Communication

Selective reactivity of diamino Fischer-type carbene complexes towards 2,6-disubstituted and 2,4,6-trisubstituted pyrylium salts and 2,4,6-trichloro-1,3,5-triazine

P. Le Poul, B. Caro *, F. Robin-Le Guen

U.M.R. Sciences Chimiques, CNRS 6226, I.U.T. Lannion, Rue E. Branly, 22300 Lannion, France

Abstract

The synthesis of new amino Fischer-type carbene complexes **2a**–**d** with amino-containing side chain is presented. The reaction of these complexes with 2,4,6-triarylpyrylium salts gave the corresponding pyridinium salt **4a**, **4c**–**e** as expected from the initial attack of the free amino group onto the pyrylium α-carbon. When using the 2,6-diphenylpyrylium salt, a γ-addition of the amino group occurred, leading – after an hydrogen migration and a ring opening step – to the new organometallic unsaturated aminoketone **5**. Finally, the reactivity of the diaminocarbene **2b** with 2,4,6-trichloro-1,3,5-triazine has been investigated. The new triazine **6** bearing a ferrocenylaminocarbene group was isolated.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Aminolysis; Pyrylium salt; 1,3-Hydride transfer; Pyridinium Fischer-type carbene complex

1. Introduction

For analytical purpose, during the last two decades various ways of derivatization of proteins with transition organometallic complexes have been explored by reaction of N-terminus function of aminoacid residue [1]. Recent success in labelling BSA and lysozyme proteins thank to alkoxy Fischer-type carbenes [2] have been achieved by Jaouen et al. [3]. Water solubility of these complexes, necessary for biological applications, has been improved by incorporating oligoethyleneglycol/polyethyleneglycol (OEG/ PEG) groups [4]. On the other hand, the reaction of pendant NH$_2$ group of organometallic complexes with C terminus function of amino acid, peptides or proteins [5a,5b] has been less developed. Alkoxy Fischer-type carbene complexes undergo a facile reaction of aminolysis with diaminoalkanes, leading to aminocarbenes bearing a free amino function [6] (Fig. 1). As amines can be used to graft biomolecules, we tested the reactivity of the free nitrogen atom of these organometallic carbenes. Two heterocyclic target molecules, known for a long time for their high affinity with primary amines, were chosen: pyrylium salts [7] and 2,4,6-trichloro-1,3,5-triazine [8].

The reaction of pyrylium salts, including organometallic ones, with the NH$_2$ group of the carbene complex could allow the formation of new complexes containing pyridinium ring. With trichlorotriazine, the successive substitutions by aminocarbene groups could be expected [9]. As the aminocarbene organometallic fragment may be comparable to an amide function, we had in mind that the obtained complexes could play the role of new receptors for anions [10].

2. Results and discussion

2.1. Synthesis of diaminocarbene complexes (Scheme 1)

We initially investigated the condensation reaction of the methoxy(phenyl)pentacarbonyltungsten carbene complex

* Corresponding author. Tel.: +33 2 96485748; fax: +33 2 96485797.
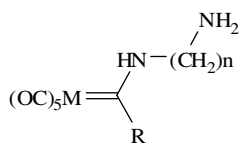*E-mail address:* bertrand.caro@univ-rennes1.fr (B. Caro).

Fig. 1. Diaminocarbene complex.

1a (Scheme 1) with ethylene diamine. To prevent the formation of the bis-aminocarbene, the diaminoalkane was wholly added to the cooled CH_2Cl_2 or THF solution of the carbene (−60 °C) as recognized by Sierra et al. [6] for the synthesis of the chromium counterpart. The diamino carbene **2a** was isolated in 40% yield as a yellow solid.

The lack of formation of the bis-aminocarbene indicates that the NH_2 group in **2a** is less reactive towards **1a** than the amino groups of the diaminoalkane precursor. The aminolysis reaction was extended without any experimental modification to the γ-methylenepyran Fischer-type carbene **1c** [11] using ethylenediamine and 1,3-diaminopropane, respectively. The new diamino heterocyclic carbenes **2c** (n = 2, Scheme 2) and **2d** (n = 3 Scheme 2) were isolated in good yield as pale yellow solids. Finally, the diaminobimetallic carbene **2b** containing a ferrocenyl group was obtained from ethylenediamine and the ferrocenylcarbene **1b** (Scheme 1) [12]. All the new compounds showed analytical and spectroscopic data in good agreement with their structure. The presence of two characteristic N–H signals in the ^1H NMR spectra indicates that as expected, compounds **2c** and **2d** were a mixture of two geometrical isomers Z and E because of the double bond character of the C–N bond [13]. For **2a** and **2b**, only one isomer was detected.

2.2. Reaction of carbene 2 with pyrylium salts and 2,4,6-trichloro-1,3,5-triazine

Having successfully synthesized a series of Fischer-type carbenes bearing amino free group, we decided to investigate their reactivity towards tri and disubstituted pyrylium salts, and 2,4,6-trichloro-1,3,5-triazine. One of the most
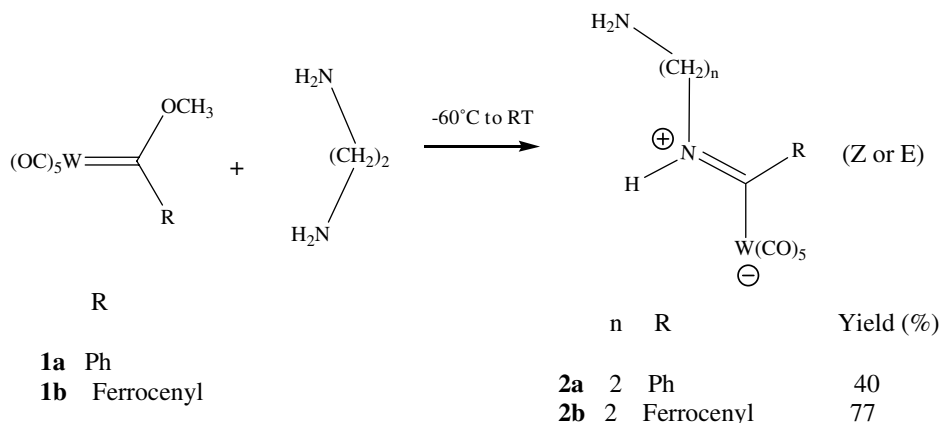
interesting general reactions of pyrylium salts is the ready exchange of oxygen atom for nitrogen atom in the pyrylium ring to form the corresponding pyridinium salt [14]. Due to the high electrophilic character of pyrylium ring, the reaction with primary alkyl amines [15], aromatic amines [15], aminoacids [15] and lysine residues of proteins [7] proceeds under mild conditions, whatever the substituent borne by the pyrylium ring.

So the treatment of a solution of carbene **2a** in degassed THF at −60 °C for 1 h, then at room temperature for 12 h, with 2,4,6-triaryl pyrylium salt **3a** or **3e** led, after elimination of the solvent under vacuum, to the new organometallic carbene pyridinium salt **4a** or to the heterodinuclear pyridinium salt **4e**, respectively (Scheme 3). The same procedure allowed the formation of the organometallic pyridinium salts **4c** and **4d**, from reaction between 2,4,6-triphenylpyrylium tetrafluoroborate and the pyran aminocarbenes **2c** and **2d**, respectively. It can be noted that the organometallic pyridinium salt **4b** was isolated in lower yield (15%). In that case, unreacted pyrylium salt was recovered from the reaction mixture.
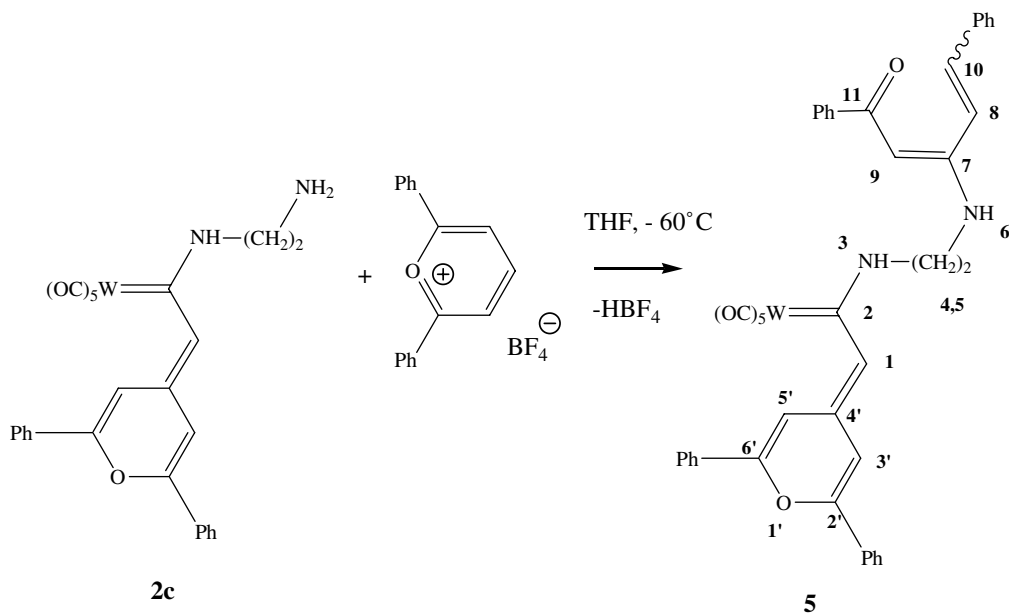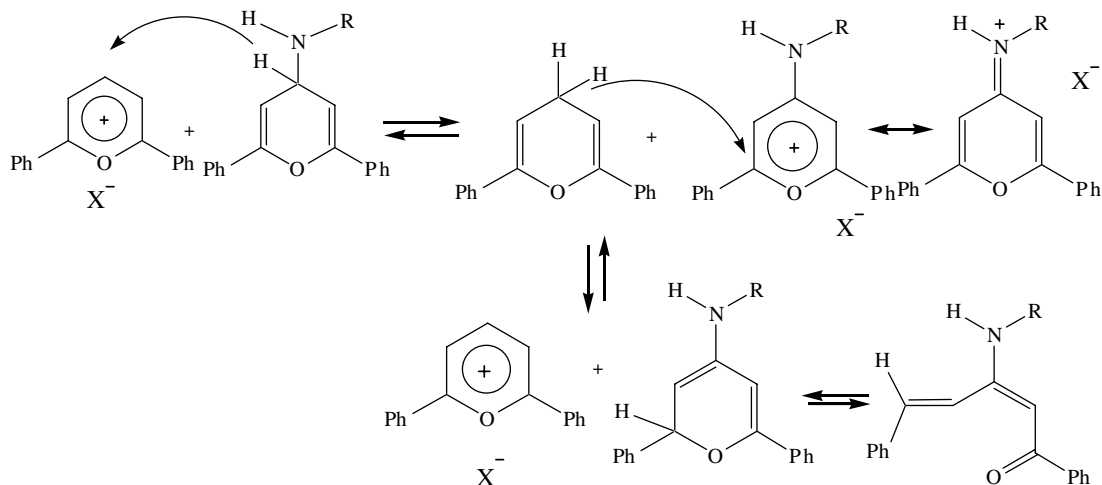
Organometallic pyridinium salts **4** were isolated as yellow precipitates and characterized by the usual spectroscopic techniquecs: ^1H, ^{13}C NMR, FTIR, HRMS and/or elemental analysis. NMR analysis showed that pyridinium salts **4a** and **4e** were obtained as one isomer about the carbene carbon–nitrogen bond. Pyridinium **4d** was obtained as a mixture of Z/E isomers.

We next turned our attention to the reactivity of the aminocarbene **2c** with 2,6-diphenylpyrylium salt. As it is repeatedly pointed out, 2,4,6-trisubstituted pyrylium salts usually favor α attack by nucleophiles, whereas 2,6-disubstituted pyrylium cations frequently undergo γ attack [15]. The formed 4H-pyrans undergo facile ring opening under acidic influence in order to give unsaturated 1,5-diketone [16]. However, the addition of primary amines to the 4-free position of 2,6-disubstituted pyrylium salts is rarely observed and pyridinium salt formation occurs.

Mixing the aminocarbene **2c** and the 2,6-diphenylpyrylium salt in THF at low temperature (−60 °C) gave, after

n	R	Yield (%)
2a 2	Ph	40
2b 2	Ferrocenyl	77

	R
1a	Ph
1b	Ferrocenyl

Scheme 1. Reaction of ethylenediamine with methoxypentacarbonyltungsten carbene complexes.

Scheme 2. Reaction of diaminoalkanes with γ-methylenepyran Fischer-type carbene complex **1c**.

	n	Y	Z	X	Yield (%)
4a	2	Ph$_{(1)}$	Ph$_{(3)}$	Ph$_{(2)}$	35
4c	2	2,6-diphenyl-4-*(4H*-pyran-4-ylidene)	Ph$_{(3)}$	Ph$_{(2)}$	15
4d	3	2,6-diphenyl-4-*(4H*-pyran-4-ylidene)	Ph$_{(3)}$	Ph$_{(2)}$	55
4e	2	Ph$_{(1)}$	2-methoxyBCT*	CH$_3$	46

*BCT: benzenechrometricarbonyl

Scheme 3. Reaction of diaminocarbene complexes with 2,4,6-trisubstituted pyrylium salts.

workup, the new unsaturated diaminocarbene **5** (72% yield, Scheme 4).

The spectra data (NMR and IR) of **5** leave no doubt about the proposed structure (Scheme 4). In particular, the chemical shift value (Scheme 4) of the carbonyl carbon ($\delta C_{11} = 188.6$ ppm) determined by 2D ^{1}H/^{13}C NMR analysis and the stretching vibration band of the carbonyl group ($\bar{v}_{CO} = 1721$ cm^{-1}) confirmed the ring opening structure.

The formation of **5**, under these experimental conditions (−60 °C), is unprecedented in pyrylium and pyran chemistry. This complex likely results from an initial attack of the amino group in **2c** onto the Cγ of the pyrylium salt. Such an attack leads to a 4H-pyran. A 1,3-hydride shift leads

to a 2H-pyran and subsequent ring opening step gives the final carbene **5** (Scheme 5).

Whereas the ring opening step is a well known process in 2H-pyran chemistry [16,17], the 4H-pyran to 2H-pyran isomerization is rarely observed (Scheme 5). Such a conversion has been only reported by Oestensen and colleagues for 2,4,6-triphenyl-4H-pyran and thiopyran [18] and by Chen and Reynolds for the diethyl (2,6-diphenyl-4H-thiopyran) phosphonate [19]. In the first case, the 1,3-hydrogen shift required heating in acetic acid. An intermolecular mechanism catalysed by the presence of a pyrylium cation, formed in the acidic medium by a disproportionation reaction involving the 4H-pyran and the corresponding protonated species, was suggested. In

Scheme 4. Reaction of diaminocarbene complex **2c** with 2,6-disubstituted pyrylium salt.

Scheme 5. Suggested intermolecular mechanism for the formation of **5**.

non-protic medium (boiling acetonitrile), isomerization of the 4H-pyran required the presence of catalytic amount of pyrylium salt. This confirmed the decisive role of pyrylium salt. On the other hand, for the thiopyranphosphonate isomerization, in boiling tetrachloroethylene solution, Chen and Reynolds favoured the prevalence of a sigmatropic rearrangement (intramolecular 1,3-hydrogen shift).

In our case, the presence of 2,6-diphenylpyrylium salt in the reaction medium, and the low reaction temperature are in favour of an intermolecular mechanism as exemplified in Scheme 5.

It can be noted that the first step of this process could be kinetically favorized by an orbital interaction between the lone pair of the nitrogen atom and the σ^* Molecular Orbital of the C–H bond.

Finally, we tested the reactivity of the ferrocenyl aminocarbene **2b** towards 2,4,6-trichloro-1,3,5-triazine. Mixing triazine and the organometallic moiety (1/3 molar ratio) in THF, at room temperature, for 1 h gave no reaction. Then, heating the mixture under reflux for 1 h produced the mono substituted organometallic triazine **6** as the major product of the reaction (53% yield) (Scheme 6).

The structure of carbene **6** was confirmed by IR spectroscopy, elemental analysis and ^1H, ^{13}C and ^{15}N NMR. In particular 2D $^1H/^{15}N$ NMR correlation shows two characteristic signals for the two nitrogen atoms of the –NH groups at $\delta = -286.0$ ppm and $\delta = -197.6$ ppm. For **2b** the NH$_2$ and NH groups resonate at $\delta = -367.3$ ppm and $\delta = -186.7$ ppm, respectively. Therefore, the signal at -197.6 ppm for **6** was assigned to the NH carbene group. In addition, ^{13}C chemical shift values for the three
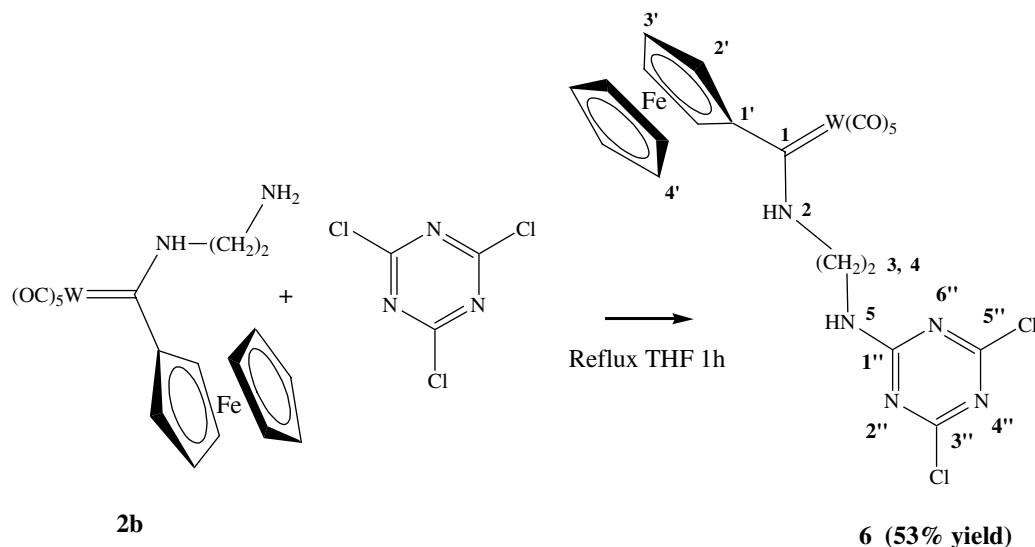
Scheme 6. Addition of diaminoferrocenylcarbene **2b** to 2,4,6-trichloro-1,3,5-triazine.

carbon atoms of the triazine ring of **6** (C_5'', C_3'': 170.8 ppm, 171.4 ppm and C_1'': 166.8 ppm) determined by 2D $^1H/^{13}C$ HMBC NMR analysis, are in accordance with the proposed structure.

3. Conclusion

We have synthesized and characterized a series of diamino Fischer-type carbene complexes with pendant NH_2. These molecules can easily react with electrophile species such as pyrylium salts or trichlorotriazine to lead to new heterocyclic organometallic carbene complexes. This suggests that these diamino carbenes could be good organometallic markers for biomolecules.

4. Experimental

All operations were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from Na/benzophenone under N_2. Chromatographic purification was performed with Silica Gel 60 (0.063–0.200 μm). NMR analysis were carried out using Brücker 400 and 500 MHz spectrometers. IR analysis were recorded on a Perkin–Elmer Spectrum 1000 FT-IR spectrophotometer using KBr plates. Mass spectroscopy and microanalysis were performed by the Centre Régional de Mesures Physiques de l'Ouest de l'Université de Rennes 1. 1,2-diaminoethane, 1,2-diaminopropane and 2,4,6-trichloro-1,3,5-triazine are commercial products from Aldrich.

4.1. General procedure for the preparation of diaminocarbenes complexes 2

An excess of 1,2-diaminopropane or 1,2-diaminoethane (2.4×10^{-3} mol) was added to a cooled solution of the methoxycarbene [11,12] (1.8×10^{-3} mol) in THF or CH_2Cl_2

at −60 °C. The yellow solution was stirred until the temperature reached 0 °C. The solvent was removed under vacuum. The residue was washed with water and extracted with diethylether. The solvent was eliminated in vacuo and the products recrystallized from CH_2Cl_2/Et_2O. The diaminocarbenes, were isolated in good yields as yellow powders (40–77%).

4.2. Procedure for the preparation of organometallic pyridinium salts 4

Diaminocarbenes **2** (6×10^{-4} mol) were diluted in 10 mL of degassed THF. The solution was cooled to −60 °C and 2,4,6-trisubstituted pyrylium tetrafluoroborates (6×10^{-4} mol) were added. The orange solutions were stirred for 12 h at room temperature. Then, the solvent was removed and the residue was recrystallized from CH_2Cl_2/Et_2O to give the corresponding pyridinium salts **4** in low to moderate yields.

Selected spectroscopic data of organometallic pyridinium salt **4a** (Scheme 3):

35% yield, FTIR (KBr) $\bar{v}$ (cm^{-1}): 3440, 3000, 2063, 1915, 1622, 1567, 1531, 1495, 1470, 1417, 1345, 1281, 1250, 1191, 1161, 1062, 878, 764, 703. ^1H NMR (acetone-d_6, 500 MHz, δ (ppm)): 3.58 (q, 2H, H_4, $^3J = 6$ Hz), 5.19 (t, 2H, H_5, $^3J = 6$ Hz), 6.49 (d, 2H, $H_{Ph(1)}$, $^3J = 7.5$ Hz), 7.30 (t, 1H, $H_{Ph(1)}$, $^3J = 7.5$ Hz), 7.38 (t, 2H, $H_{Ph(1)}$, $^3J = 8$ Hz), 7.60–7.92 (m, 11H, $H_{Ph(1)}$, $H_{Ph(2)}$), 8.24 (d, 4H, $H_{Ph(2)}$, $^3J = 8$ Hz), 8.43 (s, 2H, H_3', H_5'), 10.60 (s, 1H, H_3). ^{13}C NMR (acetone-d_6, 125 MHz, δ (ppm)): 49.4 (C_4), 53.9 (C_5), 120.2 ($C_{Ph(1)}$), 127.8 ($C_{Ph(1)}$), 129.4 ($C_{Ph(1)}$), 127.6 (C_3', C_5'), 129.4 ($C_{Ph(2)}$), 130.1, 130.4, 130.8, 136.0 ($C_{Ph(1)}$, $C_{Ph(2)}$), 134.3 (C_4'), 151.0 (C_{Ph}), 156.9 ($CPh_{(2)}$), 158.0 (C_2', C_6'), 198.8 (CO), 206.0 (CO), 262.6 (C_2). MS m/z calcd. for (C+): 763.1429. Found: 763.1463.

4.3. Procedure for the preparation of diaminocarbene 5

Aminocarbene **2c** (3.1×10^{-4} mol, 200 mg) and the 2,6-diphenylpyrylium tetrafluoroborate (3.1×10^{-4} mol, 100 mg) were mixed in THF at low temperature ($-50\ °C$). The reaction mixture was raised to room temperature. The solution was stirred during 12 h and then hydrolysed. The product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solution was concentrated under vacuum and purified by flash chromatography using CH_2Cl_2 as eluent. Aminocarbene **5** was isolated as a yellow solid in 72% yield (195 mg).

Main spectroscopic data of aminocarbene **5** (Scheme 4): FTIR (KBr) $\bar{v}$ (cm^{-1}): 3396, 3263, 2057, 1912, 1721, 1578, 1506, 1380, 1193, 1044, 768, 700. ^1H NMR (acetone-d_6, 500 MHz, δ (ppm) major isomer): 3.75 (s, 1H, H_6), 3.97 (q, 2H, H_5, $^3J = 4.5$ Hz), 4.48 (q, 2H, H_4, $^3J = 5.5$ Hz), 5.90 (d, 1H, H_8, $^3J = 12$ Hz), 6.52 (s, 1H, H_1), 6.77 (s, 1H, H'_5 or H'_3), 6.82 (s, 1H, H_9), 6.83 (s, 1H, H'_3 or H'_5), 7.37–7.51 (m, 12 H, H_{Ph}), 7.52 (d, 1H, H_{10}, $^3J = 12$ Hz), 7.81–7.92 (m, 8H, H_{Ph}), 10.25 (s, 1H, H_3). ^1H NMR (acetone-d_6, 500 MHz, δ (ppm) detected signals of the minor isomer): 3.78 (q, 2H, H_5, $^3J = 4.5$ Hz), 4.06 (q, 2H, H_4, $^3J = 5.5$ Hz), 5.80 (d, 1H, H_8, $^3J = 12$ Hz), 6.46 (s, 1H, H_1), 6.71 (s, 1H, H'_5 or H'_3), 6.81 (s, 1H, H'_3 or H'_5). ^{13}C NMR (acetone-d_6, 125 MHz), δ (ppm): 44.0 (C_5), 55.0 (C_4), 98.0 (C_8), 102.0 (C'_3 or $C_{5'}$), 108.0 ($C_{5'}$ or $C_{3'}$), 116 (C_9), 129.0 (C_1), 133.0 ($C_{4'}$), 147.0 (C_{10}), 155.0 (C'_6 or C'_2), 155.6 (C'_2 or C'_6), 159 (C_7), 123–133 (CH_{Ph}), 139, 141 (Cq_{Ph}), 188.6 (C_{11}), 199.5 (CO), 204.5 (CO), 242.0 (C_2). MS m/z calcd. for (C+): 873.1797. Found: 873.1805.

4.4. Procedure for the preparation of organometallic triazine 6

Ferrocenyl aminocarbene **2b** (3.10×10^{-4} mol, 180 mg) and 2,4,6-trichloro-1,3,5-triazine (1.03×10^{-4} mol, 20 mg) were diluted in 10 mL of freshly distilled THF at room temperature. The solution was then refluxed for 1 h. The reaction mixture was allowed to cool to room temperature and then poured into water. The product was extracted with CH_2Cl_2 and dried over $MgSO_4$. The solution was concentrated under vacuum and purified by flash chromatography with CH_2Cl_2–petroleum ether 80/20. The mono substituted organometallic triazine **6** was finally isolated as a yellow powder (53% yield, 120 mg).

Main spectroscopic data of triazine **6** (Scheme 6): FTIR (KBr) $\bar{v}$ (cm^{-1}): 3258, 2060, 1964, 1888, 1598, 1547, 1229, 1106, 998, 847, 801, 740. ^1H NMR (CDCl$_3$, 500 MHz, δ (ppm)): 3.99 (m, 2H, H_3), 4.20 (m, 2H, H_4), 4.17 (s, 5H, H'_4), 4.52 (s, 2H, H'_3), 4.61 (s, 2H, H'_2), 6.56 (s, 1H, H_5), 9.08 (s, 1H, H_2). 2D $^1H/^{15}N$ NMR (CDCl$_3$, 500 MHz, δ (ppm)): -197.6 (N_5), -286.0 (N_2). ^{13}C NMR (CDCl$_3$, 125 MHz, δ (ppm)): 40.6 (C_4), 55.2 (C_3), 70.7 (C'_2), 72.2 (C'_3), 69.7 (C'_4), 93.3 (C'_1), 166.8 (C''_1), 170.8 (C''_3), 171.4 (C''_5), 198.8 (CO), 202.4 (CO), 253.6 (C_1). Anal.

Calcd. for $_{21}H_{15}N_5O_5Cl_2FeW$: C, 34.65; H, 2.08; N, 9.62. Found: C, 35.03; H, 2.28; N, 9.57%.

Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.05.034.

References

[1] (a) G. Jaouen, A. Vessières, I.S. Butler, Acc. Chem. Res. 26 (1993) 361–369;
(b) M. Salmain, G. Jaouen, C. R. Chim. 6 (2003) 249–258;
(c) Y.K. Yan, M. Melchart, A. Habtemariam, P. Sadler, Chem. Commun. (2005) 4764–4776;
(d) M. Salmain, in: G. Jaouen (Ed.), Bioorganometallics, Wiley–VCH, 2005, p. 181;
(e) M. Salmain, J.-C. Blais, H. Tran-Huy, C. Compain, G. Jaouen, Eur. J. BioChem. 269 (2001) 5479–5487;
(f) A. Kazimierczak, J. Zakrzewski, M. Salmain, G. Jaouen, Bioconjugate 8 (1997) 489–494;
(g) K. Weiß, E.O. Fischer, Chem. Ber. 109 (1976) 1868–1886.
[2] (a) For selected reviews on the chemistry of Fischer-type carbene complexes see: K.H. Dötz, Angew. Chem., Int. Ed. Engl. 23 (1984) 587–608;
(b) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon, Oxford, 1995, p. 470;
(c) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, Pergamon, Oxford, 1995, p. 549;
(d) J.W. Herndon, Tetrahedron 56 (2000) 1257–1280;
(e) J. Barluenga, F.J. Fananas, Tetrahedron 56 (2000) 4597–4628;
(f) R. Aumann, Eur. J. Org. Chem. (2000) 17–31;
(g) J. Barluenga, J. Santamaria, M. Tomás, Chem. Rev. 104 (2004) 2259–2283.
[3] (a) M. Salmain, E. Licandro, C. Baldoli, S. Maiorana, H. Tran-Huy, G. Jaouen, J. Organomet. Chem. 617–618 (2001) 376–382;
(b) C. Baldoli, P. Cerea, L. Falciola, C. Giannini, E. Licandro, S. Maiorana, P. Mussini, D. Perdicchia, J. Organomet. Chem. 690 (2005) 5777–5787.
[4] D. Samanta, S. Sawoo, S. Patra, M. Ray, M. Salmain, A. Sarkar, J. Organomet. Chem. 690 (2005) 5581–5590.
[5] (a) A. Hess, O. Brosch, T. Weyhermüller, N. Metzler-Nolte, J. Organomet. Chem. 589 (1999) 75–84;
(b) D.R. Van Staveren, N. Metzler-Nolte, Chem. Rev. 104 (2004) 5931–5985.
[6] (a) E.O. Fischer, S. Fontana, J. Organomet. Chem. 40 (1972) 367–372;
(b) B. Alcaide, L. Casarrubios, G. Dominguez, M.A. Sierra, A. Monge, J. Am. Chem. Soc. 117 (1995) 5604–5605;
(c) V. Péron, E. Porhiel, V. Ferrand, H. Le Bozec, J. Organomet. Chem. 539 (1997) 201–203;
(d) J.M. Moreto, S. Ricart, K.H. Dötz, E. Molins, Organometallics 20 (2001) 62–70;
(e) I. Fernandez, M.J. Mancheno, M. Gomez-Gallego, M.A. Sierra, Org. Lett. 5 (2003) 1237–1240.

[7] (a) F. Robin-Le Guen, M.-C. Sénéchal-Tocquer, D. Sénéchal, B. Caro, J. Organomet. Chem. 545–546 (1997) 357–368;
(b) B. Caro, F. Robin-Le Guen, M. Salmain, G. Jaouen, Tetrahedron 56 (2000) 257–263;
(c) M. Salmain, K.L. Malisza, S. Top, G. Jaouen, M.-C. Sénéchal-Tocquer, D. Sénéchal, B. Caro, Bioconjugate Chem. 5 (1994) 655–659.

[8] (a) S. Masala, M. Taddei, Org. Lett. 1 (1999) 1355–1357;
(b) J.T. Bork, J.W. Lee, S.M. Khersonsky, H.-S. Moon, Y.-T. Chang, Org. Lett. 5 (2003) 117–120.

[9] (a) F. Chérioux, L. Guyard, P. Audebert, Chem. Commun. (1998) 2225–2226;
(b) M. Quesada, P. De Hoog, P. Gamez, O. Roubeau, G. Aromi, B. Donnadieu, C. Massera, M. Lutz, A.L. Spek, J. Reedijk, Eur. J. Inorg. Chem. (2006) 1353–1361.

[10] (a) P.D. Beer, J. Cadman, Coord. Chem. Rev. 205 (2000) 131–155;
(b) P.D. Beer, A.R. Graydon, A.O.M. Johnson, D.K. Smith, Inorg. Chem. 36 (1997) 2112–2118;
(c) P.A. Gale, Z. Chen, M.G.B. Drew, J.A. Heath, P.D. Beer, Polyhedron 17 (1998) 405–412;
(d) P.D. Beer, M.G.B. Drew, R. Jagessar, J. Chem. Soc., Dalton Trans. (1997) 881–886.

[11] (a) B. Caro, P. Le Poul, F. Robin-Le Guen, M.-C. Sénéchal-Tocquer, J. Vaisserman, Tetrahedron Lett. 39 (1998) 557–560;
(b) B. Caro, P. Le Poul, F. Robin-Le Guen, J.-Y. Saillard, S. Kahlal, C. Moinet, N. Le Poul, J. Vaissermann, Tetrahedron 58 (2002) 7519–7530;

(c) F. Robin-Le Guen, P. Le Poul, B. Caro, R. Pichon, N. Kervarec, J. Organomet. Chem. 626 (2001) 37–42.

[12] For the preparation and uses of ferrocenyl Fischer carbene complexes, see J.A. Connor, E.M. Jones, J.P. Lloyd, J. Organomet. Chem. 24 (1970) C20–C22.

[13] E. Moser, E.O. Fischer, J. Organomet. Chem. 15 (1968) 147–155.

[14] W. Schilf, B. Kolodziej, E. Grech, L. Dobrzycki, K. Wozniak, J. Mol. Struct. 707 (2004) 115–121.

[15] (a) A.T. Balaban, A. Dinculescu, G.N. Dorofeenko, G.W. Fischer, A.V. Koblik, V.V. Mezheritskii, W. Schroth, in: A.R. Katritzky (Ed.), Advances in Heterocycle Chemistry Supplement 2, Academic Press, New York, 1982;
(b) R.L. Shriner, R. Sutton, J. Am. Chem. Soc. (1963) 3989–3991.

[16] Y. Yamamoto, T. Kume, K.-Y. Akiba, Heterocycles 26 (1987) 1495–1498.

[17] (a) A. Alberola, C. Andrés, A. González Ortega, R. Pedrosa, M. Vicente, J. Chem. Soc., Perkin Trans. 1 10 (1987) 2125–2128;
(b) Y.Y. Belosludtsev, B.C. Borer, R.J.K. Taylor, Synthesis 4 (1990) 320–322;
(c) P. Charoenying, D.H. Davies, D. McKerrecher, R.J.K. Taylor, Tetrahedron Lett. 37 (1996) 1913–1916;
(d) R.J.K. Taylor, K. Hemming, E.F. De Medeiros, J. Chem. Soc., Perkin Trans. 1 19 (1995) 2385–2392.

[18] (a) E.T. Oestensen, M.M. Mishrikey, Acta Chem. Scand., B 30 (1976) 635–639;
(b) E.T. Oestensen, A.A.-A. Abdallah, S.H. Skaare, M.M. Mishrikey, Acta Chem. Scand., B 31 (1977) 496–499.

[19] C.H. Chen, G.A. Reynolds, J. Org. Chem. 45 (1980) 2453–2458.