Organometallics **1998,** *17,* 5931−5932

Cyclopentadienyl(pentamethylcyclopentadienyl)iron Derivatives. A New and Highly Selective Synthesis

Gerhard E. Herberich,* Andreas Gaffke,[1] and Hartmut J. Eckenrath

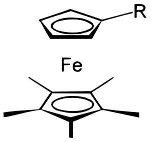
Institut für Anorganische Chemie, Technische Hochschule Aachen, D-52056 Aachen, Germany

Received August 19, 1998

*Summary: [Cp*Fe(AN)$_3$]PF$_6$ (**5**) (AN = MeCN) reacts with alkali metal cyclopentadienides M(C$_5$H$_4$R) (M = Li, Na; R = H, CHO, COMe, CH$_2$NMe$_2$) in acetonitrile at ambient temperature to produce the corresponding (known) pentamethylferrocenes Cp*Fe(C$_5$H$_4$R) (**1**−**4**) in high yields. The potential ligand scrambling products Fe(C$_5$H$_4$R)$_2$ and FeCp*$_2$ are not formed. The new method should be widely applicable; the related syntheses of the boratabenzene complex Cp*Fe(C$_5$H$_5$BMe) and of the phosphaferrocene Cp*Fe(C$_4$Me$_4$P) are pertinent examples.*

Introduction

The sequential addition of two different cyclopentadienides to a metal center is an important synthetic problem in metallocene chemistry. This paper deals with one of the more prominent examples, the synthesis of cyclopentadienyl(pentamethylcyclopentadienyl)iron FeCpCp* [2] (**1**) and its derivatives.[3]



1 : R = H
2 : R = CHO
3 : R = COMe
4 : R = CH$_2$NMe$_2$

The parent compound **1** is efficiently made by the method of Manriquez via an intermediate pentane-2,4-dionate [Cp*Fe(acac)]$_x$, which, in a second step, is treated with MCp (M = Li, Na).[2] We and others have observed that, depending on subtle details of the experimental conditions, some ligand scrambling takes place which results in the formation of ferrocene and decamethylferrocene as byproducts.[3] Ligand scrambling may become dominant for weakly nucleophilic cyclopentadienides such as [C$_5$H$_4$CHO]$^-$.[4] Therefore the Manriquez method is not recommendable for the synthesis of, for example, the formyl and acetyl derivatives, **2**[4] and **3**,[3] respectively.

We have developed a new and highly selective alternative for the preparation of pentamethylferrocene (**1**) and its derivatives such as the compounds **2**−**4**.

Results and Discussion

We use the robust salt [Cp*Fe(AN)$_3$]PF$_6$[5] (**5**) as starting material. This complex can be made in three steps (Scheme 1), commencing with the thermal reaction of Fe(CO)$_5$ with 1,2,3,4,5-pentamethylcyclopentadiene in octane to give [Cp*Fe(CO)$_2$]$_2$.[6] Subsequent oxidation with [FeCp$_2$]PF$_6$[7] in acetonitrile affords [Cp*Fe(CO)$_2$(AN)]PF$_6$,[5] and exhaustive photochemical decarbonylation in acetonitrile finally produces the desired compound **5**.[5] We find that optimized large-scale preparations give 20 g lots of spectroscopically pure **5** with an overall yield of 82%.[1,8] The material may be stored at ambient temperature over months but is rather sensitive in solvents other than acetonitrile.

When compound **5** is treated with alkali metal cyclopentadienides M(C$_5$H$_4$R) (R = H, CHO,[9] COMe,[9] CH$_2$NMe$_2$) in acetonitrile at ambient temperature, the corresponding pentamethylferrocenes **1-4** are formed in high yields (Scheme 2). This is especially remarkable for the formyl compound **2**[4] (92% isolated yield) and the acetyl derivative **3**[3] (99%), where the Manriquez method requires careful chromatographic product separation and gives only moderate yields. Our method was also applied to the synthesis of the *N*,*N*-dimethylaminomethyl derivative **4**, which has previously been made by aminomethylation of **1**.[3] The required cyclopentadienide Na(C$_5$H$_4$CH$_2$NMe$_2$) (**6**) can readily be made from 6-(*N*,*N*-dimethylamino)fulvene[10] (**7**) by hydride addition with NaBHEt$_3$ in toluene at −30 °C; the closely related reaction of 6,6-dimethylfulvene with LiAlH$_4$ to give isopropylcyclopentadienide is a long known reaction.[11] It should be noted, however, that the specified reaction conditions for the synthesis of **6** are critical; if the same hydride addition is attempted with NaBHEt$_3$ in THF or with LiAlH$_4$, the NMe$_2$ group is lost and methylcyclopentadienide is formed.

Our method is clearly advantageous in terms of efficiency and yield when complexes of weakly nucleophilic cyclopentadienides such as **2** and **3** are to be made. Other ligands that are akin to cyclopentadienides can also be linked to Cp*Fe fragments by this method. We have already published two pertinent examples. The reaction of **5** with Li(C$_5$H$_5$BMe) affords the boratabenzene complex Cp*Fe(C$_5$H$_5$BMe),[12] and the reaction with

---

[1] Gaffke, A. Doctoral Dissertation, Technische Hochschule Aachen, Aachen, Germany, 1998.

[2] (a) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680. (b) Manriquez, J. M.; Bunel, E. E.; Oelckers, B. *Inorg. Synth.* **1997**, *31*, 214.

[3] Bildstein, B.; Hradsky, A.; Kopacka, H.; Malleier, R.; Ongania, K.-H. *J. Organomet. Chem.* **1997**, *540*, 127.

[4] Calabrese, J. C.; Cheng, L.-T.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

[5] Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

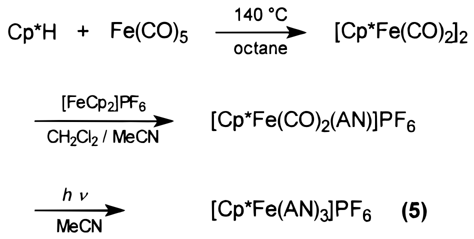
[6] (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287. (b) Salzer, A.; Marko, I. In *Synthetic Methods in Organometallic and Inorganic Chemistry*; Herrmann W. A., Ed.; Thieme Verlag: Stuttgart, 1997; Vol. 8, p 68.

[7] (a) Nesmeyanov, A. N.; Materikova, R. B.; Lyatifov, I. R.; Kurbanov, T. K.; Kochetkova, N. S. *J. Organomet. Chem.* **1978**, *145*, 241. (b) Preparation: Zybill, C. E. In *Synthetic Methods in Organometallic and Inorganic Chemistry*; Herrmann W. A., Ed.; Thieme Verlag: Stuttgart, 1997; Vol. 8, p 12. (c) Review: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

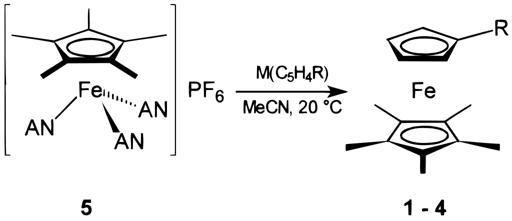
[8] Gaffke, A.; Eckenrath, H. J. Manuscript in preparation.

10.1021/om980708a CCC: $15.00

Scheme 1



Scheme 2



$Li(C_4Me_4P)$ produces the phosphaferrocene $Cp^*Fe(C_4Me_4P)$.[13]

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Hexane was distilled from potassium, CH_2Cl_2, and Et_2O from sodium benzophenone ketyl. Acetonitrile was filtered through a column with activated alumina and distilled under dinitrogen. NMR spectra were recorded on a Varian Unity 500 spectrometer (^1H, 500 MHz; $^{13}C\{^1H\}$, 125.7 MHz) and a Bruker WM-250 (^1H, 250 MHz; ^{13}C, 62.9 MHz) spectrometer.

Preparation of Cp*FeCp (1). Solid **5** (2.66 g, 5.79 mmol) was added with stirring to a suspension of NaCp (0.52 g, 6.0 mmol) in acetonitrile (40 mL) at 0 °C. The temperature was allowed to rise to ambient temperature, and stirring was continued for 1 h. The solvent was removed under vacuum, and the resulting residue was carefully extracted with pentane. Filtration through alumina (10 cm layer on a frit) and removal of the solvent left **1** (1.42 g, 96%) as an orange crystalline solid. Data are as in ref 3 and in the literature quoted therein.

Preparation of $Cp^*Fe(C_5H_4CHO)$ (2). Reaction of **5** (24.1 g, 52.5 mmol) in acetonitrile (200 mL) with $Na(C_5H_4CHO)$[9] (6.1 g, 52.5 mmol) in acetonitrile (100 mL) and workup as described for **1** gave **2** (13.8 g, 92%) as a red solid, mp 62.5−63 °C (lit. red oil[3]).

Preparation of $Cp^*Fe(C_5H_4COMe)$ (3). Reaction of **5** (10.41 g, 22.7 mmol) in acetonitrile (100 mL) and $Na(C_5H_4COMe)$[9] in acetonitrile (100 mL) at −30 °C and standard workup gave **3** (6.7 g, 99%) as a brownish red crystalline solid. Data are as in ref 3.

Synthesis of $Na(C_5H_4CH_2NMe_2)$ (6) and $Cp^*Fe(C_5H_4CH_2NMe_2)$ (4). (a) A solution of **7** (2.44 g, 20.1 mmol) in toluene (50 mL) was cooled with an efficient ice bath. $NaBHEt_3$ (22 mL, 1 M in toluene, Aldrich) was added slowly (10 min). The temperature was then allowed to rise to room temperature, and stirring was continued for 2 h. The solid formed was collected on a frit, washed several times with toluene, and thoroughly dried under high vacuum to give impure **6** (2.7 g, ca. 80% yield) as a pale yellow powder. This material contained mainly some BEt_3 (ca. 10%, NMR), presumably coordinated to the NMe_2 group, and was used as obtained.

^1H NMR (250 MHz, CD_3CN) δ 5.50 ("s", C_5H_4), 3.20 (s, CH_2), 2.09 (s, NMe_2).

(b) A suspension of **6** (1.62 g, 11.1 mmol) in acetonitrile (15 mL) was cooled to −30 °C and quickly combined with a saturated solution of **5** (5.11 g, 11.1 mmol) in acetonitrile. Workup as described for **3** gave a raw product, which was chromatographed on deactivated alumina using a pentane/NEt_3 mixture (20/1) as eluent. Removal of the eluent left **4** (2.54 g, 73%) as a red-brown liquid. Data are as in ref 3.

Acknowledgment. This work was generously supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

OM980708A

---

(9) (a) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 1196. (b) Hart, W. P.; Macomber, D. W.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1.

(10) Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Liebigs Ann. Chem.* **1961**, *641*, 2.

(11) Knox, G. R.; Pauson, P. L. *J. Chem. Soc.* **1961**, 4610.

(12) Herberich, G. E.; Englert, U.; Ganter, B.; Lamertz, C. *Organometallics* **1996**, *15*, 5236.

(13) Herberich, G. E.; Ganter, B. *Organometallics* **1997**, *16*, 522.