Inorganica Chimica Acta 370 (2011) 224–229

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

2-Pyridylmetallocenes: Part I. Electrophilic halogenation of 2-pyridylferrocene. Molecular structures of 2-pyridylferrocene and its α-brominated and -fluorinated derivatives. Synthesis of 2-pyridylruthenocene and 2-pyridylcymantrene

Karlheinz Sünkel *, Stefan Weigand

Ludwig-Maximilians-University Munich, Butenandtstr. 9, 81377 Munich, Germany

ARTICLE INFO

Article history:
Received 16 September 2010
Received in revised form 18 January 2011
Accepted 19 January 2011
Available online 4 February 2011

Keywords:
Pyridylmetallocenes
Fluoroferrocene
Electrophilic halogenation
Crystal structure determination

ABSTRACT

A new high-yield synthesis of 2-pyridylferrocene (**1**) without formation of the 1,1′-disubstituted product has been developed. Also the corresponding ruthenocene and cymantrene derivatives $[C_5H_4(2\text{-}C_5H_4N)]ML_n$ (ML_n = Ru(C_5H_5) (**2**), Mn(CO)$_3$ (**3**)) were prepared and fully characterized. *Ortho*-lithiation of **1** followed by electrophilic halogenation yielded $[C_5H_3X(2\text{-}C_5H_4N)]Fe(C_5H_5)$ [X = F (**4**), Cl (**5**), Br (**6**), I (**7**)], with **4** only being the second reported and first fully characterized fluoroferrocene. The molecular structures of **1**, **4** and **6** have been determined by X-ray crystallography.

1. Introduction

2-Phenylpyridine and its substituted derivatives have been intensively studied in the last decade due to their application as cyclometalated ligands for coordination compounds with very interesting photophysical and photochemical properties, particularly with Ir(III) [1]. It has been found that substituents on the phenyl ring and/or the pyridine ring, particularly fluorine atoms, markedly influence these properties [2]. We reasoned that substituting the phenyl moiety by a ferrocenyl or related metallocenyl group would open up an even wider field of fine-tuning possibilities due to the attached metal and further ligands. 2-Pyridylferrocene (**1**) is known for nearly 50 years [3,4] and its cyclopalladation [5] and cycloruthenation [6] have been reported as well, however no photophysical properties have been studied. While a 6-ruthenocenyl-2,2′-bipyridine has been reported ca. 20 years ago [7], the Ru analog **2** of **1** is unknown. A cymantrene derivative, with further substitution in the pyridine ring, $[C_5H_4(2\text{-}C_5H_2Ph_2N)]Mn(CO)_3$ has been mentioned in the literature, but there seems to be no full characterization [8]. This paper reports a new approach to **1** as well as the first synthesis of **2** and pyridylcymantrene $[C_5H_4(2\text{-}C_5H_4N)]Mn(CO)_3$ (**3**).

There are so far no studies on cyclometallation reactions of further ring-substituted pyridylferrocenes. With the above-mentioned high influence of halogen substituents on the properties of the cyclometallated complexes in mind, we decided also to prepare the four 1-halo-2-pyridylferrocenes via a lithiation-electrophilic halogenation sequence. The cyclometallation reactions of compounds **1**–**7** will be reported in forthcoming papers.

2. Experimental

2.1. General

All reactions were performed under an atmosphere of argon using standard Schlenk-techniques. The solvents used for the lithiation reactions (THF and Et_2O) were obtained from Aldrich in the highest available quality and used without further purification. The other solvents were of standard quality. The reagents *t*-BuLi (1.7 m in pentane); *n*-BuLi (2.5 m in hexane); "superhydride" ($LiBEt_3H$) (1.0 m in THF); 2-bromopyridine; $(PhSO_2)_2NF$; C_2Cl_6; $C_2Cl_4Br_2$ were obtained from Aldrich and used without further purification. The palladium catalyst $[PdCl_2(PPh_3)_2]$ was prepared according to a literature procedure [9].

NMR (all in $CDCl_3$): JEOL ECP-270 and ECX-400, ref. $CHCl_3$ $\delta(^1H)$ = 7.250 ppm, $\delta(^{13}C)$ = 77.0 ppm.

MS: Finnigan MAT 90 and JEOL Mstation 700.

* Corresponding author. Tel.: +49 89 2180 77773; fax: +49 89 2180 77774.
E-mail address: suenk@cup.uni-muenchen.de (K. Sünkel).

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.01.062

2.2. 2-Pyridylferrocene (**1**)

t-Butyllithium (28.2 mL, 47.9 mmol) was added slowly at −78 °C to a solution of ferrocene (4.46 g, 24.0 mmol) and potassium butoxide (0.36 g, 3.21 mmol) in THF (180 mL). The mixture was stirred for 1 h. Then a solution of zinc chloride (6.54 g, 48.0 mmol) in THF (90 mL) was added. After 5 min the mixture was allowed to reach room temperature and was further stirred for 1 h.

A suspension of $[PdCl_2(PPh_3)_2]$ (1.39 g, 1.98 mmol) and "superhydride" (2.40 mL, 2.4 mmol) in THF (45 mL) was added to the ferrocene reaction mixture. Subsequently 2-bromopyridine (5.69 mL, 59.7 mmol) was added dropwise to the dark mixture.

After 25 h a solution of sodium hydroxide (150 mL, 2.5 m) was added. The two-layer mixture was poured into a separating funnel. The aqueous phase was extracted three times with $CHCl_3$. The organic phases were combined and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue purified by column chromatography on alumina. Elution with hexane yielded remaining ferrocene as yellow, weak band. The desired product was eluted with hexane/$CHCl_3$ (1:2) as orange band. 2-Pyridylferrocene was obtained as orange-red powder (5.51 g, 87.3%).

^{1}H NMR (400 MHz) δ = 8.498 dd (1H), 7.564 dt (1H), 7.402 d (1H), 7.054 ddd (1 H), 4.910 t (2H), 4.389 t (2H), 4.040 s (5H); ^{13}C NMR (100.5 MHz) δ = 159.2, 149.1, 136.0, 120.5, 120.1; 83.4, 70.0, 69.6, 67.3.

2.3. 2-Pyridylruthenocene (**2**)

t-BuLi (5.10 mL, 8.67 mmol) was added slowly at −78 °C to a solution of ruthenocene (1.00 g, 4.32 mmol) and potassium butoxide (0.30 g, 0.54 mmol) in THF (130 mL). The mixture was stirred for 30 min. Then a solution of $ZnCl_2$ (1.18 g, 8.66 mmol) in THF (22 mL) was added. After 5 min the mixture was allowed to reach room temperature and was further stirred for 1 h.

A suspension of $[PdCl_2(PPh_3)_2]$ (0.22 g, 0.32 mmol) and "superhydride" (0.38 mL, 3.80 mmol) in tetrahydrofuran (12 mL) was added to the reaction mixture. Subsequently 2-bromopyridine (1.02 mL, 10.66 mmol) was added dropwise to the dark mixture.

After 25 h a solution of NaOH (30 mL, 2.5 m) was added. The two-layer mixture was poured into a separating funnel. The aqueous phase was extracted three times with $CHCl_3$. The organic phases were combined and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue purified by column chromatography on alumina.

Elution with hexane/$CHCl_3$ mixtures of increasing polarity yielded first unreacted ruthenocene, followed by various byproducts as colorless, blurred bands. The desired product was eluted with $CHCl_3$ as faint-yellow band. Complex **2** was obtained as yellow-grey solid (0.65 g, 49%).

Anal. Calc. for $C_{15}H_{13}NRu$: C, 58.43; H, 4.25; N, 4.54. Found: C, 57.42; H, 4.36; N, 4.41%. ^{1}H NMR (270 MHz): δ = 8.429 dd (1H), 7.501 dt (1H), 7.323 d (1H), 7.015 dt (1H), 5.283 t (2H), 4.721 t (2H), 4.454 s (5H); ^{13}C NMR (67.9 MHz): δ = 158.2, 149.0, 135.9, 120.6, 120.1; 88.1, 71.6, 71.5, 69.6.

MS (FAB$^+$): m/z = 309.3 M$^+$ (calcd. 309.9).

2.4. 2-Pyridylcymantrene (**3**)

n-BuLi (2.20 mL, 5.50 mmol) was added slowly to a solution of $[(C_5H_5)Mn(CO)_3]$ (1.00 g, 4.90 mmol) in THF (50 mL) at −78 °C in the dark. After 1 h $ZnCl_2$ (0.70 g, 5.14 mmol) was added and the mixture stirred for 1 h.

A suspension of $[PdCl_2(PPh_3)_2]$ (1.39 g, 1.98 mmol) and "superhydride" (2.40 mL, 2.4 mmol) in THF (45 mL) was added to the reaction mixture. Subsequently 2-bromopyridine (5.69 mL, 59.7 mmol) was added dropwise into the dark mixture. The suspension was allowed to reach room temperature.

After 3 days in the dark a solution of NaOH (50 mL, 5 m) was added. The two-layer mixture was poured into a separating funnel. The aqueous phase was extracted twice with THF. The organic phases were combined and dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue purified by column chromatography on silica. Remaining cymantrene was eluted with hexane, the product with $CHCl_3$ as yellow-orange band. Complex **3** was obtained as yellow oil (1.07 g, 78%).

Anal. Calc. for $C_{13}H_8MnNO_3$: C, 55.54; H, 2.87; N, 4.98. Found: C, 55.19; H, 2.77; N, 4.79%. ^{1}H NMR (400 MHz): δ = 8.528 (1H), 7.623 (1H), 7.338 (1H), 7.145 (1H), 5.513 (2H), 4.821 (2H); ^{13}C NMR (100.5 MHz): δ = 224.4; 152.2, 149.6, 136.5, 122.5, 119.7; 100.4, 82.6, 82.4.

MS (DEI$^+$): m/z = 281.1 (M$^+$, calcd. 281.0, $I_{rel.}$ = 7.5%), 225.1 (M$^+$−2CO, $I_{rel.}$ = 4.8%), 197.1 (M$^+$−3CO, $I_{rel.}$ = 100%).

2.5. 1-Fluoro-2-(2-pyridyl)ferrocene (**4**)

n-BuLi (0.55 mL, 1.4 mmol) was added slowly to a solution of **1** (0.24 g, 0.9 mmol) in Et_2O (15 mL). The mixture was stirred for 60 min and cooled to −78 °C. $(PhSO_2)_2NF$ (0.47 g, 1.5 mmol) was added and the reaction mixture was stirred for 15 min at −78 °C. Subsequently the temperature was allowed to reach −10 °C and the mixture was stirred for another 3 h.

Elution with hexane and hexane/CH_2Cl_2 mixtures with slowly increasing proportions of CH_2Cl_2 until hexane/CH_2Cl_2 (2:1) yielded unreacted **1** and byproducts as yellow, faint and blurred band. The following intensive orange band slowly spread in two very close bands, with the first containing **4** and the second butylated byproducts. Evaporation of the first eluting band yielded **4** as orange powder (0.07 g, 27%). Recrystallisation from hexane/Et_2O gave only few yellow-orange crystals.

Anal. Calc. for $C_{15}H_{12}FFeN$: C, 64.09; H, 4.30; N, 4.98. Found: C, 64.12; H, 4.57; N, 5.00%. ^{1}H NMR (400 MHz): δ = 8.542 d (1H), 7.724 d (1H), 7.627 dt (1H), 7.116 t (1H), 4.703 t (1H), 4.542 dd (1H), 4.140 s (5H), 4.014 dd (1H); ^{13}C NMR (67.9 MHz): δ = 157.0 d ($^3J_{CF}$ = 4 Hz), 149.4 s, 136.1 s, 134.4 d ($^1J_{CF}$ = 273 Hz), 121.5 d ($^4J_{CF}$ = 7 Hz), 121.0 s; 71.3 d ($^2J_{CF}$ = 7 Hz), 70.9 s (C_5H_5), 61.7 s, 61.1 d ($^3J_{CF}$ = 4 Hz), 58.0 d ($^2J_{CF}$ = 16 Hz); ^{19}F: (254 MHz): δ = −187.1 ppm. MS: (DEI$^+$) m/z = 281.2 (M$^+$, calcd. 281.0), 261.2 (M$^+$−HF).

2.6. 1-Chloro-2-(2-pyridyl)ferrocene (**5**)

n-BuLi (2.1 mL, 5.3 mmol) was added slowly to a solution of **1** (0.50 g, 1.9 mmol) in Et_2O (20 mL). The mixture was stirred for 1 h and cooled to −78 °C. A solution of hexachloroethane (1.09 g, 4.6 mmol) in Et_2O (15 mL) was added and the reaction mixture was allowed to reach room temperature.

After 3 h the solvent was evaporated and the brown residue purified by column chromatography on alumina. Elution with hexane/$CHCl_3$ mixtures of increasing polarity yielded remaining **1** and by-products as a faint yellow and blurred band. The desired product was eluted with $CHCl_3$ as intensive orange band. Complex **5** was obtained as viscous, orange oil (0.45 g, 79%). Recrystallization from Et_2O/hexane gave only few orange crystals.

^{1}H NMR (400 MHz): δ = 8.561 s (1H), 8.025 d (1 H), 7.658 t (1H), 7.137 t (1H), 4.888 s (1H), 4.592 s (1H), 4.269 s (1H), 4.145 s (5H); ^{13}C NMR (100.5 MHz): δ = 157.0, 149.2, 135.7, 122.5, 121.3; 91.8, 81.4, 71.9, 70.1, 67.0, 66.3. MS (DEP/EI) m/z = 297.2 (M$^+$, calcd. 297.0), 261.2 (M$^+$−HCl).