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$[(C_5H_5)Fe(C_5H_4CH_2NMe_2)]$ as a promoter for the synthesis of the 1,2-disubstituted ferrocenyl aldehydes $[(C_5H_5)Fe(1,2\text{-}C_5H_3(CHO)(CH_2NMe_2)]$ and $[(C_5H_5)Fe\{1,2\text{-}C_5H_3(CHO)CH_2NMe(CH_2)_2OCH{=}CH_2\}]$

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Abstract

The one pot synthesis of $[(C_5H_5)Fe\{1,2\text{-}C_5H_3(CHO)(CH_2NMe_2)\}]$ (**2**) from $[(C_5H_5)Fe(C_5H_4CH_2NMe_2)]$ (**1**) is described. The new biferrocenyl compound $[\{(C_5H_5)FeC_5H_4CH_2ONMe(CH_2)_2OCH_2\}_2]$ (**3**), whose preparation is reported, reacts successively with 2 mole equivalents of LiBu and DMF (−78 °C) to give, among other products, the aldehyde $[(C_5H_5)Fe\{1,2\text{-}C_5H_3(CHO)CH_2NMe(CH_2)_2OCH{=}CH_2\}]$ (**6**).

Keywords: Iron; Ferrocenyl aldehydes, Synthesis

We have shown recently [1] that it is possible to synthesize selectively and in high yield acyclic phosphorus ferrocenyl compounds that show a remarkable ability to complex copper(I) salts. This new class of compound of general formula $[XP\{NMeN{=}CHFc\}_nPh_{3-n}]$ (X = O or S; $n = 2$ or 3; Fc = $C_5H_5FeC_5H_4$ is obtained by condensation of ferrocene carbaldehyde with phosphohydrazines. As an extension of this work we attempted the synthesis of new 1,2-disubstituted ferrocenyl compounds containing both a (Ph)P(S)-$(NMeN{=}CH\text{-})_2$ moiety and a $(\text{-}CH_2NMe(CH_2)_2\text{-}OCH_2\text{-})_2$ moiety. This would increase the number and the nature of available binding sites for anions or cations. This new species of molecule would be well-suited for electrochemical molecular recognition studies.

An easy route to 1,2-ferrocenyl compounds was described by Slocum et al. [2]. In this method, the *N,N'* dimethylaminomethylferrocene **1** is a good precursor for the synthesis of new 1,2-disubstituted ferrocenes via ring metallation at the 2-position with butyllithium and condensation with electrophilic compounds such as ketones, benzonitrile, phenylisocyanate. The use of lithium salt of **1** has been widely developed, for example to the synthesis of a series of ferrocenyl-sulfenides and -selenides $[(C_5H_5)Fe(1,2\text{-}C_5H_3(CH_2NMe_2)(ER))]$ (E = S or Se; R = Pr^n, Bu^n, Bu^t, Bz, 4-tolyl or 4-ClPh) [3] and for the synthesis of the new aminoalkene complex $[(C_5H_5)Fe\{1,2\text{-}C_5H_3(CH_2NMe_2)(CH_2CH{=}CH_2)\}]$ [4]. However, the synthesis of the aldehyde $[(C_5H_5)\text{-}Fe\{1,2\text{-}C_5H_3(CHO)(CH_2NMe_2)\}]$ **2** has never been reported.

In this paper we report a simple and efficient synthesis of **2** and try to apply the Slocum methodology to the new biferrocenyl compound $[\{(C_5H_5)Fe(C_5H_4\text{-}CH_2N(Me)(CH_2)_2OCH_2\text{-}\}_2]$ **3**.

Successive addition of 1 equiv of LiBu at room temperature (24 h stirring) and of DMF at −78 °C to a solution of $[(C_5H_5)Fe(C_5H_4CH_2NMe_2)]$ **1** gave, after 4 h stirring at room temperature, a brown solution that, after hydrolysis and extraction with ether, appeared to be a mixture of the starting material and the new aldehyde **2** in a 1/2 ratio. Column chromatography of the solution on alumina (eluent ether/pentane: 1/2) allowed the separation of pure **2** as a red light-sensitive oil in 62% yield [5]. Replacement of one proton of the cyclopentadienyl ring by CHO induces a downfield shift of the signals in the ^1H NMR spectrum

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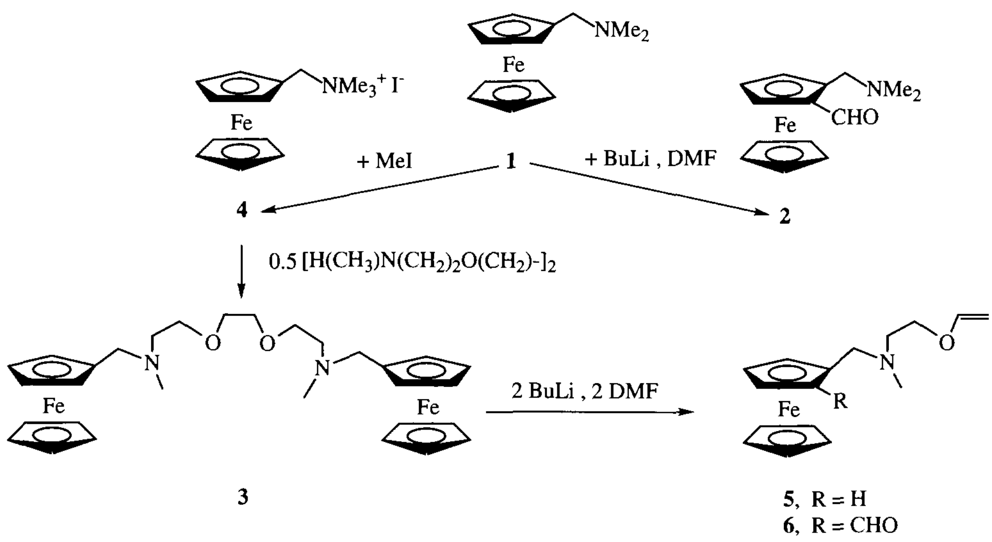

Scheme 1.

compared with those of compound **1**. The Cp signals are characteristically split into three multiplets at δ = 4.76 (m), 4.58 (m), 4.54 (t) ppm and one singlet is observed for the unsubstituted ring at $\delta = 4.21$ ppm (relative intensities 1/1/1/5). In parallel, the singlet observed for the CH_2 protons of **1** becomes an AB type signal centered at $\delta = 3.56$ ppm and the CHO signal is clearly detected at 10.08 ppm. The presence of the CHO group is evident in ^{13}C NMR spectra from a doublet $\delta = 193$ ppm ($^1J_{CH} = 173$ Hz). Finally, microanalysis and mass spectroscopy are consistent with the proposed formula. The only ferrocene derivative with both a CH_2NMe_2 and a CHO so far described is 1,1'-substituted [6].

We have also attempted to prepare first the biferrocenyl compound **3** with the diazadioxa chain and then to synthesize selectively using the Slocum methodology the dialdehyde derivative.

$[(C_5H_5)Fe(C_5H_4CH_2NMe_3)][I]$ [7] **4**, obtained by methylation reaction of **1**, is well known to undergo easily condensation reactions with nucleophiles [8], and indeed it reacts with 0.5 equiv of 1,8-bis(methylamino)-3,6-dioxaoctane to give an 82% yield of $[\{(C_5H_5)Fe(C_5H_4CH_2NMe(CH_2)_2OCH_2\text{-}\}_2]$ **3**. In contrast to the recently described $[\{(C_5H_5)Fe(C_5H_4CH_2NH(CH_2)_2SCH_2\text{-})\}_2]$ [9] and $[\{(C_5H_5)Fe(C_5H_4CH_2NHCH_2\text{-})\}_2]$ [10], this compound was synthesized only in one step in refluxing water and was isolated as a brown oil after extraction with ether. This relatively stable compound is very soluble in common organic solvents. Its structure was deduced from NMR data and microanalysis [11].

Successive treatment of a solution of **3** in ether with 2 equiv of LiBu and DMF at −78 °C did not give the expected aldehyde. The solution lightened and after hydrolysis two new products in 1:4 ratio were observed. After purification by chromatography, (eluent ether/ pentane: 3/1) $[(C_5H_5)Fe\{C_5H_4CH_2NMe(CH_2)_2OCH{=}CH_2\}]$ **5** and $[(C_5H_5)Fe\{1,2\text{-}C_5H_3(CHO)CH_2NMe(CH_2)_2OCH{=}CH_2\}]$ **6** were isolated as yellow and red oils (yield 27% and 7%) [12]. The ^1H NMR spectra of both complexes show three doublets of doublets, centered at δ = 3.98; 4.18 and 6.48 ppm for **5** and δ = 3.98; 4.16 and 6.47 ppm for **6**. These shifts and the coupling constants are characteristic of vinyl groups [13]. In the ^{13}C NMR spectra, resonances at $\delta = 86.3$ and 151.8 ppm for **5** and 86.5 and 151.7 ppm for **6** confirm the presence of the -$(OCH{=}CH_2)$ group. The new aldehyde **6** has a ^1H and ^{13}C NMR spectra characteristic singlet and doublet at δ = 10.08 and 193.0 ppm (J_{CH} = 173 Hz) respectively for the CHO function. The most reasonable mechanism by which **5** and **6** are formed is a deprotonation reaction at the β position relative to the nitrogen atom, followed by an intramolecular rearrangement which induces organic chain rupture. Organic ether deprotonations are generally difficult [14] and at −78 °C would not normally by favored, but the basicity of the LiBu is certainly increased here by interaction of the lithium with the azaoxa chain.

To conclude, two new 1,2 disubstituted ferrocenyl aldehydes **2** and **6** were obtained according to Slocum's methodology (Scheme 1). Complex **2** seems to be a good synthon for 1,2-disubstituted ferrocenyl compounds and probably for macrocycle compounds and a study of its reactivity is underway.

References and notes

[1] (a) B. Delavaux-Nicot, N. Lugan and R. Mathieu, *Inorg. Chem., 31* (1992) 334; (b) B. Delavaux-Nicot and R. Mathieu, *Phosphorus, Sulfur and Silicon, 77* (1993) 323; (c) B. Delavaux-Nicot, R.

Mathieu, D. de Montauzon, G. Lavigne and J.-P. Majoral, *Inorg. Chem.*, *33* (1994) 434.

[2] D.W. Slocum, B.W. Rockett and C.R. Hauser, *J. Am. Chem. Soc.*, *87* (1965) 1242.

[3] M.O. Okoroafor, L.H. Shen, R.V. Honeychuck and C.H. Brubaker Jr., *Organometallics* (1988) 1297.

[4] P.A. Van der Schaaf, J.P. Sutter, M. Grellier, G.P.M. van Mier, A.L. Spec, G. van Kotten and M. Pfeffer, *J. Am. Chem. Soc.*, *116* (1994) 5134.

[5] $[(\mathrm{C_5H_5})\mathrm{Fe}\{1,2\text{-}\mathrm{C_5H_3(CHO)(CH_2NMe_2)}\}]$ **2**. Anal calcd. for $\mathrm{C_{14}H_{17}FeNO}$: C, 62.00; H, 6.32; N, 5.19%. Found: C, 62.06; H, 6.40; N, 5.17%. Mass spectrum (CI), $m/z = 271$ ($\mathrm{MH^+}$). ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 2.19 (s, 6H, $\mathrm{CH_3}$), 3.56 (dd, $^2J_{\mathrm{HH}} = 13.2$ Hz, 2H, $\mathrm{CH_2}$), 4.21 (s, 5H, $\mathrm{C_5H_5}$), 4.54 (brt, 1H), 4.58 (m, 1H) 4.76 (m, 1H) ($\mathrm{C_5H_3}$), 10.08 (s, 1H, CHO). ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 44.7 (q, $J_{\mathrm{CH}} = 133$ Hz, $\mathrm{CH_3}$), 56.4 (t, $^1J_{\mathrm{CH}} = 134$ Hz, $\mathrm{CH_2}$), 70.0 (m, $^1J_{\mathrm{CH}} = 177$ Hz), 70.1 (m, $^1J_{\mathrm{CH}} = 177$ Hz), 71.7 (m, $^1J_{\mathrm{CH}} = 178$ Hz), 75.7 (M, $^1J_{\mathrm{CH}} = 175$ Hz), 86.5 (s) ($\mathrm{C_5H_5FeC_5H_3}$), 193.0 (d, $J_{\mathrm{CH}} = 173$ Hz, CHO).

[6] K. Schlögl and M. Walser, *Tetrahedron Lett., 56* (1968) 5885.

[7] D. Lednicer and C.R.Hauser, *Organic Synthesis, 40* (1960) 434.

[8] (a) G. De Santis, L. Fabbrizzi, M. Lichello, C. Mangano, P. Pallavicini and A. Poggi, *Inorg. Chem., 32* (1993) 854; (b) P.D. Beer, D.B. Crowe, M.I. Ogden, M.G.B. Drew and B. Main, *J. Chem. Soc. Dalton Trans.*, (1993) 2107.

[9] R.A. Holwenda, T.W. Robinson, R.A. Bartsch and B.P. Czech, *Organometallics, 10* (1991) 2652.

[10] A. Benito, J. Cano, R. Martinez-Manez, J. Soto, J. Paya, F. Lloret, M. Julve, J. Faus and M.D. Marco, *Inorg. Chem., 32* (1993) 1197.

[11] Compound **3**. Anal. calcd. for $\mathrm{C_{30}H_{40}Fe_2N_2O_2}$: C, 62.94; H, 7.04; N, 4.91%. Found: C, 62.54; H, 7.15; N, 4.97%. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$, δ(ppm)): 2.22 (s, 6H, $\mathrm{CH_3}$), 2.63 (t, $J_{\mathrm{HH}} = 6.1$ Hz, 4H, $\mathrm{N}CH_2\mathrm{CH_2O}$), 3.40 (s, 4H, $\mathrm{FcCH_2N}$), 3.49 (s, 4H, $\mathrm{OCH_2CH_2O}$), 3.55 (t, $^3J_{\mathrm{HH}} = 6.1$ Hz, 4H, $\mathrm{NCH_2}CH_2\mathrm{O}$), 3.97 (t, $J_{\mathrm{HH}} = 1.8$ Hz, 4H), 4.00 (s, 10H), 4.12 (t, $J_{\mathrm{HH}} = 1.8$ Hz, 4H) ($\mathrm{C_5H_5FeC_5H_4}$). ^{13}C NMR (62.9 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 42.2 (q, $J_{\mathrm{CH}} = 133$ Hz, $\mathrm{CH_3}$), 55.5 (t, $J_{\mathrm{CH}} = 132$ Hz, $\mathrm{OCH_2}CH_2\mathrm{N}$ or $\mathrm{FcCH_2N}$), 57.6 (t, $J_{\mathrm{CH}} = 136$ Hz, $\mathrm{OCH_2}CH_2\mathrm{N}$ or $\mathrm{FcCH_2N}$), 67.9 (t, $^1J_{\mathrm{CH}} = 169$ Hz, $\mathrm{OCH_2}CH_2\mathrm{N}$ or $\mathrm{FcCH_2N}$), 68.4 (m, $^1J_{\mathrm{CH}} = 175$ Hz), 70.2 (m, $^1J_{\mathrm{CH}} = 174$ Hz), 82.6 (s) ($\mathrm{C_5H_5FeC_5H_4}$), 69.6 (t, $J_{\mathrm{CH}} = 143$ Hz, $\mathrm{O}CH_2\mathrm{CH_2N}$), 70.3 (t, $J_{\mathrm{CH}} = 141$ Hz, $\mathrm{OCH_2CH_2O}$).

[12] Compound **5**. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 2.21 (s, 3H, $\mathrm{CH_3}$), 2.60 (t, $J_{\mathrm{HH}} = 5.9$ Hz, 2H, $\mathrm{N}CH_2\mathrm{CH_2O}$), 3.46 (s, 2H, $\mathrm{FcCH_2N}$), 3.73 (t, $J_{\mathrm{HH}} = 5.9$ Hz, 2H, $\mathrm{NCH_2}CH_2\mathrm{O}$), 3.98 (dd, $^2J_{\mathrm{HH}} = 2.0$ Hz, $^3J_{\mathrm{HH}} = 6.9$ Hz, 1H $\mathrm{CH{=}C}H_2$), 4.10 (s, 5H), 4.11 (t, $J_{\mathrm{HH}} = 2.0$ Hz, 2H), 4.15 (t, $J_{\mathrm{HH}} = 2.0$ Hz, 2H) ($\mathrm{C_5H_5FeC_5H_4}$), 4.18 (dd, $^2J_{\mathrm{HH}} = 2.0$ Hz, $^3J_{\mathrm{HH}} = 14.4$ Hz, $\mathrm{CH{=}CH_2}$), 6.48 (dd, $^3J_{\mathrm{HH}} = 14.4$ Hz, $^3J_{\mathrm{HH}} = 6.9$ Hz, $\mathrm{C}H\mathrm{CH_2}$). ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 42.0 (q, $J_{\mathrm{CH}} = 134$ Hz, $\mathrm{CH_3}$), 54.6 (t, $J_{\mathrm{CH}} = 135$ Hz, $\mathrm{FcCH_2N}$ or $\mathrm{N}CH_2\mathrm{CH_2O}$), 57.4 (t, $J_{\mathrm{CH}} = 137$ Hz, $\mathrm{FcCH_2N}$ or $\mathrm{N}CH_2\mathrm{CH_2O}$), 65.7 (t, $J_{\mathrm{CH}} = 137$ Hz, $\mathrm{O}CH_2\mathrm{CH_2N}$), 68.1 (m, $^1J_{\mathrm{CH}} = 176$ Hz), 68.5 (m, $^1J_{\mathrm{CH}} = 176$ Hz), 70.2 (m, $^1J_{\mathrm{CH}} = 174$ Hz), 82.3 (s) ($\mathrm{C_5H_5FeC_5H_4}$), 86.3 (ddd, $J_{\mathrm{CH}} = 157$ Hz, $^1J_{\mathrm{CH}} = 161$ Hz, $^2J_{\mathrm{CH}} = 10$ Hz, $CH\mathrm{{=}CH_2}$) 151.8 (d, $J_{\mathrm{CH}} = 185$ Hz, $\mathrm{C}H = \mathrm{CH_2}$). Mass spectrum (CI), $m/z = 300$ ($\mathrm{MH^+}$).

Compound **6**. ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 2.23 (s, 3H, $\mathrm{CH_3}$), 2.67 (t, $J_{\mathrm{HH}} = 5.8$ Hz, 2H, $\mathrm{N}CH_2\mathrm{CH_2O}$), 3.76 (dd, $J_{\mathrm{HH}} = 13.4$ Hz, 2H), ($\mathrm{FcCH_2N}$), 3.76 (t, $J_{\mathrm{HH}} = 5.8$ Hz, 2H, $\mathrm{NCH_2}CH_2\mathrm{O}$), 3.98 (dd, $^2J_{\mathrm{HH}} = 2.1$ Hz, $^3J_{\mathrm{HH}} = 6.8$ Hz, $\mathrm{CH{=}}CH_2$), 4.16 (dd, $^2J_{\mathrm{HH}} = 2.1$ Hz, $^3J_{\mathrm{HH}} = 14.4$ Hz, 1H, $\mathrm{CH{=}}CH_2$), 4.21 (s, 5H), 4.54 (m, 1H), 4.58 (m, 1H), 4.76 (m, 1H) ($\mathrm{C_5H_5FeC_5H_3}$), 6.47 (dd, $^3J_{\mathrm{HH}} = 14.4$ Hz, $^3J_{\mathrm{HH}} = 6.8$ Hz, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$), 10.08 (s, 1H, CHO). ^{13}C NMR (50.3 MHz, $\mathrm{CDCl_3}$, δ(ppm)): 42.1 (q, $J_{\mathrm{CH}} = 134$ Hz, $\mathrm{CH_3}$), 55.0 (t, $J_{\mathrm{CH}} = 135$ Hz, $\mathrm{N}CH_2\mathrm{CH_2O}$ or $\mathrm{FcCH_2N}$), 55.1 (t, $J_{\mathrm{CH}} = 135$ Hz, $\mathrm{N}CH_2\mathrm{CH_2O}$ or $\mathrm{FcCH_2N}$), 55.1 (t, $J_{\mathrm{CH}} = 135$ Hz, $\mathrm{N}CH_2\mathrm{CH_2O}$ or $\mathrm{FcCH_2N}$), 65.9 (t, $J_{\mathrm{CH}} = 143$ Hz, $\mathrm{NCH_2}CH_2\mathrm{O}$), 70.2 (m, $^1J_{\mathrm{CH}} = 177$ Hz), 70.3 (m, $^1J_{\mathrm{CH}} = 177$ Hz), 71.8 (m, $^1J_{\mathrm{CH}} = 177$ Hz), 76.0 (m, $^1J_{\mathrm{CH}} = 184$ Hz), 83.2 (s) ($\mathrm{C_5H_5FeC_5H_3}$), 86.5 (ddd, $^1J_{\mathrm{CH}} = 157$ Hz, $^1J_{\mathrm{CH}} = 161$ Hz, $^2J_{\mathrm{CH}} = 10$ Hz, $\mathrm{CH{=}}CH_2$), 151.7 (dm, $^1J_{\mathrm{CH}} = 182$ Hz, $CH\mathrm{{=}CH_2}$), 193 (d, $J_{\mathrm{CH}} = 173$ Hz, CHO). Mass spectrum (CI), $m/z = 328$ ($\mathrm{MH^+}$).

[13] R.M. Sylverstein, G.C. Bassler, T.C. Morril, in *Spectrometric Identification of Organic Compounds*, Wiley, 4th edn., 1981, Chap. 4, pp. 260–269.

[14] J. March, *Advanced Organic Chemistry*, Wiley Interscience, 3 edn., 1985, Chap. 17, p. 904.