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Selective mono- and di{(perfluoroalkyl)acylation} of ferrocene

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Abstract

The selective synthesis of mono- and 1,1′-di{(perfluoroalkyl)acylated} ferrocenes by Friedel–Crafts acylation with (perfluoroalkyl)acyl halides is described. The acyl derivatives were further converted to the corresponding (perfluoroalkyl)alkyl ferrocenes by reduction of the carbonyl group with $LiAlH_4/AlCl_3$. Electrochemical studies of all the obtained substituted ferrocenes were carried out to assess the influence of the perfluoroalkyl ponytails on their redox behavior.

Keywords: Perfluoroalkylation; Perfluoroacylation; Ferrocene; Perfluoroalkylated ferrocenes

1. Introduction

A recent demand for environmentally benign technologies has led to the development of homogeneous catalysis in biphasic systems with fluorous phase [1] and, consequently, has initiated a search for catalytically active, fluorophilic transition–metal complexes. As the latter are derived mostly from the classical, non-fluorophilic complexes by a modification of their ligands with perfluoroalkyl substituents, a careful choice of the parent ligand backbone and its proper modification are vital for obtaining of efficient catalytic systems.

Among the compounds so far tested, cyclopentadienyl complexes are of particular importance because the cyclopentadienyl ligand is usually firmly bound to the metal. There have been reported preparation of perfluoralkylated cyclopentadienes and the formation of some transition metal complexes thereof. However, a directly attached perfluoroalkyl moiety, due to its strong electron-withdrawing nature, dramatically changes electronic properties and reactivity of the cyclopentadienyl ligands and their complexes [2]. Hence, it is of general interest to develop methods for the preparation of new perfluoroalkylated cyclopentadienes and their complexes with a spacer inserted between the cyclopentadienyl ring and the perfluoroalkyl chain that would shield the cyclopentadienyl ring from the inductive effect of the perfluoroalkyl chain. There has been some progress achieved in the recent years in the development of methods for the preparation of (perfluoroalkyl)alkylated cyclopentadienes by alkylation of cyclopentadienes with $R^fCH_2CH_2I$ but these procedures has been usually plagued by relatively low yields and selectivity [3,4].

The preparation of (perfluoroalkyl)alkylcyclopentadienes could be circumvented by a direct (perfluoroalkyl)alkylation of cyclopentadienyl compounds. One of the possible approaches is Friedel–Crafts acylation of metallocenes with acyl halides followed by reduction of the acyl to an alkyl group. Although there have been reported a number of acylation reactions with cyclopentadienyl complexes of iron [5], cobalt [6], manganese [6a], this approach has not yet been applied for (perfluoroalkyl)acylation. The only exception is acylation of ferrocene with (perfluoroalkyl)acyl chloride with a 10-carbon atom spacer [7]. Herein we would like to report our results on selective mono and diacylation of ferrocene with 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl chloride **1** ($C_6F_{13}CH_2CH_2C(O)Cl$).

2. Results and discussion

Although there are several synthetic routes [8] leading to the starting (perfluoroalkyl)acyl chloride **1**, we used the procedure outlined in Scheme 1 as it allows to use a readily accessible starting material: the reaction sequence started

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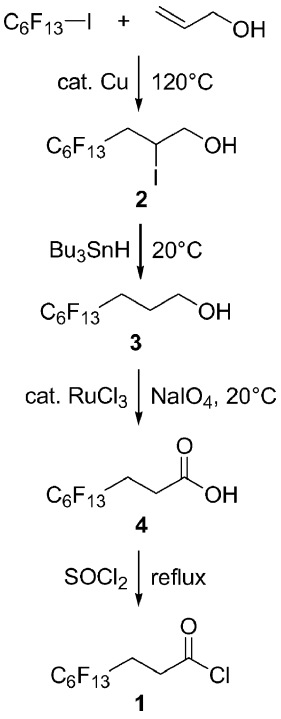
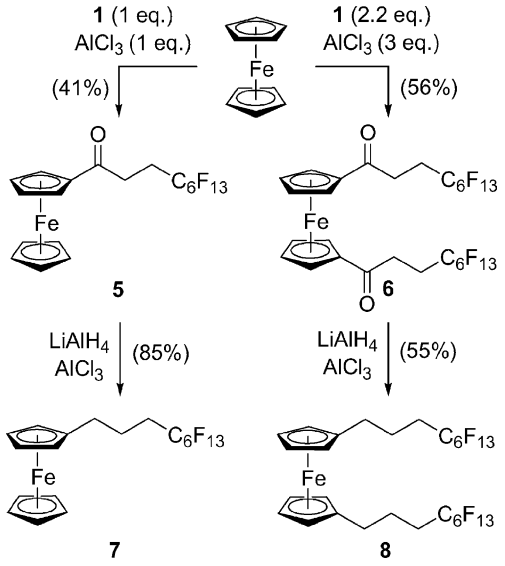


Scheme 1. Preparation of acyl chloride **1**.



Scheme 2. Mono- and diacylation of ferrocene.

with copper-catalyzed radical addition of perfluorohexyl iodide to propenol to give 2-iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-ol (**2**) followed by reduction with tributylstannane to 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononano-1-ol (**3**) [9]. Alcohol **3** was easily oxidized to 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoic acid (**4**) under mild conditions by using a $RuCl_3$(cat.)/$NaIO_4$ catalytic system and biphasic conditions [10]. Finally, 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl chloride **1** was prepared by reaction of acid **4** with thionyl chloride [11].

Initially, monoacylation of ferrocene with 1 eq. of (perfluoroalkyl)acyl chloride **1** was carried out in the presence of $AlCl_3$ in tetrachloromethane under the same reaction conditions as previously reported (Scheme 2) [7]. However, the reaction did not proceed well, resulting in a mixture of mono- and di(perfluoroalkyl)acylated products **5** and **6** in a rather low yield. This could be attributed to the precipitation of (perfluoroalkyl)acyl aluminate which formed upon the addition of (perfluoroalkyl)acyl chloride **1** into a suspension of $AlCl_3$ in tetrachloromethane. Heterogeneous condition thus influenced the distribution and the overall yield of the products. Our assumption to change the solvent proved correct and a replacement of tetrachloromethane with dichloromethane enabled us to prepare a solution of (perfluoroalkyl)acyl aluminate and to carry out the acylation reaction under homogenous conditions. Although the reaction time was in comparison with the usual acylations rather long (5 days), (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononano1-oyl)ferrocene (**5**) was formed selectively in 48% yield (after work-up). Unreacted ferrocene was recovered in 37% yield and the formation of di(perfluoroalkyl)acylated product **6** was observed only in a negligible extent (ca. 1%). Diacylation was carried out under the same conditions but with 2.2 eq. of **1** and gave selectively 56% of bis(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl)ferrocene (**6**). The formation of mono(perfluoroalkyl)acylated product **5** was not observed. Interestingly, an attempt to carry out acylation directly by using a mixture $POCl_3$/$AlCl_3$ and carboxylic acid **4** did not afford any acylated ferrocenes [5d].

The next step was the reduction of the carbonyl group to a methylene group. In both cases the reduction was achieved with a mixture of $LiAlH_4$/$AlCl_3$ to give the corresponding products **7** and **8** in 85 and 55% yields, respectively [12].

3. Electrochemistry

As revealed by voltammetric and cyclovoltammetric measurements (Table 1), compounds **5**–**8** are reversible, one-electron redox systems though the peak separations in cyclovoltammograms (ΔE_p) of the disubstituted ferrocenes are notably higher in the series. Whereas compounds **5** and **7** show ΔE_p close to the value expected for an ideal, reversible one-electron system (ca. 60 mV, cf. $\Delta E_p = 65$ mV for ferrocene under identical conditions), ferrocene-1,1′-diyl derivatives **6** and **8** exhibit significantly larger peak separations (95 and 120 mV, respectively) and, accordingly, slightly tilted voltammetric waves. This points to some chemical complications accompanying the electrochemical oxidation in the latter case such as slow diffusion expectable for large molecules [3], sorption processes or rather slow subsequent reactions.

In accordance with the electron-withdrawing nature of their substituents, ketones **5** and **6** are shifted to higher redox potentials compared to ferrocene itself, the potential shift for **6** being nearly twice of that observed for **5**. This points to an

Table 1
Electrochemical data for **5**–**8**[a]

Metallocene	E° (V)	ΔE_p (mV)
5	0.30	80
6	0.56	95
7	0.00	70
8	−0.01	120
$Fe(CpR^f)_2$-I[b]	0.03[c]	–
$Fe(CpR^f)_2$-II[b]	0.04[c]	–

E° is the redox potential determined by cyclic voltammetry as $E^\circ = (1/2)(E_{pa} + E_{pc})$ while ΔE_p denotes the separation of the cyclovoltammetric counter peaks, $\Delta E_p = E_{pa} - E_{pc}$, E_{pa} and are the anodic and cathodic peak potentials, respectively. The half-wave potentials determined from voltammetric curves are identical with E° and, therefore, only cyclovoltammetric date are listed in the Table. For conditions see Section 5.

[a] The potentials are given relative to internal ferrocene/ferrocenium.

[b] $Fe(CpR^f)_2$-I = [Fe{η^5-$C_5H_4(CH_2CH_2C_6F_{13})$}$_2$), $Fe(CpR^f)_2$-II = [Fe{η^5-$C_5H_4(CH_2CH_2C_{10}F_{21})$}$_2$].

[c] In THF data from ref. [3].

additivity of the electronic influences of the substituents at the ferrocene unit with the deviation from simple additivity attributable to an electron buffering effect of the cyclopentadienyl π-electron systems. On the other hand, the ferrocene/ferrocenium potentials observed for **7** and **8** do not virtually differ from that of unsubstituted ferrocene. This implies that 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroct-1-yl substituent has virtually no electronic influence on the ferrocene core [H ≈ $(CH_2)_3(CF_2)_5CF_3$] and that the propane-1,3-diyl spacer is long enough to compensate efficiently an electron-withdrawing effect of the perfluorohexyl chain. A comparison of our data for trimethylene-spaced compound **7** with its dimethylene analogue, [Fe{η^5-$C_5H_4(CH_2CH_2C_6F_{13})$}$_2$], and the related compound [Fe{η^5-$C_5H_4(CH_2CH_2C_{10}F_{21})$}$_2$] (Table 1) indicates that the propane-1,3-diyl spacer assists in insulating the ferrocene unit from the perfluoroalkyl chain slightly more efficiently than the shorter bridge, acting as an ''electronically neutral'', not yet electron-donating substituent (cf. E° for 1,1′-bis(alkylated)ferrocene, [Fe(η^5-$C_5H_4Me)_2$], of ca. −0.05 V in MeCN [13]).

4. Conclusion

We may conclude that the acylation of metallocenes (ferrocenes) with (perfluoroalkyl)acyl chlorides may constitute an alternative approach for the preparation of cyclopentadienyl metal complexes with (perfluoroalkyl)alkyl ponytails with and without polar carbonyl group(s). In the case of ferrocene it is possible to control mono- and di(perfluoroalkyl)acylation selectively and simply by changing the amount of (perfluoroalkyl)acyl halides and aluminium chloride. In addition, electrochemical studies have shown that propane-1,3-diyl spacer separates efficiently the ferrocene unit from an electron-withdrawing influence of the perfluoroalkyl chain.

5. Experimental

Perfluorohexyl iodide, ferrocene, aluminium chloride, tributylstannane, thionyl chloride were purchased from Aldrich and used as obtained. Propenol and dichloromethane (dried over CaH_2) were distilled prior to use. 2-Iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-ol acid (**2**) [9], 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-ol (**3**) [9], 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl chloride (**4**) [11] were prepared according to the previously published procedures.

NMR spectra were measured on a Varian UNITY Inova 400 spectrometer (^{1}H, 400.0, ^{13}C, 100.6, and ^{19}F, 376.3 MHz). Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H, ^{13}C) or to neat external $CFCl_3$ (^{19}F, $\delta = 0$). IR spectra were recorded on a Perkin-Elmer PE 640 spectrometer. High resolution, electron impact (EI) mass spectra were measured on a ZAB SEQ spectrometer. Positive ion FAB mass spectra were recorded on the same instrument in a glycerol-thioglycerol matrix. Elemental analyses were obtained on a Perkin-Elmer 2400 elemental analyzer. Melting points were determined on a Kofler apparatus and are uncorrected. TLC was performed on Merck Silica Gel 60 F_{254} aluminium sheets and column chromatography was carried out on Merck Silica Gel 60.

Electrochemical measurements were carried out at 20 °C with a multipurpose polarograph PA3 connected to an XY Recorder 4103 (Laboratorní přístroje, Prague) using a three-electrode consisting of a platinum disc working, platinum wire auxiliary, and Ag/AgCl (1 M KCl) reference electrodes (the reference electrode was separated from the measuring compartment by a salt bridge filled with 1 M aqueous KCl). The analyzed solutions contained 4×10^{-4} M of the analyzed compounds and 0.1 M Bu_4NPF_6 as the base electrolyte (Fluka, puriss. for electrochemistry) dissolved in dichloromethane (Merck p.a., used without any further purification). The solutions were purged with argon and then kept under an argon blanket. Cyclic voltammograms were recorded on the stationary disc electrode at 100 mV s^{-1} while the voltammograms were measured with rotating electrode (1000 min^{-1}) at a scan rate of 20 mV s^{-1}. The potentials are given in Volts relative to the redox potential of an internal ferrocene/ferrocenium standard (E°(FcH/FcH$^+$) = 0.48 V versus Ag/AgCl).

5.1. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-oic acid (4)

A mixture of CCl_4/MeCN/H_2O (8/8/12 ml), tridecafluorononan-1-ol **3** (1.55 g, 4 mmol), $RuCl_3{\cdot}xH_2O$ (22 mg, 0.1 mmol as trihydrate), and $NaIO_4$ (3.42 g, 16 mmol) was stirred at 20 °C for 24 h. Then, the reaction mixture was extracted with Et_2O (5 ml × 20 ml), organic fractions were collected and dried over $MgSO_4$. Evaporation of the solvent followed by distillation of the residue under reduced pressure (115 °C/100 Pa) afforded 1 g (64%) of the title

compound as a colorless solid. Its spectral characteristics were identical with the previously published data [8a].

5.2. (4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-oyl)ferrocene (**5**)

To a suspension of aluminium chloride (135 mg, 1 mmol) in dichloromethane (3 ml) was added dropwise a solution of 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl chloride **1** (411 mg, 211 μl, 1 mmol) in dichloromethane (3 ml) at 0 °C. The reaction mixture was stirred at the same temperature for 45 min, then ferrocene (188 mg, 1 mmol) was gradually added in small portions, and the reaction mixture was stirred for 5 days at 20 °C. The resulting solution was treated with ice and 3 M HCl (5 ml). Organic layer was separated, aqueous phase was extracted with hexane (3 ml × 10 ml), and the combined organic fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (1/1 hexane/$CDCl_3$) to afford 68 mg (37%) of ferrocene and 228 mg (41%) of the title compound as an orange solid: mp 96–97 °C; ^{1}H NMR ($CDCl_3$) δ 2.48–2.66 (m, 2H, CH_2C(O)), 3.10 (filled-in t, $J' = 7.5$ Hz, 2H, CH_2CF$_2$), 4.23 (s, 5H, C$_5H_5$), 4.57 (apparent t, 2H, C$_5H_4$), 4.84 (apparent t, 2H, C$_5H_4$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 25.5 (t, $^2J_{FC} = 12$ Hz, CH$_2$CF$_2$), 30.2 (unresolved t, CH$_2$C(O)), 69.3 (CH of C$_5$H$_4$), 69.9 (C$_5$H$_5$), 72.6 (CH of C$_5$H$_4$), 78.1 (C_{ipso} of C$_5$H$_4$), 200.5 (C=O); ^{19}F NMR ($CDCl_3$) δ −126.3 (m, 2F, CF$_2$), −123.6 (m, 2F, CF$_2$), −123.2 (m, 2F, CF$_2$), −122.1 (m, 2F, CF$_2$), −114.3 (m, 2F, CF$_2$), −81.1 (t, $^3J_{FF} = 10$ Hz, 3F, CF$_3$); IR ($CHCl_3$) 1674 s ($\nu_{C=O}$), 1458 m, 1243 s, 1146 m, 1066 w cm^{-1}; HR MS (EI) calcd for $C_{19}H_{13}F_{13}FeO$ 560.01082, found 560.01174. Anal. calcd for $C_{19}H_{13}F_{13}FeO$: C, 40.74; H, 2.34; F, 44.09; Fe, 9.97; O, 2.86. Found: C, 41.29; H, 2.31.

5.3. bis(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-oyl)ferrocene (**6**)

To a suspension of aluminium chloride (405 mg, 3 mmol) in dichloromethane (6 ml) was added dropwise a solution of 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl chloride **4** (904 mg, 532 μl, 2.2 mmol) in dichloromethane (4 ml) at 0 °C. The reaction mixture was stirred at the same temperature for 45 min, then ferrocene (188 mg, 1 mmol) was gradually added in small portions. After that the reaction mixture was stirred for 5 days at 20 °C. The resulting solution was treated with ice and 3 M HCl (5 ml). Organic layer was separated, aqueous phase was extracted with hexane (3 ml × 10 ml), and the combined organic fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (8/1 hexane/Et_2O) to give 520 mg (56%) of the title compound as an orange solid: mp 76–77 °C; ^{1}H NMR ($CDCl_3$) δ 2.48–2.64 (m, 4H, CH$_2$C(O)), 2.90–2.96 (filled-in t, $J' = 7.5$ Hz, 4H, CH_2CF$_2$), 4.55 (apparent t, 4H, C$_5H_4$), 4.86 (apparent t, 4H, C$_5H_4$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 25.0 (t, $^2J_{FC} = 12$ Hz, CH$_2$CF$_2$), 30.9 (CH$_2$C(O)), 70.7 (CH of C$_5$H$_4$), 73.6 (CH of C$_5$H$_4$), 79.6 (C_{ipso} of C$_5$H$_4$), 199.7 (C=O); ^{19}F NMR ($CDCl_3$) δ −126.5 (m, 4F, CF$_2$), −123.9 (m, 4F, CF$_2$), −123.2 (m, 4F, CF$_2$), −122.2 (m, 4F, CF$_2$), −114.4 (m, 4F, CF$_2$), −81.1 (t, $^3J_{FF} = 10$ Hz, 6F, CF$_3$); IR ($CHCl_3$) 1679 m ($\nu_{C=O}$), 1243 s, 1146 m, 1066 w cm^{-1}; HR MS (FAB+) calcd for $C_{28}H_{17}F_{26}FeO_2$ ($M + 1$) 935.01628, found 935.01495. Anal. calcd for $C_{28}H_{16}F_{26}FeO_2$: C, 36.00; H, 1.73; F, 52.87; Fe, 5.98; O, 3.43. Found: C, 36,18; H, 1,67.

5.4. (4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-yl)ferrocene (**7**)

To a stirred suspension of lithium aluminium hydride (20 mg, 0.5 mmol) in dry diethylether (6 ml) was added slowly aluminium chloride (67 mg, 0.5 mmol). After vigorous reaction had subsided, a solution of (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl)ferrocene **5** (146 mg, 0.26 mmol) in diethylether (2 ml) was added dropwise. The reaction mixture was refluxed for 30 min, followed by addition of ice water (2 ml) and 3 M HCl (2 ml). The ether layer was separated, aqueous phase was extracted with diethylether (2 ml × 10 ml), organic fractions were collected, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel (1/1 hexane/$CDCl_3$) to afford 120 mg (85%) of the title compound as an orange solid: mp 49–50 °C; ^{1}H NMR ($CDCl_3$) δ 1.76–1.86 (m, 2H, CH_2), 2.00–2.16 (m, 2H, CH_2), 2.43 (t, $^3J_{FH} = 7.6$ Hz, 2H, CH_2CF$_2$), 4.08 (bs, 4H, C$_5H_4$), 4.12 (s, 5H, C$_5H_5$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.9 (t, $^3J_{CF} = 3$ Hz, CH$_2$CH$_2$CF$_2$), 29.2 (FcCH$_2$), 30.7 (t, $^2J_{CF} = 12$ Hz, CH$_2$CF$_2$), 67.9 (CH of C$_5$H$_4$), 68.5 (CH of C$_5$H$_4$), 69.0 (C$_5$H$_5$), 88.0 (C_{ipso} of C$_5$H$_4$); ^{19}F NMR ($CDCl_3$) δ −126.4 (m, 2F, CF$_2$), −123.7 (m, 2F, CF$_2$), −123.1 (m, 2F, CF$_2$), −122.2 (m, 2F, CF$_2$), −114.4 (m, 2F, CF$_2$), −81.0 (t, $^3J_{FF} = 10$ Hz, 3F, CF$_3$); IR ($CHCl_3$) 1242 s, 1145 m, 1121 w, 1106 w, 1003 w cm^{-1}; HR MS (EI) calcd for $C_{19}H_{13}F_{13}FeO$ 546.03156, found 546.03282. Anal. calcd for $C_{19}H_{15}F_{13}Fe$: C, 41.78; H, 2.77; F, 45.22; Fe, 10.23. Found: C, 42.16; H, 2.66.

5.5. bis(4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononan-1-yl)ferrocene (**8**)

To a stirred suspension of lithium aluminium hydride (38 mg, 0.1 mmol) in diethylether (6 ml) was added slowly aluminium chloride (135 mg, 1 mmol). After a vigorous reaction had subsided, a solution of bis(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-1-oyl)ferrocene **6** (234 mg, 0.25 mmol) in diethylether (2 ml) was added dropwise. The reaction mixture was refluxed for 30 min, followed by addition of ice water (2 ml) and 3 M HCl (2 ml). The ether layer was separated, aqueous phase was extracted with

diethylether (2 ml × 10 ml), organic fractions were collected, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure and subsequent column chromatography on silica gel (8/1 hexane/toluene) afforded 125 mg (55%) of the title compound as an orange solid: mp 40–41 °C; ^{1}H NMR ($CDCl_3$) δ 1.76–1.86 (m, 4H, CH_2), 2.00–2.16 (m, 4H, CH_2), 2.42 (t, $^3J_{FH} = 7.6$ Hz, 4H, CH_2CF$_2$), 3.99 (apparent t, 4H, C$_5H_4$), 4.03 (apparent t, 4H, C$_5H_4$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.0 (unresolved t, CH$_2$CH$_2$CF$_2$), 29.0 (FcCH$_2$), 30.7 (t, $^2J_{CF} = 12$ Hz, CH$_2$CF$_2$), 68.2 (CH of C$_5$H$_4$), 68.7 (CH of C$_5$H$_4$), 87.5 (C_{ipso} of C$_5$H$_4$); ^{19}F NMR ($CDCl_3$) δ −126.5 (m, 4F, CF_2), −123.8 (m, 4F, CF_2), −123.2 (m, 4F, CF_2), −122.2 (m, 4F, CF_2), −114.4 (m, 4F, CF_2), −81.1 (t, $^3J_{FF} = 10$ Hz, 6F, CF_3); IR ($CHCl_3$) 1242 s, 1145 m, 1120 m cm^{-1}; HR MS (FAB+) calcd for $C_{28}H_{20}F_{26}FeO_2$ 906.04993, found 906.05472. Anal. calcd for $C_{28}H_{20}F_{26}Fe$: C, 37.11; H, 2.22; F, 54.51; Fe, 6.16. Found: C, 37.47; H, 2.13.

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References

[1] (a) I.T. Horváth, J. Rábai, Science 266 (1994) 72–75;
(b) I.T. Horváth, Acc. Chem. Res. 31 (1998) 641–650;
(c) E.G. Hope, A.M. Stuart, J. Fluorine Chem. 100 (1999) 75–83;
(d) R.H. Fish, Chem. Eur. J. 5 (1999) 1677–1680.
[2] (a) T. Olsson, O. Wennerström, Acta Chem. Scand. Ser. B B32 (1978) 293–296;
(b) P.G. Gasmann, C.H. Winter, J. Am. Chem. Soc. 108 (1986) 4228–4229;
(c) P.G. Gasmann, J.W. Mickelson, J.R. Sowa Jr., J. Am. Chem. Soc. 114 (1992) 6942–6944.
[3] R.P. Hughes, H.A. Trujillo, Organometallics 15 (1996) 286–294.
[4] (a) J. Čermák, K. Auerová, H.T.T. Nguyen, V. Blechta, P. Vojtíšek, J. Kvíčala, Collect. Czech. Chem. Commun. 15 (2001) 382–396;
(b) T. Bříza, J. Kvíčala, O. Paleta, J. Čermák, Tetrahedron 58 (2002) 3841–3846;
(c) J. Kvíčala, T. Bříza, O. Paleta, K. Aureová, J. Čermák, Tetrahedron 58 (2002) 3847–3854.
[5] (a) M. Sališová, Š. Toma, Chem. Papers 40 (1986) 619–629;
(b) A.F. Cunningham Jr., Organometallics 13 (1994) 2480–2485;
(c) V.A. Darin, A.F. Neto, J. Miller, M.M.F. Afonso, H.C. Fonsatti, A.D.L. Borges, J. Prakt. Chem. 341 (1999) 588–591;
(d) R.D. Vukevic, M. Vukevic, Z. Ratkovic, S. Konstantonovic, Synlett (1998) 1329–1330.
[6] (a) W.P. Hart, M.D. Rausch, J. Organomet. Chem. 355 (1988) 455–471;
(b) S.T. Mabrouk, W.P. Hart, M.D. Rausch, J. Organomet. Chem. 527 (1997) 43–49.
[7] C. Guillon, P. Vierling, J. Organomet. Chem. 506 (1996) 211–220.
[8] (a) A.M. Jouani, F. Szönyi, A. Cambon, J. Fluorine Chem. 56 (1992) 85–92;
(b) Y. Chaudier, F. Zito, P. Barthélémy, D. Stroebel, B. Améduri, J.-L. Popot, B. Puccia, Bioorg. Med. Chem. Lett. 12 (2002) 1587–1590.
[9] M. Kotora, M. Hájek, B. Ameduri, B. Boutevin, J. Fluorine Chem. 68 (1994) 49–56.
[10] P.H.J. Carlsen, T. Katsuki, V.S. Martin, K.B. Sharpless, J. Org. Chem. 46 (1981) 3936–3938.
[11] H. Urata, Y. Kinoshita, T. Asanuma, O. Kosukegawa, T. Fuchikami, J. Org. Chem. 56 (1991) 4996–4999.
[12] Y.-P. Wang, J.-M. Hwu, J. Organomet. Chem. 385 (1990) 61–71.
[13] J.K. Bashkin, P.J. Kinlen, Inorg. Chem. 29 (1990) 4507–4509.