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Group 4 and Group 8 unbridged metallocene derivatives with a pendant fluorenyl group. X-ray structure of 1,1′-bis[2-(2-fluorenyl)propyl]ferrocene

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Abstract

The action of one equivalent of BuLi on 2-cyclopentadienyl-2-fluorenylpropane ($C_5H_5CMe_2C_{13}H_9$) led to the monoanionic salt $LiC_5H_4CMe_2C_{13}H_9$. This anion was reacted with $Fe_2Cl_4(THF)_3$, $TiCl_3(THF)_3$, $ZrCl_4$, $HfCl_4$ or $CpZrCl_3$, DME and, in a mixture with CpLi, with $Fe_2Cl_4(THF)_3$ afffording the corresponding metallocenes and metallocene dichlorides. The X-ray structure of $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2$ is described. The first results about the reactivity of the fluorenyl group are reported together with the synthesis of $Zr(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8Rh(cod)]Cl_2$, which has been tested using hydroformylation and cyclotrimerisation catalysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene; Group IV metallocene; Fluorenyl; X-ray structure; Hydroformylation; Cyclotrimerisation

1. Introduction

During the last few years, the synthesis of bimetallic compounds has been of interest in the field of organometallic chemistry. However, the use of cyclopentadienyl rings substituted by a cyclopentadienyl group as precursors to bimetallic compounds has been rarely described. The literature reports anions belonging essentially to the fulvalene class $-C_5H_4-C_5H_4-$ [1] and to ligands with a substituted carbon (Me_2C) or silicon (Me_2Si) atom bridging two cyclopentadienyls [2].

The dianions of ligands containing two cyclopentadienyl, indenyl or fluorenyl groups connected by carbon or silicium-containing units have been frequently used for the synthesis of *ansa*-metallocenes especially of Group 4 transition metals. In a typical synthesis, despite the difference of reactivity, a double deprotonation of 2-cyclopentadienyl-2-fluorenylpropane (or substituted analogues) gives the corresponding dilithium salt which in turn is used to afford the corresponding *ansa*-metallocene dichloride [3].

Recently, one example of cyclopentadienide salt with a pendant fulvenoid fluorenyl group has been described and used to generate the corresponding ferrocene [4].

This paper prompts us to report our results concerning the monolithium salt of 2-cyclopentadienyl-2-fluorenylpropane which precisely gives the above mentioned ferrocenyl complex. Our results are based mainly on a different preparative approach and the successful single-crystal X-ray study as well as the implication of the monolithioligand in bent metallocene chemistry.

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2. Experimental section

All the manipulations were carried out under argon. Solvents were dried over sodium benzophenone ketyl. The ^{1}H- and ^{13}C{^{1}H}-NMR spectra were registered on a Brucker AC 200 instruments in C_6D_6 or $CDCl_3$ at r.t. Elemental analyses were performed by the service de microanalyses du CNRS, Vernaison. $C_5H_5CMe_2C_{13}H_9$ [5] and $[ClRh(cod)]_2$ [6] were prepared by the literature procedure. $Fe_2Cl_4(THF)_3$ was prepared by soxhlet extraction of $FeCl_2$ in THF. Chromatography was performed on Silice Merck 9385.

2.1. *LiC$_5$H$_4$CMe$_2$C$_{13}$H$_9$* (**1**)

A 10 ml volume of butyllithium (2 M in hexane, 20 mmol) was added, at −40°C, to a solution of 5.42 g (20 mmol) of 2-cyclopentadienyl-2-fluorenylpropane in 50 ml of THF. The red solution was stirred for 3 h and then evaporated. The residue was dried and 5.56 g of a yellow powder was obtained (quantitative yield).

^{1}H-NMR, THF-d_8, δ ppm: $C_{13}H_8$, 7.59 (d, 2); 7.13 (t, 2); 6.97 (t, 2); 6.67 (d, 2); Cp, 5.71 (s, 4); $C_{13}H_8$–H, 4.71 (s, 1); Me, 1.13 (s, 6).

No additional THF was observed.

2.2. *Fe(η^5-C$_5$H$_4$CMe$_2$C$_{13}$H$_9$)$_2$* (**2**)

A solution of 5.56 g (20 mmol) of **1** in 50 ml of THF was added, at r.t., to a suspension of 2.35 g (5 mmol) of $Fe_2Cl_4(THF)_3$ in 10 ml of THF. The reaction mixture was stirred for 3 h and then hydrolyzed with 50 ml of water. The product was extracted by 150 ml of dichloromethane and the organic layer was washed twice with 50 ml of water and then dried over $MgSO_4$. Solvent was evaporated and the orange powder was washed by 15 ml of diethylether. A total of 9 g of orange crystals were obtained by recrystallization using the diffusion of hexane in a saturate toluene solution of **2** (yield: 75%).

$F > 250$°C.

Anal. Found: C, 84.06; H, 6.39. $C_{42}H_{38}Fe$. Calc.: C, 84.27; H, 6.4.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.58 (d, 4); 7.23 (t, 4); 7.06 (t, 4); 6.92 (d, 4); Cp, 4.13 (pt, 4); 3.95 (pt, 4); $C_{13}H_8$–H, 3.70 (sl, 2); Me, 1.24 (s, 12).

^{13}C-NMR, $CDCl_3$, δ ppm: $C_{13}H_9$, 145.5; 142.0; 127.05; 126.95; 125.5; 119.1; 38.5; Cp, 100.5; 68.1; 67.5; CMe_2, 60.4; 26.4.

2.3. *Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$CMe$_2$C$_{13}$H$_9$)* (**3**)

A solution of 1.39 g (5 mmol) of **1** and 0.36 g (5 mmol) of cyclopentadienyllithium in 50 ml of THF was added, at r.t., to a suspension of 1.18 g (2.5 mmol) of $Fe_2Cl_4(THF)_3$ in 10 ml of THF. The reaction mixture was stirred for 3 h and then hydrolyzed with 100 ml of water. The product was extracted by 150 ml of dichloromethane and the organic layer was washed twice with 50 ml of water and then dried over $MgSO_4$. Solvent was evaporated and the orange powder was washed by 20 ml of hexane and then chromatographied with dichloromethane/hexane (1/10) as eluent. A total of 0.68 g of orange powder was obtained (yield: 35%).

$F = 198$°C.

Anal. Found: C, 79.95; H, 5.92. $C_{26}H_{24}Fe$. Calc.: C, 79.62; H, 6.12.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.63 (d, 2); 7.27 (t, 2); 7.09 (t, 2); 6.96 (d, 2); Cp, 4.14 (sl, 7); 4.00 (pt, 2); $C_{13}H_8$–H, 3.70 (sl, 1); Me, 1.28 (s, 6).

^{13}C-NMR, $CDCl_3$, δ ppm: $C_{13}H_9$, 146.1; 141.1; 127.7; 127.6; 126.1; 119.8; 38.5; Cp, 69.0; C_5H_4, 101.5; 68.4; 67.4; CMe_2, 61.0; 26.7.

2.4. *Ti(η^5-C$_5$H$_4$CMe$_2$C$_{13}$H$_9$)$_2$Cl$_2$* (**4**)

A solution of 0.56 g (2 mmol) of **1** in 15 ml of THF was added, at r.t., to a suspension of 0.41 g (1 mmol) of $TiCl_3(THF)_3$ in 10 ml of THF. The reaction mixture was stirred for 3 h and then evaporated. The residue was dissolved in 30 ml of toluene and the resulting solution was treated with an excess of saturated ethereal solution of HCl, about 30 ml. The solvent was removed and the resulting red solid was recrystallized in toluene/hexane (4/1) to give 0.29 g of red crystals (yield 44%).

$F = 220$°C.

Anal. Found: C, 75.98; H, 5.81. $C_{42}H_{38}TiCl_2$. Calc.: C, 76.24; H, 5.80.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.49 (d, 4); 7.19 (t, 4); 7.08 (t, 4); 6.92 (d, 4); Cp, 6.19 (s, 8); $C_{13}H_8$–H, 3.77 (s, 2); Me, 1.31 (s, 12).

2.5. *Zr(η^5-C$_5$H$_4$CMe$_2$C$_{13}$H$_9$)$_2$Cl$_2$* (**5**)

A solution of 2.78 g (10 mmol) of **1** in 30 ml of THF was added, at r.t., to a suspension of 1.16 g (5 mmol) of $ZrCl_4$ in 20 ml of THF. The reaction mixture was stirred for 3 h and then evaporated. The white powder was extracted by 50 ml of dichloromethane and the filtrate was evaporated. A total of 2.29 g of white needle were obtained using the diffusion of hexane in a saturated solution of **5** in toluene (yield: 65%).

$F > 250$°C.

Anal. Found: C, 71.31; H, 5.40. $C_{42}H_{38}ZrCl_2$. Calc.: C, 71.55; H, 5.44.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.59 (d, 4); 7.25 (t, 4); 7.06 (t, 4); 6.92 (d, 4); Cp, 6.25 (s, 8); $C_{13}H_8$–H, 3.90 (s, 2); Me, 1.42 (s, 12).

^{13}C-NMR, $CDCl_3$, δ ppm: $C_{13}H_9$, 143.8; 142.7; 124.3; 123.6; 123.0; 119.4; 40.7; Cp, 139.5; 117.5; 109.9; CMe_2, 60.5; 22.9.

2.6. $Hf(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2Cl_2$ (**6**) and $Zr(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)(\eta^5\text{-}C_5H_5)Cl_2$ (**7**)

The same procedure was used to prepare complex **6** using $HfCl_4$ (yield 57%) and **7** using $CpZrCl_3$, DME (yield 65%) as white powders.

6: $F > 250$°C.

Anal. Found: C, 63.41; H, 4.70. $C_{42}H_{38}HfCl_2$. Calc.: C, 63.68; H, 4.83.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.59 (d, 4); 7.26 (t, 4); 7.10 (t, 4); 6.87 (d, 4); Cp, 6.18 (s, 8); $C_{13}H_8$–H, 3.90 (sl, 2); Me, 1.40 (s, 12).

^{13}C-NMR, $CDCl_3$, δ ppm: $C_{13}H_9$, 143.8; 142.7; 124.3; 123.6; 123.0; 119.4; 40.7; Cp, 139.5; 117.5; 109.9; CMe_2, 60.5; 25.8.

7: $F > 250$°C.

Anal. Found: C, 62.46; H, 4.58. $C_{26}H_{24}ZrCl_2$. Calc.: C, 62.62; H, 4.86.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.60 (d, 4); 7.28 (t, 4); 7.12 (t, 4); 6.91 (d, 4); C_5H_5, 6.44 (s, 5); C_5H_4, 6.26 (s, 4); $C_{13}H_8$–H, 3.90 (sl, 1); Me, 1.42 (s, 6).

^{13}C-NMR, $CDCl_3$, δ ppm: $C_{13}H_9$, 145.2; 142.7; 128.0; 127.0; 126.6; 120.1; 41.2; C_5H_5, 116.5; C_5H_4, 142.2; 118.6; 112.5; CMe_2, 61.7; 25.8.

2.7. $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_8Me)_2$ (**9**)

To a solution of 0.6 g (1 mmol) of **2** in 30 ml of THF was added, at -78°C, a solution of 1 ml (2 M in hexane, 10 mmol) of BuLi. The reaction mixture was stirred 1 h and then left to warm to ambient temperature, affording a solution of $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_8)_2\text{-}Li_2$ **8**. Then 2 ml of a solution of iodomethane (1 M in THF, 2 mmol) was added. After 3 h stirring, volatiles were removed. The product was extracted using 50 ml of diethylether. The diethylether was evaporated and the residue was recrystallized in toluene/hexane (1/1). Orange crystals (0.5 g) of **9** were isolated (yield: 80%.).

8: ^{1}H-NMR, THF-d_8, δ ppm: $C_{13}H_8$, 7.61 (d, 4); 7.18 (t, 4); 6.96–7.04 (m, 8); Cp, 4.18 (pt, 4); 4.04 (pt, 4); Me, 1.27 (s, 12).

9: $F = 192$°C.

Anal. Found: C, 84.21; H, 6.82. $C_{44}H_{42}Fe$. Calc.: C, 84.33; H, 6.77.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.58 (d, 4); 7.23 (t, 4); 7.07 (t, 4); 6.93 (d, 4); Cp,; 4.13 (pt, 4); 3.95 (pt, 4); $C_{13}H_8$–H, 3.70 (sl, 2); Me, 1.38 (s, 6); Me_2C, 1.24 (s, 12).

2.8. $Zr(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2Me_2$ (**10**)

A solution (1 ml) of MeLi (2 M in diethylether, 2 mmol) was added dropwise, at 0°C, to a solution of 0.70 g (1 mmol) of **5** in 30 ml of toluene. The reaction mixture was stirred for 2 h and then filtered. Volatiles were removed and the residue was washed using 10 ml of hexane and then recrystallized in toluene/hexane (2/1), leading to 0.6 g of a white powder (90%).

Anal. Found: C, 79.18; H, 6.59. $C_{44}H_{44}Zr$. Calc.: C, 79.61; H, 6.64.

^{1}H-NMR, $CDCl_3$, δ ppm: $C_{13}H_8$, 7.59 (d, 4); 7.25 (t, 4); 7.06 (t, 4); 6.92 (d, 4); Cp, 6.25 (pt, 4); $C_{13}H_8$–H, 3.70 (sl, 2); Me_2C, 1.42 (s, 12); Me, -0.23 (s, 12).

2.9. $Zr(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8Rh(cod)]Cl_2$ (**13**)

The dilithium salt $LiC_5H_4CMe_2C_{13}H_8Li$ was obtained in quantitative yield by the reaction of two equivalents of butyllithium with an ethereal solution of $C_5H_5CMe_2C_{13}H_9$. The yellow powder contains 1.5 molecules of diethylether per molecule of dilithium salt. A solution of 2 g (9.2 mmol) of Me_2SnCl_2 in 20 ml of THF was added dropwise, at -78°C, to a solution of 3.64 g (9.2 mmol) of dilithium salt in 30 ml of THF. The solution became green. The following day, the THF was evaporated and the residue was extracted twice with 40 ml of CH_2Cl_2. Volatiles were removed leading to 2.47 g of **11** as a mixture of isomers (yield 64%). The product was used without any purification and the solution in 60 ml of THF was added to a suspension of 2.09 g (5.89 mmol) of $CpZrCl_3$ and DME in 30 ml of THF. The reaction mixture was heated under reflux for 1 day. The solvent was evaporated and the residue was washed twice with 30 ml of hexane affording 3.04 g of **12** (4.47 mmol; yield 76%) as a fawn powder. Then 1.10 g (2.23 mmol) of $[ClRh(cod)]_2$ in 15 ml of THF was added dropwise to a solution of **12** in 25 ml of THF and the reaction mixture was heated under reflux for 5 days. The volatiles were removed and the residue was washed twice with 20 ml of cold pentane. A total of 1.68 g (53%) of beige powder of **13** was isolated by recrystallisation in heptane.

^{1}H-NMR, $CDCl_3$, δ ppm: **12**: $C_{13}H_8$, 7.72 (m, 4); 7.31 (m, 4); Cp, 6.29 (s, 5); C_5H_4, 5.77 (pt, 2); 5.68 (pt, 2); Me_2C, 2.04 (s, 6); Me_2Sn, 0.13 (s, 12). **13**: $C_{13}H_8$, 7.60 (d, 2); 7.29 (t, 2); 7.11 (t, 2); 6.94 (d, 2); Cp, 6.45 (s, 5); C_5H_4, 6.27 (s, 4); cod, 4.22 (sl, 4); 2.48 (m, 4); 1.74 (m, 4); Me, 1.42 (s, 6).

2.10. Hydroformylation of 1-octene

A solution of 600 µmol rhodium complex **13**, 1.35 g (12.0 mmol) 1-octene, 1.12 g (3.60 mmol) triphenylphosphite in 30 ml toluene was transferred, under a slight pressure of nitrogen, into a 150 ml stainless steel autoclave. The mixture was heated under 1 bar nitrogen to 80°C by means of oil circulating trough a double-envelope in the wall of the autoclave. The autoclave was pressurised to 10 bar with an equimolar mixture of carbon monoxide and hydrogen, and kept at this pressure throughout the reaction (60 min) by a constant pressure feed from a ballast tank. After the reaction, the autoclave was allowed to cool to room temperature and slowly depressurised. Products yields were determined by gas chromatography (Econo-Cap® FFAP column; Alltech, Deerfield, IL) with anisole as the internal standard.

2.11. Cyclotrimerisation of dimethyl acetylenedicarboxylate

A total of 3.42 ml of a 2.38 mM solution of **13** in toluene (8.14 μmol) was added to a solution of 1.00 ml (1.156 g, 8.14 mmol) dimethyl acetylenedicarboxylate in 20 ml toluene in a Schlenk tube. The tube was immediately placed in a preheated oil bath at 50°C and the solution stirred for 60 min. At the end of this time, a few crystals of iodine were added to destroy the catalyst, the mixture was allowed to cool to r.t., and the solvent and unreacted alkyne removed under vacuum to yield 10.6 mg (29.9 μmol) crude hexamethyl mellitate.

2.12. X-ray structure determination of $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2$

Crystal and experimental data for $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2$ are summarized in Table 1. Data were collected at 293 K with a KM-4 diffractometer, using an orange irregular-shaped crystal with the dimension of 0.06 × 0.03 × 0.40 mm. Diffracted intensities were measured using graphite-monochromated Mo–K_α ($\lambda = 0.71069$ Å) radiation. The $\omega/2\theta$ scan mode was employed and stationary background counts were recorded on each side of the reflection. Data were measured for $2 < \theta < 25°$. Correction was made for Lorentz-polarization effects. The space group $P2_1$ was identified from the systematic absence observed in the data.

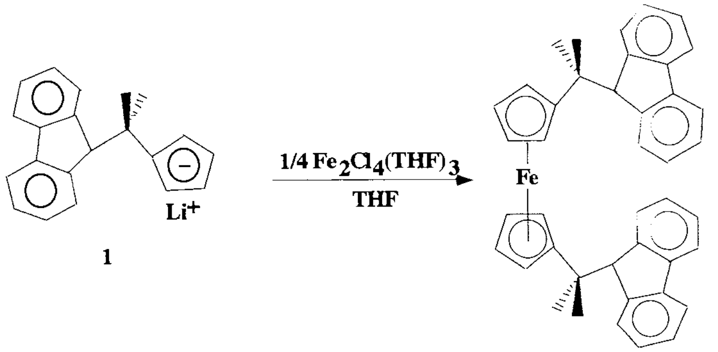
The structure was solved by direct methods. Following anisotropic refinement of the non-hydrogen atoms and isotropic for hydrogen atoms were made. Full-matrix least-squares cycles based upon the minimization of $\Sigma\, w_i(F_o^2 - F_c^2)^2$, with $w_i^{-1} = \sigma^2(F_o^2) + (0.1572P)^2$ where $P = (F_o^2 + 2F_c^2)/3$, converged to give final discrepancy indices of $R = 0.0432$, $wR = 0.1112$ and GOF = 1.099 for 817 reflections with $I > 3\sigma(I)$ where $R = \Sigma\|F_o| - |F_c\||F_o|$ and the S.D. of an observation of unit weight (GOF) is equal to $[\Sigma(w_i(F_o^2 - F_c^2)^2)|\Sigma(n - p)]^{1/2}$ where n is the number of reflections and p is the number of parameters varied during the last refinement cycle.

3. Results and discussion

3.1. Preparation of mono- and bis(substituted) ferrocenes

To date, the preparation and the spectroscopic characterization of monolithium salt $LiC_5H_4CMe_2C_{13}H_9$ **1** have not been described fully. Thus **1** was synthesized without isolation from the stoichiometric reaction of fluorenyllithium and 6,6-dimethylfulvene and was converted to the equivalent thallium salt [7] and to 2-cyclopentadienyl-2-fluorenylpropane [5]. We prepared **1** by the selective metalation of 2-cyclopentadienyl-2-fluorenylpropane on a multigramme scale.

The reaction of two equivalents of monolithium salt **1** with $Fe_2Cl_4(THF)_3$ in THF afforded the 1,1′-bis(substituted) ferrocene **2** in 75% yield (Eq. (1)). It was identified by ^{1}H- and ^{13}C-NMR spectroscopy, microanalysis and X-ray analysis.



1

2

(1)

The monosubstituted ferrocene **3** (Eq. (2)) was obtained by reaction of a mixture of the monolithium salt **1** and the lithium cylopentadienide with $Fe_2Cl_4(THF)_3$ at r.t. An NMR spectrum analysis of the reaction mixture showed the presence of ferrocene/disubstituted ferrocene/monosubstituted ferrocene in a 1:1:1.5 ratio. Complex **3** was isolated by chromatography (yield 35%) and identified by ^{1}H- and ^{13}C-NMR spectroscopy and by microanalysis.

$$\mathbf{1} \xrightarrow[\text{THF, 25°C}]{\text{CpLi, 0.25Fe}_2\text{Cl}_4\text{(THF)}_3} \underset{\mathbf{3}}{Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)} \qquad (2)$$

Note that a mixture of ferrocene and bis(substituted) ferrocene was only obtained when the reaction was performed at low temperature (−40°C). This result is

Table 1
Crystallographic data of $Fe(C_5H_4CMe_2C_{13}H_9)_2$

Empirical formula	$C_{42}H_{38}Fe$
Molecular weight	598.6
Temperature (K)	293(2)
Space group	$P2_1$
a (Å)	9.915(3)
b (Å)	6.293(3)
c (Å)	23.987(2)
V (Å^3)	1483.8(8)
Z	2
$D_{\text{calc.}}$ (g cm^{-3})	1.335
Absorption coefficient (mm^{-1})	0.54
Independent reflections with $[I > 3\sigma]$	1242
Reflections unique	1214
Reflections used	817
Diffractometer	KM-4
Radiation	Mo–K$_\alpha$ graphite
Scan	$2 < \theta < 25$
Solution method	Direct
Refinement	Full-matrix anisotropic
Program	SHELXL
R	0.0432
wR	0.1112
Index ranges	$-10 \leq h \leq 10$, $0 \leq k \leq 6$, $0 \leq 1 \leq 28$
Goodness-of-fit	1099

probably in close relation with the structure of the monolithium salt **1**. Effectively, the NMR spectrum of the monolithium salt shows the absence of coordinated THF on the lithium cation. It was suggested that the structure of this salt is similar to the arrangement described in the case of the equivalent thallium derivative [7]. We propose that, in solution at low temperature, the monolithium salt **1** is stabilized by weak interactions between the lithium cation and the fluorenyl group, which leads to a lower reactivity towards iron chloride than the lithium cyclopentadienide itself.

3.2. Preparation of Group 4 unbridged metallocenes

In the past, much effort has been devoted to the preparation of Group 4 unbridged metallocene dichlorides with bulky substituents or unsymmetric coordination sphere [8]. Instead of cyclopentadienyl ligands, fluorenyl precursors have been used leading to η^5-fluorenyl complexes [9] and the synthesis of $(C_9H_7CMe_2C_5H_4)(C_5H_5)ZrCl_2$ shown the utilisation of the indenyl group as a substituent on the cyclopentadienyl ring [10]. However, dicyclopentadienyl Group 4 complexes with a pendant fluorenyl group on the cyclopentadienyl remain unknown.

The metallocene dichlorides **4**, **5** and **6** were obtained by reaction of two equivalents of monolithium salt **1** on $TiCl_3(THF)_3$, $ZrCl_4$ and $HfCl_4$, respectively (Eq. (3)).

$$\mathbf{1} \xrightarrow[\text{THF}]{\text{TiCl}_3,\ \text{ZrCl}_4 \text{ or HfCl}_4} \text{M}(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_{13}\text{H}_9)_2\text{Cl}_2;\ \text{where M} = \text{Ti } \mathbf{4},\ \text{Zr } \mathbf{5} \text{ and Hf } \mathbf{6}. \qquad (3)$$

The dissymmetric zirconocene dichloride was prepared as described in Eq. (4).

$$\mathbf{1} \xrightarrow[\text{THF}]{\text{CpZrCl}_3(\text{THF})_2} \underset{\mathbf{7}}{\text{Zr}(\eta^5 - \text{C}_5\text{H}_5)(\eta^5 - \text{C}_5\text{H}_5\text{CMe}_2\text{C}_{13}\text{H}_9)_2\text{Cl}_2} \qquad (4)$$

All of these complexes were characterized by ^{1}H- and ^{13}C-NMR spectroscopy, and by elemental analysis.

3.3. Reactivity of $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2$

Presented hereafter is the first result showing the reactivity of the fluorenyl group in **2**. The dilithium salt **8** was obtained by reaction of two equivalents of butyllithium with **2** in THF. Reaction of the dilithium salt with iodomethane led to the complex **9** (Eq. (5)).

$$\underset{\mathbf{8}}{\text{Fe}(\eta^5 - \text{C}_5\text{H}_4\text{CMe}_2\text{C}_{13}\text{H}_8)_2\text{Li}_2} \xrightarrow{\text{MeI}} \underset{\mathbf{9}}{\text{Fe}(\eta^5 - \text{C}_5\text{H}_4\text{CMe}_2\text{-C}_{13}\text{H}_8\text{Me})_2} \qquad (5)$$

Note that this complex is a lot more soluble than the parent compound. This is probably due to the presence, in the parent ferrocene, of the two acid hydrogens of the two fluorenyl groups inducing intermolecular van der Waals interactions.

3.4. X-ray structure of $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2$

The atomic coordinates for $Fe(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2$ are given in Table 2, the structure characterized is shown in Fig. 1 and selected interatomic distances and angles are listed in Table 3.

This compound crystallizes in the monoclinic space group $P2_1$ with two molecules per unit cell.

The molecule is not centrosymmetric. The two substituents adopt the classic *anti* position. The corresponding dihedral C(11)···C(1)···C(6)···C(27) is equal to 171.3°.

The distances between the Fe atom and the centroïd of the cyclopentadienyls C(1–5) and C(6–10) are 1.63 and 1.68 Å, respectively. The quaternary carbons of the isopropylidene groups are located out of the plane of the corresponding cyclopentadienyls and fluorenyls. The angles C(11)–C(1)–Cp(1), C(27)–C(6)–Cp(2), C(11)–C(14)–Fp(1) and C(27)–C(30)–Fp(2), where Cp and Fp represent the mean plane least-squares of the cyclopentadienyl and the fluorenyl groups, are 1.5, 8.7, 30, and 40.4°, respectively.

3.5. Reactivity of the zirconocene **5** and formation of the bimetallic Rh–Zr species **13**

The reactivity of the zirconocene dichloride **5** was studied by the two successive additions, of two equiva-

Table 2
Atomic coordinates and temperature factors of $Fe(C_5H_4CMe_2C_{13}H_9)_2$

Atom	x	y	z	U_{iso}/U_{eq}
Fe	0.7472(8)	0.5000(0)	0.2481(4)	0.041
C(1)	0.836(1)	0.644(1)	0.186(1)	0.048
C(2)	0.731(1)	0.782(1)	0.199(1)	0.047
C(3)	0.603(1)	0.666(1)	0.193(1)	0.050
C(4)	0.634(1)	0.457(1)	0.1740(9)	0.050
C(5)	0.776(1)	0.443(1)	0.170(1)	0.050
C(6)	0.659(1)	0.366(1)	0.317(1)	0.047
C(7)	0.779(1)	0.254(1)	0.304(1)	0.048
C(8)	0.887(1)	0.402(1)	0.314(1)	0.049
C(9)	0.838(1)	0.598(1)	0.328(1)	0.051
C(10)	0.697(1)	0.578(1)	0.329(1)	0.049
C(11)	0.979(1)	0.728(1)	0.184(1)	0.047
C(12)	1.006(1)	0.953(1)	0.2167(9)	0.051
C(13)	1.099(1)	0.580(1)	0.2107(9)	0.049
C(14)	1.000(1)	0.780(1)	0.120(1)	0.043
C(15)	0.890(1)	0.913(1)	0.0824(9)	0.047
C(16)	0.752(1)	0.859(1)	0.0725(9)	0.049
C(17)	0.671(1)	1.004(1)	0.0373(8)	0.051
C(18)	0.712(1)	1.201(1)	0.0270(9)	0.051
C(19)	0.857(1)	1.252(1)	0.0377(9)	0.049
C(20)	0.942(1)	1.115(1)	0.0699(9)	0.047
C(21)	1.098(1)	1.071(1)	0.0826(9)	0.047
C(22)	1.175(1)	1.251(1)	0.0742(9)	0.052
C(23)	1.322(1)	1.194(1)	0.088(1)	0.051
C(24)	1.355(1)	0.980(1)	0.115(1)	0.052
C(25)	1.264(1)	0.831(1)	0.124(1)	0.049
C(26)	1.133(1)	0.903(1)	0.112(1)	0.048
C(27)	0.513(1)	0.294(1)	0.319(1)	0.047
C(28)	0.483(1)	0.117(1)	0.280(1)	0.051
C(29)	0.423(1)	0.489(1)	0.3011(9)	0.050
C(30)	0.505(1)	0.260(1)	0.385(1)	0.045
C(31)	0.383(1)	0.125(1)	0.389(1)	0.047
C(32)	0.237(1)	0.155(1)	0.370(1)	0.051
C(33)	0.133(1)	0.018(1)	0.387(1)	0.052
C(34)	0.172(1)	−0.162(1)	0.412(1)	0.049
C(35)	0.300(1)	−0.212(1)	0.4303(8)	0.049
C(36)	0.415(1)	−0.094(1)	0.4153(8)	0.047
C(37)	0.554(1)	−0.058(1)	0.4323(8)	0.048
C(38)	0.631(1)	−0.229(1)	0.4651(8)	0.050
C(39)	0.760(1)	−0.199(1)	0.4790(8)	0.050
C(40)	0.828(1)	−0.028(1)	0.4558(8)	0.052
C(41)	0.749(1)	0.145(1)	0.4278(8)	0.049
C(42)	0.612(1)	0.110(1)	0.4091(8)	0.047

studied by the two successive additions, of two equivalents of methyllithium. The reaction which begins by the substitution of the chlorine atoms is followed by the aromatisation of the fluorenyl groups.

$$\mathbf{5} \xrightarrow{2\mathrm{MeLi}} \underset{\mathbf{10}}{\mathrm{Zr}(\eta^5\text{-}C_5H_4CMe_2C_{13}H_9)_2Me_2}$$

$$\mathbf{10} \xrightarrow{2\mathrm{MeLi}} \mathrm{Zr}(\eta^5\text{-}C_5H_4CMe_2C_{13}H_8)_2Me_2Li_2 \qquad (6)$$

In the near future, the reactivity of such a lithium salt will be investigated to prepare heteropolymetallic species. In this field, we succeeded in the synthesis of an heterobimetallic complex with a fluorenyl–rhodium pentahapto bond by a classical way [11] using a stanna derivative (Eq. (7)).

$$\underset{\mathbf{11}}{\mathrm{Sn}(\eta^1\text{-}C_5H_4CMe_2\text{-}\eta^1\text{-}C_{13}H_8)Me_2} \xrightarrow{\mathrm{CpZrCl_3,\ DME}}$$

$$\underset{\mathbf{12}}{\mathrm{Zr}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^1\text{-}C_{13}H_8SnMe_2Cl)Cl_2}$$

$$\xrightarrow{0.5[\mathrm{RhCl(cod)}]_2}$$

$$\underset{\mathbf{13}}{\mathrm{Zr}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8Rh\text{-}(cod)Cl_2)} \qquad (7)$$

The stanna derivative **11** was obtained as a mixture of isomers by the addition of Me_2SnCl_2 to the dilithium salt $LiC_5H_4CMe_2C_{13}H_8Li$. The reaction of **11** with $CpZrCl_3 \cdot DME$ in refluxing THF led to the zirconocene **12**, which reacted with $[RhCl(cod)]_2$ to give **13**. This last

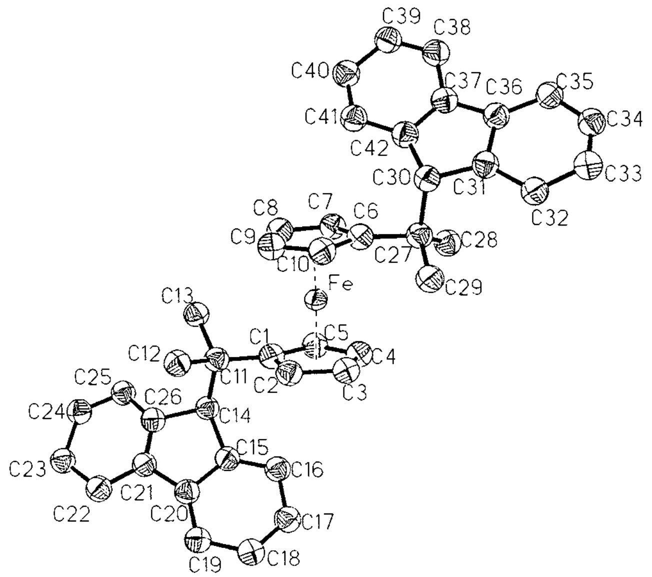


Fig. 1. Molecular structure of complex **2** $Fe(C_5H_4CMe_2C_{13}H_9)_2$.

Table 3
Selected bond lengths (Å) and bond angles (°) at the isopropylidene connections in $Fe(C_5H_4CMe_2C_{13}H_9)_2$

Bond length (Å)			
Fe–C(1)	2.03(2)	Fe–C(6)	2.14(2)
C(1)–C(11)	1.52(2)	C(6)–C(27)	1.52(2)
C(11)–C(14)	1.61(3)	C(27)–C(30)	1.62(3)
C(14)–C(15)	1.57(2)	C(30)–C(31)	1.49(2)
C(14)–C(26)	1.57(2)	C(30)–C(42)	1.48(2)
Bond angle (°)			
C(1)–C(11)–C(14)	110(1)	C(6)–C(27)–C(30)	103(1)
Cp(1)–C(11,12,13)	136.1	Cp(2)–C(27,28,29)	124.9
Flu(1)–C(11,12,13)	128.5	Flu(2)–C(27,28,29)	117.9

Table 4
The hydroformylation of 1-octene in the presence of **13** and of $[Rh(OH)(cod)]_2$

Catalyst	Conversion[a]	Yield[a]		Specificity[b]
		Nonanal	2-Methyloctanal	
13	2.5	2.1	0.4	83.2
$[Rh(OH)(cod)]_2$	95.8	78.2	17.6	81.6

Conditions, [Rh] = 20 mM; [1-octene] = 400 mM; $[P(OPh)_3]$ = 120 mM; [Rh]/[P] = 6, p = 10 bar; $p(CO)/p(H_2) = 1$; T = 80°C; t = 60 min.

[a] Based on 1-octene, determined by gas chromatography: no hydrogenation or double bond isomerisation was observed.

[b] Specificity = [nonanal]/([nonanal] + [2-methyloctanal]).

complex was somewhat sensitive to atmospheric moisture and readily hydrolysed to give **7**.

3.6. Catalytic activity of ***13***

3.6.1. Hydroformylation of 1-octene

Recently prepared samples of **13** showed negligible catalytic activity for the hydroformylation of octene under anhydrous conditions. Tests carried out using old samples of **13**, or under conditions where water was not rigorously excluded, gave spurious results: this was ascribed to the partial hydrolysis of **13**, yielding **7** and $[Rh(OH)(cod)]_2$. The results of the hydroformylation of 1-octene in the presence of **13** and of $[Rh(OH)(cod)]_2$ [12] are shown in Tables 4–7.

Table 5
Bond lengths (Å) of $Fe(C_5H_4CMe_2C_{13}H_9)_2$

Fe–C(1)	2.03(2)	Fe–C(2)	2.12(2)
Fe–C(3)	2.09(2)	Fe–C(4)	1.99(2)
Fe–C(5)	1.96(2)	Fe–C(6)	2.14(2)
Fe–C(7)	2.05(2)	Fe–C(8)	2.05(2)
Fe–C(9)	2.10(2)	Fe–C(10)	2.13(2)
C(1)–C(2)	1.42(2)	C(1)–C(5)	1.43(2)
C(1)–C(11)	1.52(2)	C(2)–C(3)	1.45(2)
C(3)–C(4)	1.44(2)	C(4)–C(5)	1.43(2)
C(6)–C(7)	1.45(2)	C(6)–C(10)	1.41(1)
C(6)–C(27)	1.52(2)	C(7)–C(8)	1.41(2)
C(8)–C(9)	1.39(2)	C(9)–C(10)	1.41(2)
C(11)–C(12)	1.62(2)	C(11)–C(13)	1.58(2)
C(11)–C(14)	1.61(3)	C(14)–C(15)	1.57(2)
C(14)–C(26)	1.57(2)	C(15)–C(16)	1.40(2)
C(15)–C(20)	1.42(1)	C(16)–C(17)	1.42(2)
C(17)–C(18)	1.34(1)	C(18)–C(19)	1.46(2)
C(19)–C(20)	1.36(2)	C(20)–C(21)	1.57(2)
C(21)–C(22)	1.39(1)	C(21)–C(26)	1.29(2)
C(22)–C(23)	1.49(2)	C(23)–C(24)	1.52(2)
C(24)–C(25)	1.34(2)	C(25)–C(26)	1.37(2)
C(27)–C(28)	1.45(2)	C(27)–C(29)	1.54(2)
C(27)–C(30)	1.62(3)	C(30)–C(31)	1.49(2)
C(30)–C(42)	1.48(2)	C(31)–C(32)	1.47(2)
C(31)–C(36)	1.53(2)	C(32)–C(33)	1.44(2)
C(33)–C(34)	1.31(2)	C(34)–C(35)	1.33(2)
C(35)–C(36)	1.45(2)	C(36)–C(37)	1.40(2)
C(37)–C(38)	1.48(2)	C(37)–C(42)	1.36(2)
C(38)–C(39)	1.30(2)	C(39)–C(40)	1.42(2)
C(40)–C(41)	1.46(2)	C(41)–C(42)	1.39(2)

Table 6
Bond angles (deg) of $Fe(C_5H_4CMe_2C_{13}H_9)_2$

C(2)–C(1)–C(5)	108(1)	C(1)–C(2)–C(3)	109(1)
C(2)–C(3)–C(4)	106(1)	C(3)–C(4)–C(5)	109(1)
C(1)–C(5)–C(4)	108(1)	C(7)–C(6)–C(10)	107(1)
C(6)–C(7)–C(8)	106(1)	C(7)–C(8)–C(9)	110(1)
C(8)–C(9)–C(10)	108(1)	C(6)–C(10)–C(9)	109(1)
C(1)–C(11)–C(12)	112(1)	C(1)–C(11)–C(13)	116(1)
C(1)–C(11)–C(14)	110(1)	C(12)–C(11)–C(13)	105(1)
C(12)–C(11)–C(14)	105(1)	C(13)–C(11)–C(14)	109(1)
C(15)–C(14)–C(26)	101(1)	C(14)–C(15)–C(20)	111(1)
C(16)–C(15)–C(20)	124(1)	C(15)–C(16)–C(17)	114(1)
C(16)–C(17)–C(18)	123(1)	C(17)–C(18)–C(19)	119(1)
C(18)–C(19)–C(20)	119(1)	C(15)–C(20)–C(19)	118(1)
C(15)–C(20)–C(21)	100(1)	C(20)–C(21)–C(22)	112(1)
C(20)–C(21)–C(26)	116(1)	C(22)–C(21)–C(26)	129(1)
C(21)–C(22)–C(23)	108(1)	C(22)–C(23)–C(24)	117(1)
C(23)–C(24)–C(25)	125(1)	C(24)–C(25)–C(26)	112(1)
C(14)–C(26)–C(21)	108(1)	C(21)–C(26)–C(25)	125(1)
C(6)–C(27)–C(28)	109(1)	C(6)–C(27)–C(29)	106(1)
C(6)–C(27)–C(30)	103(1)	C(28)–C(27)–C(29)	112(1)
C(27)–C(30)–C(42)	110(1)	C(31)–C(30)–C(42)	99(1)
C(30)–C(31)–C(36)	114(1)	C(32)–C(31)–C(36)	113(1)
C(32)–C(33)–C(34)	118(1)	C(33)–C(34)–C(35)	124(1)
C(34)–C(35)–C(36)	123(1)	C(31)–C(36)–C(35)	116(1)
C(31)–C(36)–C(37)	97(1)	C(36)–C(37)–C(42)	117(1)
C(38)–C(37)–C(42)	125(1)	C(37)–C(38)–C(39)	117(1)
C(38)–C(39)–C(40)	121(1)	C(39)–C(40)–C(41)	120(1)
C(40)–C(41)–C(42)	118(1)	C(30)–C(42)–C(37)	110(1)
C(37)–C(42)–C(41)	116(1)		

The almost complete inactivity (the slight activity being ascribed to hydrolysis by traces of water in the dried reactants or on the walls of the reactor) was somewhat unexpected, as [RhCp(cod)] has been claimed to be a catalyst for alkene hydroformylation [13], and fluorenyl-type compounds are usually more active in reactions involving ligand exchange and displacement than their cyclopentadienyl homologues [14].

3.6.2. Cyclotrimerisation of dimethyl acetylenedicarboxylate

[Rh(fluorenyl)(cod)] is a known catalyst for the [2 + 2 + 2] cycloaddition of alkynes [15], showing a turnover of 280 h^{-1} for the conversion of dimethyl acetylenedicarboxylate to hexamethyl mellitate under the conditions used here (50°C, [alkyne]/[Rh] = 1000). The activity of **13** is very much lower (3.7 h^{-1}), although this is still more active than the cyclopentadienyl complex, [RhCp(cod)], which does not catalyse this reaction at all temperatures < 100°C.

Table 7
Anisotropic temperature factors ($\times 10^4$) of $(C_{13}H_9C(CH_3)_2C_5H_4)_2Fe$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	358(10)	592(11)	272(10)	67(12)	30(9)	−41(12)
C(1)	484(10)	479(13)	479(13)	4(13)	60(13)	1(13)
C(2)	474(13)	483(13)	460(13)	17(13)	90(13)	4(13)
C(3)	494(13)	500(13)	490(13)	12(13)	49(13)	7(13)
C(4)	510(13)	505(13)	488(13)	8(13)	54(13)	−27(13)
C(5)	500(13)	502(13)	485(13)	−3(13)	66(13)	−1(13)
C(6)	474(13)	474(13)	473(13)	2(13)	64(13)	−3(13)
C(7)	485(13)	489(13)	473(13)	18(13)	82(13)	10(13)
C(8)	478(13)	506(13)	488(13)	11(13)	62(13)	9(13)
C(9)	508(13)	508(13)	499(13)	1(13)	51(13)	−32(13)
C(10)	492(13)	496(13)	476(13)	−4(13)	72(13)	−3(13)
C(11)	468(13)	481(13)	471(13)	16(13)	73(13)	6(13)
C(12)	518(13)	498(13)	507(13)	−5(13)	75(13)	−9(13)
C(13)	486(13)	499(13)	497(13)	1(13)	60(13)	16(13)
C(14)	430(13)	448(13)	426(13)	15(13)	80(13)	7(13)
C(15)	466(13)	494(13)	462(13)	−3(13)	66(13)	−2(13)
C(16)	486(13)	497(13)	482(13)	7(13)	69(13)	8(13)
C(17)	505(13)	526(13)	500(13)	−4(13)	63(13)	1(13)
C(18)	516(13)	524(13)	502(13)	6(13)	60(13)	15(13)
C(19)	499(13)	502(13)	487(13)	5(13)	83(13)	15(13)
C(20)	474(13)	469(13)	460(13)	7(13)	60(13)	8(13)
C(21)	463(13)	477(13)	468(13)	8(13)	74(13)	−1(13)
C(22)	521(13)	516(13)	513(13)	2(13)	77(13)	−8(13)
C(23)	503(13)	520(13)	504(13)	−1(13)	87(13)	−13(13)
C(24)	511(13)	531(13)	523(13)	6(13)	74(13)	−6(13)
C(25)	485(13)	497(13)	485(13)	8(13)	73(13)	−2(13)
C(26)	473(13)	482(13)	478(13)	1(13)	79(13)	3(13)
C(27)	463(13)	480(13)	463(13)	10(13)	83(13)	−6(13)
C(28)	514(13)	501(13)	506(13)	−9(13)	73(13)	−11(13)
C(29)	491(13)	508(13)	500(13)	7(13)	52(13)	5(13)
C(30)	448(13)	471(13)	440(13)	29(13)	71(13)	−2(13)
C(31)	469(13)	474(13)	481(13)	3(13)	75(13)	9(13)
C(32)	503(13)	521(13)	504(13)	6(13)	80(13)	−4(13)
C(33)	509(13)	528(13)	518(13)	12(13)	73(13)	−8(13)
C(34)	491(13)	497(13)	488(13)	0(13)	75(13)	−13(13)
C(35)	496(13)	501(13)	492(13)	−3(13)	84(13)	−1(13)
C(36)	477(13)	476(13)	471(13)	2(13)	67(13)	4(13)
C(37)	486(13)	482(13)	477(13)	4(13)	61(13)	6(13)
C(38)	512(13)	507(13)	491(11)	6(13)	69(13)	18(13)
C(39)	502(11)	508(11)	490(11)	14(11)	78(11)	9(11)
C(40)	515(11)	523(11)	513(11)	−6(11)	63(11)	0(11)
C(41)	485(11)	499(11)	477(11)	6(11)	66(11)	6(11)
C(42)	473(11)	493(11)	463(11)	−7(11)	77(11)	−1(11)

Two hypotheses may be proposed for this relative lack of activity. The steric hindrance of the $-CMe_2C_5H_4ZrCpCl_2$ group may inhibit the coordination of alkyne to the supposed metallocyclopentadiene intermediate [16]. Alternatively, the bulk of the $-CMe_2-$ bridge may inhibit the 'ring slippage' coordination isomerism of the fluorenyl ring which has been proposed as the reason for the high activity of [Rh(fluorenyl)(cod)] in this reaction [16]. Although attempts to grow single crystals of **13** have proved unsuccessful, the crystal structure of [Rh(fluorenyl)(cod)] shows an asymmetric coordination of the five-membered ring in the solid state, with the rhodium atom substantially closer to C9 than to the other ring carbons [17]. The bulk of the bridging group and of the zirconocene portion of the molecule would disfavor such a ground state ring slippage in **13**.

4. Supplementary material

Tables of fractional atomic coordinates for H are available from the authors upon request.

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