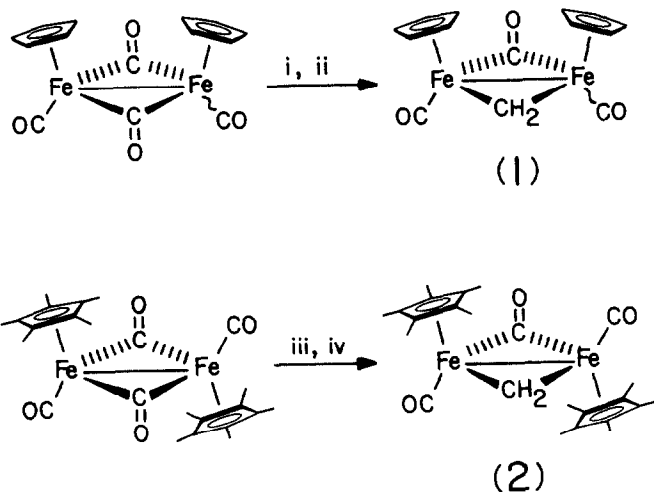
The compounds  $(\eta^5\text{-C}_5\text{R}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$  (R = H, CH<sub>3</sub>) have been prepared through the reaction of chloromethyl pivalate with the appropriate metal anions,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{K}$  and  $\eta^5\text{-C}_5\text{Me}_5\text{Fe}(\text{CO})_2\text{K}$ .

In recent years, the synthesis and chemistry of binuclear transition metal compounds containing a  $\mu\text{-CH}_2$  ligand have attracted considerable attention from organometallic chemists [1]. Several reagents have been utilized for the introduction of the  $\mu\text{-CH}_2$  group such as  $\text{CH}_2\text{I}_2$  [2],  $\text{CH}_2\text{N}_2$  [3],  $\text{CH}_2(\text{OTs})_2$  [4], and  $\text{CH}_2\text{PPh}_3$  [5]. In addition, the iron complex  $\text{Fp}(\eta^1\text{-CH}_2\text{O}_2\text{CCH}_3)$  (Fp =  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ) has been used by Casey [6] to prepare  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$  (**1**) in 20% yield. We wish to report a new and convenient method for the synthesis of **1** using chloromethyl pivalate and  $\text{FpK}$ . This methodology has also been employed to prepare the new analog  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$  (**2**).

The  $\text{FpK}$  was generated from the reaction of  $\text{Fp}_2$  with 2.1 equiv of  $\text{K}(\text{sec-C}_4\text{H}_9)_3\text{BH}$  in refluxing tetrahydrofuran (THF) for 1 h [7]. One equiv of chloromethyl pivalate,  $\text{ClCH}_2\text{O}_2\text{CC}(\text{CH}_3)_3$ , was slowly added to the mixture which was then refluxed for an additional 2 h. The crude reaction product was found to contain a mixture of **1** and  $\text{Fp}_2$  in a molar ratio of 3/1, respectively (55% crude yield of **1**). Complex **1** was separated from the  $\text{Fp}_2$  using the method previously reported [6] which afforded **1** (*cis/trans*, 3.5/1) in 35% isolated yield based upon the starting compound,  $\text{Fp}_2$ .

The  $\text{Fp}'\text{K}$  ( $\text{Fp}' = \eta^5\text{-C}_5\text{Me}_5\text{Fe}(\text{CO})_2$ ) was prepared in the following manner [8]. A THF solution that contained  $\text{Fp}'_2$  and 3.5 equiv of Na/K alloy (22/78%) [9] was heated at reflux for 1 h. Chloromethyl pivalate (0.30 g, 2.0 mmol) was added to the  $\text{Fp}'\text{K}$  solution after removal of excess Na/K alloy, and the mixture was refluxed for 2 h. Chromatography of the crude product under nitrogen on a column of

\* Presently located at Research Laboratories, Tennessee Eastman Co., Kingsport, TN 37662 (U.S.A.).



SCHEME 1. Reagents: (i) 2.1 equiv  $\text{K}(\text{sec-C}_4\text{H}_9)_3\text{BH}$ , THF, reflux, 1 h; (ii) 1.0 equiv chloromethyl pivalate, reflux, 2 h; (iii) 3.5 equiv Na/K alloy (22/78%), THF, reflux, 1 h; (iv) 1.0 equiv chloromethyl pivalate, reflux, 2 h.

alumina(III) with hot hexanes afforded analytically pure **2** as air-stable purple crystals in 15% isolated yield. The single resonance at  $\delta$  8.57 for the  $\mu\text{-CH}_2$  protons indicates that **2** exists completely as the *trans*-isomer\*. The single terminal carbonyl IR band at  $1909\text{ cm}^{-1}$  is consistent with only the *trans*-isomer which possesses  $C_{2h}$  symmetry (ignoring rotational orientation about the  $C_5\text{Me}_5$   $C_5$  axes) [10]. The observation of the carbonyl IR bands of **2** at lower wavenumbers is undoubtedly due to the additional electron donation through the  $C_5\text{Me}_5$  ligands.

From this work we have provided experimental proof that chloromethyl pivalate is a readily available source of a methylene unit for the bimetallic systems **1** and **2**. In addition, we feel this reagent may be one of choice because of its commercial availability and the property of undergoing substitution reactions versus electron transfer.

## Experimental

### General

All manipulations of solvents and compounds were carried out under a purified nitrogen atmosphere using standard Schlenk techniques. The following instrumentation was utilized:  $^1\text{H}$  NMR (250 MHz) and  $^{13}\text{C}$  NMR (62.9 MHz), Bruker WM 250 FT; IR, Perkin-Elmer 983. Carbon-13 chemical shifts were referenced to the  $\text{CDCl}_3$  resonance at  $\delta$  77.00 ppm and  $^1\text{H}$  NMR chemical shifts were relative to  $\text{Me}_4\text{Si}$ . The  $\text{K}(\text{sec-C}_4\text{H}_9)_3\text{BH}$  (purchased as K-selectride), Na/K alloy (22/78%), and chloromethyl pivalate were purchased from Aldrich Chemical Company and used as received. The  $\text{Fp}_2$  was obtained from Strem Chemical Company and was used without purification. The  $[\eta^5\text{-C}_5\text{Me}_5\text{Fe}(\text{CO})_2]_2$  was prepared by a literature method [11].

\* The NMR spectrum of the crude reaction mixture also exhibited only a single  $\mu\text{-CH}_2$  resonance at  $\delta$  8.57 ppm.

### Preparation of 1

A THF (50 ml) solution containing  $\text{Fp}_2$  (1.00 g, 2.8 mmol) and K-selectride (0.5 M in THF, 12.0 ml, 6.0 mmol) was refluxed for 1 h. Chloromethyl pivalate (0.42 g, 2.8 mmol) was added to the mixture via syringe and the mixture was then refluxed for 2 h. The solution was cooled to 25°C, filtered, and the solvent volume reduced to ~ 10 ml under vacuum. This mixture was treated with pentane (50 ml) and set aside at -25°C overnight. The solid was collected by filtration, washed with cold pentane (2 × 25 ml), and finally dried in vacuo to afford a mixture of **1** and  $\text{Fp}_2$  (3/1, respectively) as seen by  $^1\text{H}$  NMR. Separation of **1** from  $\text{Fp}_2$  utilized column chromatography eluting with hot hexanes as discussed previously by Casey and co-workers [6]. This gave pure **1** (0.32 g, 35%) by  $^1\text{H}$  NMR as mixture of *cis* and *trans* isomers (3.5/1, respectively).

### Preparation of 2

In a glove box, a flask was charged with THF (50 ml), Na/K alloy (0.34 g, 7.0 mmol), and  $\text{Fp}_2'$  (1.00 g, 2.0 mmol). The mixture was taken out of the glove box and heated at reflux for 1 h. The mixture was cooled to 25°C and filtered through Celite to remove the excess Na/K alloy. Chloromethyl pivalate (0.30 g, 2.0 mmol) was added to the filtrate and the mixture heated at reflux for an additional 2 h. The solution was then allowed to cool to 25°C, filtered, and the solvent removed in vacuo. Column chromatography (2 × 30 cm) of the residue on alumina III eluting with hot hexanes gave purple and red bands, in that order. The solvent was removed from the purple band to afford analytically pure **2** (0.15 g, 15%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.57 (s, 2,  $\text{CH}_2$ ), 1.68 (s, 15,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  280.63 ( $\mu\text{-CO}$ ), 216.12 ( $\text{C}\equiv\text{O}$ ), 159.26 ( $\mu\text{-CH}_2$ ), 97.15 ( $\text{C}_5\text{Me}_5$ ), 9.24 ( $\text{CH}_3$ ); IR ( $\text{cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{CO})$  1909 and 1758. Anal. Found: C, 59.97; H, 6.77.  $\text{C}_{24}\text{H}_{32}\text{Fe}_2\text{O}_3$  calcd.: C, 60.03; H, 6.72%.

### Acknowledgment

G.O.N. gratefully acknowledges support of this work through a grant from the National Science Foundation (CHE-8102918).

### References

- 1 For a leading reference and excellent review of the literature see: W.A. Herrmann, *Adv. Organomet. Chem.*, 20 (1982) 160.
- 2 C.E. Sumner, Jr., P.E. Riley, R.E. Davis and R. Petit, *J. Am. Chem. Soc.*, 102 (1979) 1752; C.E. Sumner, Jr., J.A. Colier and R. Petit, *Organometallics*, 1 (1982) 1350.
- 3 W.A. Herrmann and Ch. Bauer, *J. Organomet. Chem.*, 204 (1981) C21.
- 4 K.M. Motyl, J.R. Norton, C.K. Schauer and O.P. Anderson, *J. Am. Chem. Soc.*, 104 (1982) 7325.
- 5 R. Kirswagen, R. Alt, S. Dieter and M.L. Ziegler, *Angew. Chem.*, 93 (1981), 1073.
- 6 C.P. Casey, P.J. Fagen and W.H. Miles, *J. Am. Chem. Soc.*, 104 (1982) 1134.
- 7 J.A. Gladysz, G.M. Williams, W. Tam and D.K. Johnson, *J. Organomet. Chem.*, 140 (1977) C1.
- 8 The preparation of  $\text{Fp}'\text{K}$  has been reported previously using a K-mirror: D. Catheline and D. Astruc, *J. Organomet. Chem.*, 226 (1982) C52.
- 9 J.E. Ellis, R.W. Fennell and E.A. Flom, *Inorg. Chem.*, 15 (1976), 2031.
- 10 F.A. Cotton, *Chemical Applications of Group Theory*, Wiley, New York, 2nd Ed. Chapter 10.
- 11 R.B. King and M.B. Bisnette, *J. Organomet. Chem.*, 8 (1967) 287.