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Journal of Organometallic Chemistry 689 (2004) 2770–2775
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Aminocarbonylation of 1,1′-diiodoferrocene, two-step synthesis of heterodisubstituted ferrocene derivatives via homogeneous catalytic carbonylation/coupling reactions

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Received 23 January 2004; accepted 12 May 2004

Abstract

Detailed investigation of the catalytic carbonylation of 1,1′-diiodoferrocene has been carried out. The importance of the 1′-iodoferrocenecarboxamide- or 1′-iodo-ferroceneglyoxylic amide-type products as starting materials for the synthesis of various heterodisubstituted ferrocenes, that can serve as starting materials for ferrocene-based biosensors, was also proved. The potential of this reaction sequence was shown by the high-yielding synthesis of 1′-vinyl ferrocenecarboxamide/glyoxylic amide and 1′-acyl ferrocencarboxamide derivatives.

Keywords: Disubstituted ferrocenes; Ferrocene amides; Homogeneous catalysis; Carbonylation; Pd-catalysts

1. Introduction

In the past few years there has been an increasing interest in the design of new compounds incorporating the ferrocene skeleton, owing to their utility in diverse fields of chemistry, such as organic synthesis, catalysis and materials science [1]. At the same time, relatively few reports have been published concerning the synthesis of unsymmetrically 1,1′-disubstituted ferrocene derivatives. Although there are some examples for the selective functionalisation of the 1′-position of a monosubstituted ferrocene [2–4], in most cases the heterodisubstituted compounds are obtained via the transformation of one of the two substituents of a symmetrical 1,1′-disubsituted ferrocene derivative. These reactions may involve the selective transmetalation of one tributylstannyl group of 1,1′-bis (tributylstannyl)-ferrocene [5], the reaction of 1,1′-ferrocenedicarboxylic acid with oligoproline-benzylesters, hydroxybenzotriazole and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide [6], but in most cases the first step of the syntheses is the selective monolithiation of 1,1′-dibromo- or 1,1′-diiodoferrocene [7–10].

As palladium-catalysed coupling reactions of 1,1′-diiodoferrocene with organotin [11] and organozinc compounds [12] have been reported to lead to mixtures of 1-substituted-1′-iodo-ferrocenes and symmetrical 1,1′-disubstituted derivatives, we decided to explore the palladium-catalysed aminocarbonylation of the same substrate in detail.

Recently, we have found that using iodoferrocene as substrate, either ferrocene α-ketoamides or ferrocene amides can be synthesised by homogeneous catalytic carbonylation in good yields [13,14]. Optimal conversion

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doi:10.1016/j.jorganchem.2004.05.046

was achieved at 40–50 bar CO pressure. The use of relatively low temperatures (40–60 °C) favoured the formation of α-ketoamides, while amides were formed with high selectivity at 100 °C in most cases.

Now we report on the investigation of the carbonylation reaction of 1,1′-diiodoferrocene in the presence of secondary amines. It is shown that by the proper choice of the reaction conditions the 1′-iodo-ferrocenecarboxamide- or 1′-iodo-ferroceneglyoxylic amide-type products can be isolated in reasonable yields. These compounds can serve as starting material for the synthesis of unsymmetrical 1,1′-disubstituted ferrocene derivatives of practical importance.

2. Results and discussion

2.1. Carbonylation of 1,1′-diiodoferrocene in the presence of secondary amines

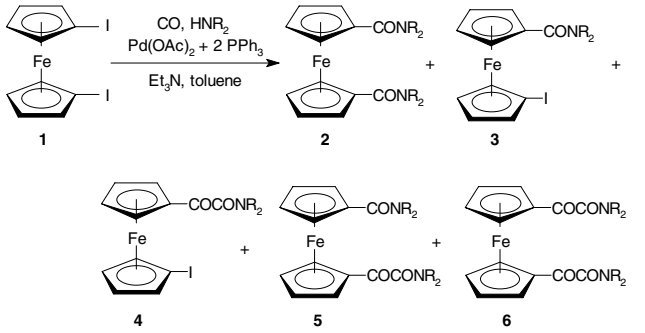
As the next step in our series of investigations concerning the carbonylation reactions of ferrocene derivatives, the aminocarbonylation of 1,1′-diiodoferrocene has been explored.

1,1′-Diiodoferrocene (**1**) [15] was reacted with various secondary amines in the presence of an in situ Pd-catalyst in an autoclave under CO pressure Eq. (1). At 100 °C and 40 bar CO pressure **1** could be converted into diamides **2a**–**d** with excellent selectivity. At the same time, the presence of iodo derivatives **3** and **4** could also be observed with shorter reaction times. This observation prompted us to investigate the effects of the changes in the reaction conditions in order to isolate these compounds.

Using Et_2NH (**a**) as the nucleophile, it was observed that although the decrease of the temperature led to a dramatic decrease of the conversion, products **3a** and **4a** were obtained in considerable amounts. Beside **2a** another disubstituted derivative (**5a**) featuring simple and double carbon monoxide insertion was also formed. It should be mentioned that the 1,1′-bis(glyoxylic amide) type compounds (**6**) could never be detected using either Et_2NH or other secondary amines.

An increase in the pressure resulted in somewhat lower conversion and an increase in the ratio of double carbonylated products **4a** and **5a**, as it was expected (compare entries 2 and 4). Using a lower amine/1,1′-diiodoferrocene ratio (3/1 instead of 10/1) led to a marked improvement in the relative amount of **3a** in the reaction mixture together with a fall of the conversion. Although higher conversions could be achieved by the use of longer reaction times, the isolated yield of **3a** remained approximately the same (35–37%) because the second carbonylation step leading to **2a** became more favoured.

Aminocarbonylation of **1** in the presence of Bu_2NH (**b**) led to **3b** with good selectivity, but due to the lower reactivity of this amine compared to Et_2NH which was evident even at 100 °C, **3b** could be isolated only in 31% yield.



(1)

In the reaction of the cyclic secondary amines, morpholine (**c**) and piperidine (**d**), double carbonylation leading to α-ketoamide type products **4c** and **4d** prevailed over monocarbonylation at lower temperatures. This is in accordance with our previous results obtained during the carbonylation of iodoferrocene [14], where α-ketoamides were the main products of the reaction of sterically less hindered secondary amines at 60 °C. In the present case, formation of **4a** and **4b** may be not favoured because the flexible alkyl groups of the amines and the presence of the iodo substituent on the second ring may lead to a more crowded palladium-complex which makes the coordination of a second carbon monoxide less feasible.

From the point of view of synthetic applications, it is of special interest, that one of the two iodo-aryl moieties remained intact resulting in the formation of **3d**, **4c** and **4d**, and might serve as an appropriate functionality in further reactions. The symmetric diamide **2d** could not be detected when the piperidine/**1** ratio was kept at 5/1.

After isolation of the monosubstituted products, **3a**, **4c** and **4d** were chosen as substrates for further functionalisation via homogeneous catalytic coupling and carbonylation reactions.

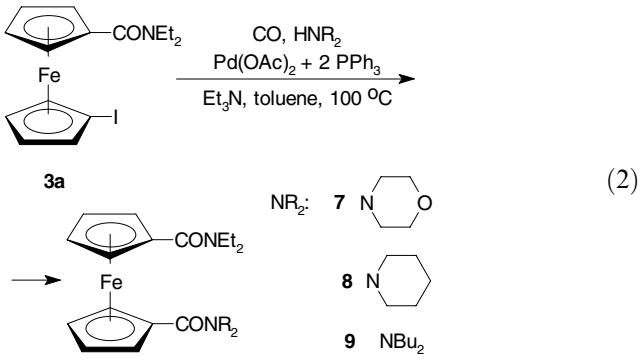
2.2. Carbonylation and coupling reactions of 1′-iodo-ferrocenecarboxamide- or 1′-iodo-ferroceneglyoxylic amide derivatives

In order to explore the scope of applicability of the above-mentioned compounds in the synthesis of heterodisubstituted derivatives, they were subjected to various homogeneous catalytic reactions, namely aminocarbonylation, carbonylative coupling in the presence of $NaBPh_4$ and Stille-coupling.

Monoamide **3a** could be totally converted into diamides **7**–**9** (isolated yields 77–92% after column chromatography) by reacting it with various secondary amines Eq. (2) under carbonylation conditions (40 bar CO, 100 °C, 8–16 h). It should be mentioned that in this

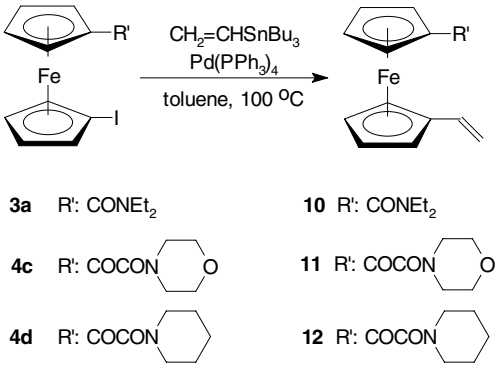
reaction no products with ketoamide functionality due to double carbonylation could be detected even at lower temperatures (40–60 °C).

It should be added, that in spite of the high conversion and excellent selectivity of the aminocarbonylation reaction, this two-step procedure for the synthesis of unsymmetrically substituted ferrocene diamides seems to be inferior to the one-pot aminocarbonylation starting from 1,1′-diiodoferrocene in the presence of two different amines, due to the moderate yield of **3a** in the first step [16].



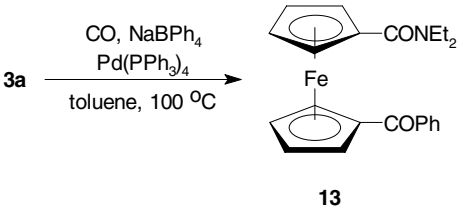
(2)

Stille-coupling of **3a**, **4c** and **4d** with vinyltributyltin in the presence of $Pd(PPh_3)_4$ led to functionalised vinylferrocenes **10**–**12** in a smooth reaction. The formation of no byproducts was observed.



(3)

The carbonylative coupling reaction elaborated for the synthesis of steroidal phenyl ketones [17] could also be successfully used for the conversion of **3a**. The substrate was reacted with $NaBPh_4$ under atmospheric CO pressure using $Pd(PPh_3)_4$ catalyst. The reaction resulted in the selective formation of **13** (isolated yield: 78%).



(4)

3. Conclusion

We have found that 1′-iodo-ferrocenecarboxamide- or 1′-iodo-ferroceneglyoxylic amide-type products can be isolated in reasonable yields from the reaction mixtures produced via aminocarbonylation of 1,1′-diiodoferrocene under CO pressure. The products were successfully used as substrates in palladium-catalysed aminocarbonylation, coupling and carbonylative coupling reactions. These reactions led to the selective formation of unsymmetrical ferrocene 1,1′-diamides, or 1′-vinyl-1-amide/glyoxylic amide- and 1′-benzoyl-1-amide-type products, respectively.

4. Experimental

The ^1H and ^{13}C NMR spectra were recorded on a VARIAN INOVA 400 spectrometer at 400 and 100.58 MHz, respectively. GLC analyses were carried out with a HP-5890/II gas chromatograph using a 15 m HP-5 column. Infrared (IR) spectra were recorded in KBr pellets using a Specord-IR 75 instrument. GC–MS measurements were performed with a Hewlett–Packard 5971A GC–MSD using HP-1 column.

4.1. Carbonylation of 1,1′-diiodoferrocene (*1*)

1,1′-Diiodoferrocene (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.1 mmol), the secondary amine (1.5 or 2.5 or 5 mmol, as indicated in Table 1.), Et_3N (0.5 mL) and toluene (12.5 mL) were transferred under an inert atmosphere into a stainless steel autoclave. It was charged with carbon monoxide and heated with stirring in an oil bath. Then the volatile components were removed in vacuo. The residue was dissolved in toluene (20 mL), washed with 5% H_3PO_4 (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL) and dried over Na_2SO_4. The products were separated after removal of the solvent by chromatography (aluminium oxide, benzene/EtOAc = 3/1). The structures of the isolated compounds were determined by ^1H, ^{13}C NMR and IR spectroscopy, elemental analysis, and MS.

Physical properties and spectra of **2a**, **2c** and **2d** corresponded well to literature data [18].

4b and **5a** were not isolated and were characterised by GC–MS. **4b**: MS (*m*/*z*/rel. int.): 495(M^+)/100; 339/94; 311/22; 247/13; 213/22; 183/81. **5a**: MS (*m*/*z*/rel. int.): 412(M^+)/100; 312/32; 241/75; 220/42; 121/33.

4.1.1. 1,1′-Bis(N,N-dibutyl carboxamido) ferrocene(*2b*)

^1H NMR($CDCl_3$) δ: 4.59 (t, 1.9 Hz, 4H, Cp); 4.34 (t, 1.9 Hz, 4H, Cp); 3.35 (t, 7.8Hz, 8H, NCH_2); 1.58 (m, 8H, NCH_2CH_2); 1.15 (m, 8H, $N(CH_2)_2CH_2$); 0.89 (m, 12H, $N(CH_2)_3CH_3$). IR (KBr (cm^{-1})): 1618. MS (*m*/*z*/rel. int.): 496(M^+)/100; 368/12; 340/17; 241/32; 128/35;

Table 1
Carbonylation of 1,1′-diiodoferrocene in the presence of amines

Entry	Amine	Temperature (°C)	Pressure (bar)	Reaction time (h)	Conv.[a] (%)	Ratio of the products[a] (%)				Isolated yields (%) (compound)
						2	**3**	**4**	**5**	
1	Et_2NH (**a**)	100	40	8	95[b]	100	–	–	–	92 (**2a**) [14]
2	Et_2NH (**a**)	60	40	8	88[b]	64	18	5	13	
3	Et_2NH (**a**)	50	40	8	52[b]	48	24	20	8	
4	Et_2NH (**a**)	60	50	8	83[b]	50	22	16	12	11 (**4a**)
5	Et_2NH (**a**)	40	40	26	58[c]	28	66	5	1	
6	Et_2NH (**a**)	40	40	34	68[c]	31	62	5	2	35 (**3a**)
7	Et_2NH (**a**)	40	40	48	81[c]	43	49	6	2	
8	Bu_2NH (**b**)	100	40	8	75[b]	100	–	–	–	70 (**2b**)
9	Bu_2NH (**b**)	60	40	8	48[b]	27	66	7	–	
10	Bu_2NH (**b**)	40	40	40	68[d]	35	57	8	–	31 (**3b**)
11	Morpholine (**c**)	100	40	8	88[b]	91	9	–	–	72 (**2c**)
12	Morpholine (**c**)	60	40	36	78[d]	19	23	58	–	14 (**3c**), 40 (**4c**)
13	Piperidine (**d**)	100	40	8	84[b]	100	–	–	–	75 (**2d**)
14	Piperidine (**d**)	60	40	36	70[d]	–	35	65	–	19 (**3d**), 38 (**4d**)

[a] Determined by GC.
[b] mmol R_2NH/mmol diiodoferrocene = 10/1.
[c] mmol R_2NH/mmol diiodoferrocene = 3/1.
[d] mmol R_2NH/mmol diiodoferrocene = 5/1.

121/32; 57/38; 56/12. Anal. Calc. for $C_{28}H_{44}FeN_2O_2$ (496.52): C, 67.73; H, 8.93; N, 5.64. Found: C, 67.51; H, 8.79; N, 5.51%. Yield: 70%.

*4.1.2. 1′-Iodo-N,N-diethyl ferrocenecarboxamide (**3a**)*

^{1}H NMR($CDCl_3$) δ: 4.58 (brs, 2H, Cp-2,5); 4.45 (brs, 2H, Cp-2′,5′); 4.25 (brs, 2H, Cp-3,4); 4.20 (brs, 2H, Cp-3′,4′); 3.50 (m, 4H, NCH_2CH_3); 1.20 (m, 6H, NCH_2CH_3). ^{13}C NMR($CDCl_3$) δ: 168.7; 81.0; 76.3; 72.9; 72.6; 71.1; 41.2; 40.1; 39.9; 14.2; 13.8. IR (KBr (cm^{-1})): 1609. MS (*m*/*z*/rel. int.): 411(M^+)/100; 339/26; 311/19; 284/37; 247/19; 213/78; 183/63; 56/4. Anal. Calc. for $C_{15}H_{18}FeINO$ (411.07): C, 43.83; H, 4.41; N, 3.41. Found: C, 44.05; H, 4.29; N, 3.57%. Yield: 35%.

*4.1.3. 1′-Iodo-N,N-dibutyl ferrocenecarboxamide (**3b**)*

^{1}H NMR($CDCl_3$) δ: 4.53 (t, 1.8 Hz, 2H, Cp); 4.41 (t, 1.8 Hz, 2H, Cp); 4.26 (t, 1.8 Hz, 2H, Cp); 4.22 (t, 1.8 Hz, 2H, Cp); 3.37 (t, 7.9Hz, 4H, NCH_2); 1.57 (q, 4H, 7.9 Hz, NCH_2CH_2); 1.31 (m, 4H, $N(CH_2)_2CH_2$); 0.92 (t, 6H, 7.9Hz, $N(CH_2)_3CH_3$). IR (KBr (cm^{-1})): 1610. MS (*m*/*z*/rel. int.): 467(M^+)/100; 339/92; 311/85; 247/62; 213/123;183/169. Anal. Calc. for $C_{19}H_{26}FeINO$ (467.17): C, 48.85; H, 5.61; N, 3.00. Found: C, 48.97; H, 5.47; N, 3.12%. Yield: 31%.

*4.1.4. 1′-Iodo-morpholino ferrocenecarboxamide (**3c**)*

^{1}H NMR($CDCl_3$) δ: 4.51 (t, 1.6 Hz, 2H, Cp); 4.43 (t, 1.6 Hz, 2H, Cp); 4.35 (t, 1.6 Hz, 2H, Cp);4.25 (t, 1.6 Hz, 2H, Cp); 3.68 (m, 8H, NCH_2CH_2O). ^{13}C NMR($CDCl_3$) δ: 168.8; 80.3; 76.6; 73.1; 72.6; 71.2; 66.9; 40.1. IR (KBr (cm^{-1})): 1618. MS (*m*/*z*/rel. int.): 425(M^+)/100; 339/15; 311/8;213/13; 183/13; 56/10. Anal. Calc. for $C_{15}H_{16}FeINO_2$ (425.05): C, 42.39; H, 3.79; N, 3.30. Found: C, 42.60; H, 3.87; N, 3.19%. Yield: 14%.

*4.1.5. 1′-Iodo-piperidino ferrocenecarboxamide (**3d**)*

^{1}H NMR($CDCl_3$) δ: 4.5 (t, 1.6 Hz, 2H, Cp); 4.43 (t, 1.6 Hz, 2H, Cp); 4.26 (t, 1.6 Hz, 2H, Cp);4.25 (t, 1.6 Hz, 2H, Cp); 3.59 (m, 4H, NCH_2); 1.57 (m, 6H, $NCH_2(CH_2)_3$). ^{13}C NMR($CDCl_3$) δ: 168.3; 81.5; 76.4; 73.0; 72.4; 71.2; 46.2; 43.1; 40.1; 29.7; 26.1; 24.8. IR (KBr (cm^{-1})): 1616. MS (*m*/*z*/rel. int.): 423(M^+)/100; 339/11; 311/11, 296/35; 247/11; 213/45; 183/35; 56/15. Anal. Calc. for $C_{16}H_{18}FeINO$ (423.08): C, 45.42; H, 4.29; N, 3.31. Found: C, 45.27; H, 4.12; N, 3.45%. Yield: 19%.

*4.1.6. 1′-Iodo-N,N-diethyl ferroceneglyoxylic amide (**4a**)*

^{1}H NMR($CDCl_3$) δ: 4.82 (brs, 2H, Cp); 4.58 (brs, 2H, Cp); 4.53 (brs, 2H, Cp); 4.38 (brs, 2H, Cp); 3.46 (q, 6.8 Hz, 2H, NCH_2CH_3); 3.25 (q, 6.8 Hz, 2H, NCH_2CH_3); 1.23 (t, 6.8 Hz, 3H, NCH_2CH_3); 1.14 (t, 6.8 Hz, 3H, NCH_2CH_3). ^{13}C NMR($CDCl_3$) δ: 197.7; 166.3; 77.5; 76.4; 76.1; 72.4; 72.3; 42.3; 39.9; 39.0; 14.2; 12.8. IR (KBr (cm^{-1})): 1642, 1661. MS (*m*/*z*/rel. int.): 439(M^+)/100; 339/83; 311/39; 275/15; 183/27; 128/18; 100/43; 72/68; 56/32. Anal. Calc. for $C_{16}H_{18}FeINO_2$ (439.08): C, 43.77; H, 4.13; N, 3.19. Found: C, 43.52; H, 4.01; N, 3.31%. Yield: 11%.

*4.1.7. 1′-Iodo-morpholino ferroceneglyoxylic amide (**4c**)*

^{1}H NMR($CDCl_3$) δ: 4.85 (t, 1.5 Hz, 2H, Cp); 4.60 (t, 1.5 Hz, 2H, Cp); 4.52 (t, 1.5 Hz, 2H, Cp); 4.35 (t,

1.5 Hz, 2H, Cp); 3.69 (m, 6H, morpholine); 3.45 (m, 2H, morpholine). ^{13}C NMR($CDCl_3$) δ: 196.4; 165.0; 76.7; 76.1; 72.6; 72.1; 70.7; 66.8; 66.7; 46.5; 41.7; 39.8. IR (KBr (cm^{-1})): 1646; 1667. MS (*m*/*z*/rel. int.): 453(M^+)/91; 339/100; 311/40; 183/21; 128/15; 56/12. Anal. Calc. for $C_{16}H_{16}FeINO_3$ (453.06): C, 42.42; H, 3.56; N, 3.09. Found: C, 42.55; H, 3.67; N, 3.21%. Yield: 40%.

4.1.8. 1′-Iodo-piperidino ferroceneglyoxylic amide (**4d**)

^{1}H NMR($CDCl_3$) δ: 4.82 (brs, 2H, Cp); 4.55 (brs, 2H, Cp); 4.50 (brs, 2H, Cp); 4.35 (brs, 2H, Cp); 3.59 (m, 2H, NCH_2); 3.30 (m, 2H, NCH_2); 1.62 (m, 4H, NCH_2CH_2); 1.54 (m, 2H, $N(CH_2)_2CH_2$). IR (KBr (cm^{-1})): 1644; 1662. MS (*m*/*z*/rel. int.): 451(M^+)/22; 339/62; 311/32; 183/48; 128/54; 121/39; 56/100. Anal. Calc. for $C_{17}H_{18}FeINO_2$ (451.09): C, 45.27; H, 4.02; N, 3.11. Found: C, 45.45; H, 4.15; N, 3.21%. Yield: 38%.

4.2. Aminocarbonylation of **3a**

3a (0.25 mmol, 203 mg), $Pd(OAc)_2$ (0.0125 mmol,), PPh_3 (0.025 mmol), the secondary amine (1.25 mmol), Et_3N (0.125 mL) and toluene (5 mL) were transferred under an inert atmosphere into a stainless steel autoclave. It was charged with carbon monoxide (40 bar) and heated with stirring in an oil bath at 100 °C. Then the volatile components were removed in vacuo. The residue was dissolved in toluene (15 mL), washed with 5% H_3PO_4 (15 mL), saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL) and dried over Na_2SO_4. The products were purified after removal of the solvent by chromatography (aluminium oxide, benzene/EtOAc = 3/1). The structures of the isolated compounds were determined by ^{1}H, ^{13}C NMR and IR spectroscopy, elemental analysis, and MS.

Analytical data of **7** and **8** have been reported elsewhere [16].

4.2.1. 1′-(N′,N′-Dibutyl-carbamoyl)-N,N-diethyl ferrocenecarboxamide (**9**)

^{1}H NMR($CDCl_3$) δ: 4.62 (brs, 2H, Cp); 4.58 (brs, 2H, Cp); 4.35 (brs, 2H, Cp); 4.27 (brs, 2H, Cp); 3.44 (q, 6.4 Hz, 4H, NCH_2CH$_3$); 3.35 (t, 8Hz, 4H, NCH_2CH$_2$); 1.54 (m, 4H, NCH_2CH_2); 1.26 (m, 4H, $N(CH_2)_2CH_2$); 1.17 (t, 6.4 Hz, 6H, NCH_2CH_3); 0.91 (t, 8Hz, 6H, $N(CH_2)_3CH_3$). ^{13}C NMR($CDCl_3$) δ: 169.2; 169.0; 81.1; 80.6; 71.7; 71.6; 71.5; 71.3; 48.5; 46.4; 42.5; 40.9; 31.4; 29.6; 20.2; 20.1; 13.8. IR (KBr (cm^{-1})): 1614. MS (*m*/*z*/rel. int.): 440(M^+)/100; 241/37; 220/43; 128/65; 121/80; 70/63; 57/35; 56/32. Anal. Calc. for $C_{24}H_{36}FeN_2O_2$ (440.41): C, 65.45; H, 8.24; N, 6.36. Found: C, 65.63; H, 8.31; N, 6.28%. Yield: 77%.

4.3. Stille-coupling of **3a**, **4c** and **4d**

$Pd(PPh_3)_4$ (0.005 mmol) and the iodoferrocene-derivative (0.25 mmol) were added to a flask equipped with a reflux condenser and a septum inlet. The flask was flushed with argon and charged with 2.5 mL of toluene. 0.3 mmol of vinyltributyltin was added by means of a hypodermic syringe through the septum inlet. The mixture was stirred at 100 °C. The reaction was followed by GC and TLC. After completion of the vinylation an aqueous solution of 0.6 mmol KF was added and the mixture was stirred overnight. The organic layer was separated, dried over Na_2SO_4. The product was purified after removal of the solvent by chromatography on aluminium oxide (eluent: benzene/EtOAc 85/15). The structures of the isolated compounds were determined by ^{1}H, ^{13}C NMR and IR spectroscopy, elemental analysis, and MS.

4.3.1. 1′-Vinyl-N,N-diethyl ferrocenecarboxamide (**10**)

^{1}H NMR($CDCl_3$) δ: 6.42 (dd, 10.8 Hz, 17.6 Hz, 1H, CH=CH$_2$); 5.35 (dd, 1.2 Hz, 17.6 Hz, 1H, CH=CH_AH$_B$); 5.05 (dd, 1.2 Hz, 10.8 Hz, 1H, CH=CH$_A$$H_B$); 4.53 (t, 2 Hz, 2H, Cp); 4.37 (t, 2 Hz, 2H, Cp); 4.26 (t, 2 Hz, 2H, Cp); 4.22 (t, 2 Hz, 2H, Cp); 3.49 (q, 6.8 Hz, 4H, NCH_2CH$_3$); 1.20 (t, 6.8Hz, 6H, NCH$_2$CH_3). ^{13}C NMR($CDCl_3$) δ: 169.2; 133.8; 112.1; 84.7; 79.5; 71.4; 70.7; 70.6; 68.4; 42.6; 40.4; 14.3; 12.8. IR (KBr (cm^{-1})): 1608. MS (*m*/*z*/rel. int.): 311(M^+)/100; 239/56; 212/51; 210/50; 121/55; 56/34. Anal. Calc. for $C_{17}H_{21}FeNO$ (311.21): C, 65.61; H, 6.80; N, 4.50. Found: C, 65.78; H, 6.71; N, 4.57%. Yield: 69%.

4.3.2. 1′-Vinyl-morpholino ferroceneglyoxylic amide (**11**)

^{1}H NMR($CDCl_3$) δ: 6.34 (dd, 10.8 Hz, 17.6 Hz, 1H, CH=CH$_2$); 5.36 (dd, 1.2 Hz, 17.6 Hz, 1H, CH=CH_AH$_B$); 5.11 (dd, 1.2 Hz, 10.8 Hz, 1H, CH=CH$_A$$H_B$); 4.76 (brs, 2H, Cp); 4.55 (brs, 2H, Cp); 4.46 (brs, 2H, Cp); 4.38 (brs, 2H, Cp); 3.74 (m, 2H, morpholine); 3.69 (m, 2H, morpholine); 3.64 (m, 2H, morpholine); 3.42 (m, 2H, morpholine). ^{13}C NMR($CDCl_3$) δ: 196.9; 165.2; 132.6; 113.4; 86.0; 75.5; 75.2; 71.6; 71.2; 68.9; 66.8; 66.7; 46.4; 41.7. IR (KBr (cm^{-1})): 1630, 1652. MS (*m*/*z*/rel. int.): 353(M^+)/36; 239/100; 211/82; 121/57; 56/55. Anal. Calc. for $C_{18}H_{19}FeNO_3$ (353.20): C, 61.21; H, 5.42; N, 3.97. Found: C, 61.37; H, 5.31; N, 3.85%. Yield: 85%.

4.3.3. 1′-Vinyl-piperidino ferroceneglyoxylic amide (**12**)

^{1}H NMR($CDCl_3$) δ: 6.36 (dd, 10.4 Hz, 17.6 Hz, 1H, CH=CH$_2$); 5.36 (dd, 1.2 Hz, 17.6 Hz, 1H, CH=CH_AH$_B$); 5.11 (dd, 1.2 Hz, 10.4 Hz, 1H, CH=CH$_A$$H_B$); 4.74 (t, 2 Hz, 2H, Cp); 4.52 (t, 2 Hz, 2H, Cp); 4.47 (t, 2 Hz, 2H, Cp); 4.39 (t, 2 Hz, 2H,

Cp); 3.6 (m, 2H, NCH_2); 3.31 (m, 2H, NCH_2); 1.62 (m, 4H, NCH_2CH_2); 1.55 (m, 2H, $N(CH_2)_2CH_2$). ^{13}C NMR($CDCl_3$) δ: 198.0; 165.3; 132.8; 113.2; 85.9; 75.7; 74.9; 71.7; 71.1; 68.9; 47.1; 42.2; 26.2; 25.5; 24.5. IR (KBr (cm^{-1})): 1630, 1650. MS (*m*/*z*/rel. int.): 351(M^+)/56; 239/100; 211/52; 121/32; 56/27. Anal. Calc. for $C_{19}H_{21}FeNO_2$ (351.23): C, 64.97; H, 6.03; N, 3.99. Found: C, 65.11; H, 6.11; N, 4.10%. Yield: 82%.

4.4. Carbonylation of **3a** in the presence of $NaBPh_4$

3a (0.25 mmol), $NaBPh_4$ (0.25 mmol), $Pd(OAc)_2$ (0.0125 mmol) and PPh_3 (0.025 mmol) were placed in a three-necked flask equipped with a magnetic stirrer, a septum inlet, a gas inlet and a reflux condenser with a balloon on the top. It was placed under carbon monoxide, and Et_3N (0.25 mL) and toluene (5 L) was added. The reaction mixture was heated at 90 °C for 8 h. The reaction was monitored by GC and TLC. When the carbonylation was complete, the volatile components were removed in vacuo. The residue was dissolved in toluene (15 mL), washed with 5% H_3PO_4 (15 mL), saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), and dried over Na_2SO_4. The product (**13**) was purified after removal of the solvent by chromatography (aluminium oxide, benzene/EtOAc = 3/1).

4.4.1. 1′-Benzoyl-N,N-diethyl ferrocenecarboxamide (**13**)

^1H NMR($CDCl_3$) δ: 7.88 (d, 6 Hz, 2H, Ph); 7.52 (t, 6 Hz, 1H, Ph); 7.44 (t, 6 Hz, 2H, Ph); 4.93 (brs, 2H, Cp); 4.65 (brs, 2H, Cp); 4.59 (brs, 2H, Cp); 4.29 (brs, 2H, Cp); 3.37 (q, 7.2 Hz, 4H, NCH_2CH_3); 1.12 (t, 7.2 Hz, 6H, NCH_2CH_3). ^{13}C NMR($CDCl_3$) δ: 198.6; 168.2; 139.5; 131.7; 128.2; 127.5; 81.6; 79.1; 74.9; 73.0; 71.8; 71.5; 42.5; 40.7; 14.3; 12.8. IR (KBr (cm^{-1})): 1610; 1632. MS (*m*/*z*/rel. int.): 389(M^+)/100; 317/30; 290/27; 260/31; 133/38; 72/28; 56/62. Anal. Calc. for $C_{22}H_{23}FeNO_2$ (389.28): C, 67.88; H, 5.96; N, 3.60. Found: C, 67.95; H, 5.85; N, 3.72%. Yield: 78%.

Acknowledgement

The authors thank the Hungarian National Science Foundation for financial support (OTKA T032111, TS044742, T035047).

References

[1] A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH Weinheim, 1995.
[2] D.W. Hall, J.H. Richards, J. Org. Chem. 28 (1963) 1549.
[3] M. Rosenblum, N.N. Brawn, D. Ciapanelli, J. Tancrede, J. Organomet. Chem. 24 (1970) 469.
[4] G. Iftime, C. Moreau-Bossuet, E. Manoury, G.G.A. Balavoine, Chem. Commun. (1996) 527.
[5] M.E. Wright, Organometallics 9 (1990) 853.
[6] Y. Xu, P. Saweczko, H.-B. Kraatz, J. Organomet. Chem. 637–639 (2001) 335.
[7] L.-L. Lai, T.-Y. Dong, J. Chem. Soc. Chem. Commun. (1994) 2347.
[8] I.R. Butler, R.L. Davies, Synthesis (1996) 1350;
I.R. Butler, S.C. Quayle, J. Organomet. Chem. 552 (1998) 63.
[9] I.R. Butler, A.L. Boyes, G. Kelly, S.C. Quayle, T. Herzig, J. Szewczyk, Inorg. Chem. Commun. 2 (1999) 403.
[10] I.R. Butler, M.G.B. Drew, A.G. Caballero, P. Gerner, C.H. Greenwell, J. Organomet. Chem. 679 (2003) 59.
[11] S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 470 (1994) 153.
[12] R.F.W. Jackson, D. Turner, M.H. Block, Synlett (1996) 862.
[13] Z. Szarka, R. Skoda-Földes, L. Kollár, Tetrahedron Lett. 42 (2001) 739.
[14] Z. Szarka, R. Skoda-Földes, A. Kuik, Z. Berente, L. Kollár, Synthesis (2003) 545.
[15] 1,1′-Diiodoferrocene was synthesised via lithiation according to: M.D. Rausch, D.J. Ciappanelli, J. Organomet. Chem. 10 (1967) 127 and subsequent reaction with iodine.
[16] A. Kuik, Z. Szarka, R. Skoda-Földes, L. Kollár, Lett. Org. Chem. 1 (2004) 151.
[17] R. Skoda-Földes, Z. Székvölgyi, L. Kollár, Z. Berente, J. Horváth, Z. Tuba, Tetrahedron 56 (2000) 3415.
[18] P.J. Hammond, P.D. Beer, C. Dudman, I.P. Danks, C.D. Hall, J. Organomet. Chem. 306 (1986) 367.