Evaluation of heterocumulenic ferrocene derivatives for "click" chemistry type reactions ☆

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ABSTRACT

Azidoferrocene (**1**), 1,1′-diazidoferrocene (**2**) and 1,1′-diisothiocyanatoferrocene (**3**) were subjected to reactions from the repertoire of "click" chemistry, with a view to applications in the post-functionalisation of self-assembled monolayers. The copper-catalysed 1,3-dipolar cycloaddition of **1** and FcC≡CH (Fc = ferrocenyl) afforded the expected 1,2,3-triazole derivative under anhydrous and anaerobic conditions. Analogous reactions also succeeded with **2** and RC≡CH (R = Ph, Fc). The Staudinger reaction of **2** with 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) gave the expected bis(iminophosphoranyl)ferrocene in high yield. The nucleophilic addition of 2 equiv. of NHR_2 (R = Et, *i*Pr) to **3** afforded the corresponding thiourea derivative in quantitative yield.

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1. Introduction

Research into ferrocene-based compounds continues apace, largely stimulated by their successful application in such diverse fields as, for example, catalysis, materials science and biochemistry [1]. We have developed a strong interest in self-assembled monolayers (SAMs) [2] containing ferrocene-based adsorbate molecules [3]. Owing to the reversible redox-chemical behaviour of ferrocene derivatives, such functional SAMs may exhibit 'smart' properties [4]. We have utilised dipodal 1,1′-di(heteroatom)-functionalised ferrocene derivatives [5] such as, for example, fc(NC)$_2$, fc(PPh$_2$)$_2$ and fc(SR)$_2$ (fc = 1,1′-ferrocenediyl) as adsorbate species for SAMs on gold in this context [3a]. An alternative strategy for the fabrication of such redox-functionalised SAMs is the chemical attachment of ferrocene derivatives a posteriori to a SAM which contains terminal reactive groups suitable for high-yield attachment reactions under mild conditions. This approach therefore calls for "click" chemistry [6] of reactive SAMs with ferrocene derivatives. Surprisingly, ethynylferrocene (FcC≡CH) and the closely related propynoylferrocene (FcC(O)C≡CH) appear to be the only ferrocene derivatives to date which have been utilised for "click" reactions, namely copper-catalysed 1,3-dipolar azide–alkyne cycloadditions (CuAACs). This approach has already been successfully applied [7] to surface-related redox-functionalisations of dendrimers [8] and peptoid oligomers on solid-phase support [9] as well as to re-dox-functionalisations of solid graphitic surfaces [10], thin films of conducting polymer on platinum [11], monolayers on silicon [12] and SAMs on gold [13]. The use of ethynylferrocene and related acetylenic ferrocene derivatives for SAM modification by CuAAC methodology requires surface-immobilisation of a suitable azide component. However, recent work by Kleinert et al. strongly emphasises that azido-terminated monolayers do not react readily with alkynes, probably because the formation of an insoluble copper(I) alkyne complex occurs, which removes the catalyst from the reaction solution [14]. Similar results were obtained by Meldal and coworkers in a closely related study utilising a solid support resin for CuAAC chemistry [15]. Consequently, it appears much more desirable to immobilise terminal acetylenes and react them with suitable organic azides. This has prompted us to investigate CuAAC reactions of azido-functionalised ferrocenes as an alternative to the corresponding well-studied acetylenic derivatives. In addition, we have briefly investigated Staudinger reactions with these compounds. We have further extended our study to another type of "click" chemistry reactions, viz. the nucleophilic addition of amines to isothiocyanates, which affords thiourea derivatives. We here report on our findings obtained in this context with the heterocumulenic ferrocene derivatives azidoferrocene (**1**), 1,1′-diazidoferrocene (**2**) and 1,1′-diisothiocyanatoferrocene (**3**).

2. Results and discussion

A single report exists which concerns a Huisgen 1,3-dipolar cycloaddition of **1**, viz. its reaction with the potent dipolarophile dimethyl acetylenedicarboxylate [16]. CuAAC "click" reactions of **1** and **2** have not been described before. Initial attempts to react

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1 and **2** with an alkyne RC≡CH (R = Ph, Fc) under published [17] aqueous CuAAC reaction conditions utilising a copper(II)–ascorbate catalyst system failed. Instead, considerable amounts of the respective Glaser coupling product (RC≡C)₂ were obtained. Formation of such compounds is well known in this context [15], and exclusion of oxygen and use of a nitrogen-containing base are recommended to minimise this particular side reaction. Unfortunately, our attempts to modify the aqueous "click" protocol accordingly by exclusion of oxygen and the use of ammonia as a base were unsuccessful. The reactions succeeded, however, under anhydrous and anaerobic conditions in the absence of a base (THF, room temperature, ca. 10 mol% CuI), affording the 1,2,3-triazole derivatives **4–6** (Scheme 1), which were isolated in analytically pure form after chromatographic work-up. Unfortunately, due to severe tailing on the column, isolated yields were only moderate. 1,1′-Diazidoferrocene (**2**) proved to react rather sluggishly, so that yields were further affected by incomplete reaction. Attempts to drive the reactions of **2** more to completion by utilising prolonged reaction times and/or higher temperatures proved to be unsuccessful, since unspecific decomposition was increasingly observed under such conditions.

The identity of the new compounds was confirmed by elemental analyses and by NMR spectroscopy. In the case of the ferrocenylated derivatives **5** and **6**, the triazole proton gives rise to a characteristic singlet at ca. 7.6 ppm in the ^{1}H NMR spectrum, while this signal is found at 7.76 ppm in the case of **4**. The ^{13}C{^{1}H} NMR signal of the triazole CH unit is located at ca. 118.4 ppm in all three cases. Although there are no examples of 1,2,3-triazole derivatives suitable for direct comparison (i.e. with a nitrogen-bound ferrocenyl substituent in the 1-position), these NMR spectroscopic data for the triazole CH unit appear to be unexceptional. They compare well with those of related 1,2,3-triazole derivatives which bear a carbon-bound ferrocenyl substituent in the 4-position and a second, nitrogen-bound, substituent in the 1-position such as, for example, Fc–C₂HN₃–p-C₆H₄–SO₂NH₂ (δ_H 9.00, δ_C 119.2 ppm) [18], Fc–C₂HN₃–CH₂–p-C₆H₄–OMe (δ_H 8.17, δ_C 120.4 ppm) [19] and Fc–C₂HN₃–n-C₅H₁₁ (δ_H 7.42, δ_C 118.8 ppm) [7].

The CuAAC reactions just described have failed to a certain extent in terms of "click" chemistry (moderate yields, anaerobic and anhydrous conditions). However, the conditions for such reactions occurring at the solid–liquid interface of a SAM will be different from those in isotropic solution. This is especially true for the local concentrations of the reactants, which can be adjusted to be considerably higher than in solution. This may have dramatic consequences as has been shown by Rozkiewicz et al. who found that 1,3-dipolar azide–alkyne cycloaddition "click" chemistry is possible on a monolayer by microcontact printing at room temperature even in the absence of a Cu catalyst [20]. We will report on the results of related experiments with **1** and **2** in due course.

Staudinger reactions [21] of organic azides [22] with phosphanes are high-yield reactions potentially suitable for surface
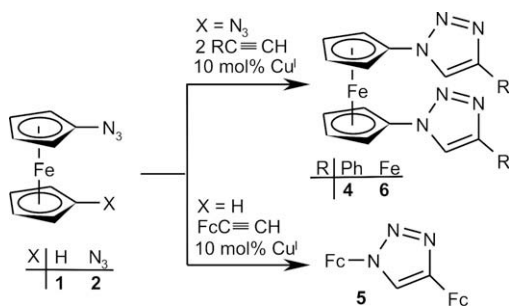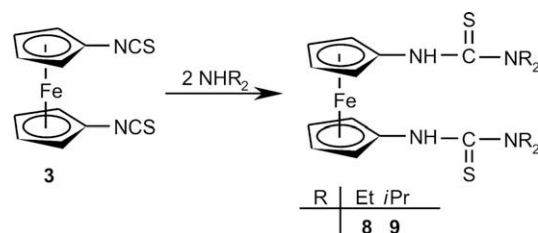
Scheme 2.

anchoring [23]. We have therefore briefly investigated the reaction of **1** and **2** with fc(PPh₂)₂ (dppf), which mimics two adjacent reactive sites in a SAM which contains terminal phosphanyl groups. Related reactions of **2** with monophosphanes PR₃ (R = Ph, Cy) were reported by Metallinos et al. to afford the respective bis(iminophosphorane) fc(N = PR₃)₂ in moderate isolated yields [24], while Otón et al. described an almost quantitative yield of crude product in the reaction of **2** with PPh₃ [25]. We performed the reaction of **1** (2 equiv.) with fc(PPh₂)₂ under the conditions previously described for Staudinger reactions of **2** with monophosphanes. The bis(iminophosphorane) product fc(PPh₂ = NFc)₂ (**7**) was obtained in 82% yield after work-up. The compound proved to be quite air-sensitive. It was characterised by elemental analysis and NMR spectroscopy. A characteristic NMR spectroscopic feature is the single signal in the ^{31}P NMR spectrum of **7**, whose chemical shift of 5.9 ppm is very similar to the value of 8.5 ppm reported for fc(N = PR₃)₂ [25]. The analogous reaction of **2** (1 equiv.) with fc(PPh₂)₂ afforded only intractable material whose insoluble nature prevented further characterisation. Obviously, a polymer was obtained in this reaction and no evidence for the formation of the [2.2]ferrocenophane fc(N = PPh₂)₂fc or related discrete cyclic oligomers could be found.

Nucleophilic additions of alcohols or amines to isocyanates and isothiocyanates are high-yield reactions which belong to the "click" chemistry repertoire [6]. Such "click" reactions on SAMs have been reported frequently for isocyanates [26], while, to the best of our knowledge, the use of isothiocyanates has been described only once to date [26d]. We have reacted 1,1′-diisothiocyanatoferrocene (**3**) with secondary amines NHR₂ (R = Et, iPr) (2 equiv.) in diethyl ether. These reactions proceeded smoothly and swiftly at room temperature and afforded the respective thiourea derivative fc{NH–C(S)–NR₂}₂ (**8**: R = Et, **9**: R = iPr) (Scheme 2), which precipitated from the reaction solution in quantitative yield and proved to be already analytically pure. Compounds **8** and **9** are essentially insoluble in diethyl ether and n-hexane, while their solubility in acetone and chlorocarbon solvents (CH₂Cl₂, CHCl₃) is rather high. Both compounds proved to be slightly air-sensitive in solution. They were characterised by elemental analyses and NMR spectroscopy, a notable ^{13}C NMR spectroscopic feature being the thiourea carbon signal at ca. 180 ppm.

3. Conclusion

We have evaluated the heterocumulenic ferrocene derivatives **1–3** for "click" chemistry type reactions with a view to the postfunctionalisation of reactive SAMs. Copper-catalysed 1,3-dipolar azide–alkyne cycloadditions, which are commonly known as the "cream of the crop" of all "click" reactions [27], gave somewhat unsatisfactory results with **1** and **2**, since it was necessary to work under anaerobic and anhydrous conditions and yields were far from quantitative. In terms of yield, the Staudinger reaction proved to be superior to these cycloadditions. However, strictly anaerobic and anhydrous conditions were mandatory, too. In comparison to the reactions performed with the azides **1** and **2**, the nucleophilic

Scheme 1.

addition of secondary amines to the isothiocyanate **3** worked much better in terms of "click" chemistry. Yields were quantitative and the compounds involved proved to be only slightly air-sensitive. This augurs well for applications of **3** and related compounds for surface post-functionalisation.

4. Experimental

All reactions were performed in an inert atmosphere (dinitrogen) by using standard Schlenk techniques. Solvents and reagents were procured from standard commercial sources and appropriately dried and purified prior to use. 1,1′-Diazidoferrocene (**2**) [28] and 1,1′-diisothiocyanatoferrocene (**3**) [3a] were prepared according to published procedures. Azidoferrocene [29] was prepared from bromoferrocene [30] in analogy to 1,1′-diazidoferrocene [28]. NMR spectra were recorded with a Varian Unity INOVA 500 spectrometer (500.13 MHz for ^{1}H). Elemental analyses were performed by the microanalytical laboratory of the University of Kassel.

4.1. Synthesis of **4**

Ethynylbenzene (205 mg, 2.00 mmol) and CuI (38 mg, 0.20 mmol) were added to a solution of **2** (268 mg, 1.0 mmol) in THF (30 mL). The mixture was stirred in the dark for 14 h. The yellow precipitate was isolated by filtration and purified by column chromatography on neutral alumina (activity grade II, CH_2Cl_2 eluent). Yield: 141 mg (30%). Anal. Calc. for $C_{26}H_{20}N_6Fe$ (472.3): C, 66.12; H, 4.27; N, 17.79. Found: C, 64.40; H, 4.60; N, 17.42%. ^{1}H NMR (CDCl$_3$): δ = 7.76 (s, 2H, C_2HN_3), 7.65 (d, J = 6.8 Hz, 4H, Ph), 7.27 (m, 6H, Ph), 4.96 (s, 4H, C_5H_4), 4.39 (s, 4H, C_5H_4). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 129.7, 128.7, 128.1, 125.6, 118.5, 68.3, 63.6; C_{ipso} signals could not be detected.

4.2. Synthesis of **5**

Ethynylferrocene (105 mg, 0.50 mmol) and CuI (10 mg, 0.05 mmol) were added to a solution of **1** (114 mg, 0.50 mmol) in THF (15 mL). The mixture was stirred in the dark for 3 d. The yellow precipitate was isolated by filtration and purified by column chromatography on neutral alumina (activity grade II, CH_2Cl_2 eluent). Yield: 90 mg (41%). Anal. Calc. for $C_{22}H_{19}N_3Fe_2$ (437.1): C, 60.45; H, 4.38; N, 9.61. Found: C, 60.13; H, 4.40; N, 9.58%. ^{1}H NMR (CDCl$_3$): δ = 7.64 (s, 1H, C_2HN_3), 4.86 (s, 2H, C_5H_4), 4.75 (s, 2H, C_5H_4), 4.31 (s, 2H, C_5H_4), 4.26 (s, 2H, C_5H_4), 4.21 (s, 5H, Cp), 4.08 (s, 5H, Cp). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 118.3, 70.4, 69.8, 69.0, 66.9, 66.8, 62.2; C_{ipso} signals could not be detected.

4.3. Synthesis of **6**

Ethynylferrocene (420 mg, 2.00 mmol) and CuI (38 mg, 0.20 mmol) were added to a solution of **2** (268 mg, 1.00 mmol) in THF (20 mL). The mixture was stirred in the dark for 14 h. The yellow precipitate was isolated by filtration and purified by column chromatography on neutral alumina (activity grade II, CH_2Cl_2 eluent). Yield: 262 mg (38%). Anal. Calc. for $C_{34}H_{28}N_6Fe_3$ (688.2): C, 59.34; H, 4.10; N, 12.21. Found: C, 58.71; H, 4.07; N, 12.00%. ^{1}H NMR (CDCl$_3$): δ = 7.61 (s, 2H, C_2HN_3), 4.85 (s, 4H, C_5H_4), 4.70 (s, 4H, C_5H_4), 4.36 (s, 4H, C_5H_4), 4.27 (s, 4H, C_5H_4), 4.05 (s, 10H, Cp). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 118.3, 69.5, 68.7, 68.4, 66.8, 64.0; C_{ipso} signals could not be detected.

4.4. Synthesis of **7**

1,1′-Bis(diphenylphosphanyl)ferrocene (138 mg, 0.25 mmol) was added to a solution of **1** (113 mg, 0.50 mmol) in dichloromethane (25 mL). The mixture was stirred in the dark for 14 h. Volatile components were removed in vacuo and the crude product titurated with *n*-hexane (3 × 10 mL). Yield 208 mg (87%). Anal. Calc. for $C_{54}H_{46}N_2Fe_3P_2$ (952.5): C, 68.10; H, 4.87; N, 2.94. Found: C, 66.27; H, 4.95; N, 2.58%. ^{1}H NMR (CDCl$_3$): δ = 7.61 (m, 8H, Ph), 7.50 (t, J = 7.2 Hz, 4H, Ph), 7.41 (m, 8H, Ph), 4.39 (s, 4H, C_5H_4), 4.14 (s, 4H, C_5H_4), 4.04 (s, 4H, C_5H_4), 3.91 (s, 10H, Cp), 3.69 (s, 4H, C_5H_4). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 132.4 (d, $|J_{CP}|$ = 9.0 Hz), 131.5, 128.3 (d, $|J_{CP}|$ = 11.3 Hz), 74.4 (d, $|J_{CP}|$ = 9.8 Hz), 73.7 (d, $|J_{CP}|$ = 9.4 Hz), 68.6, 67.9, 62.3; C_{ipso} signals could not be detected. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 5.9.

4.5. Synthesis of **8**

Diethylamine (74 mg, 1.01 mmol) was added to a solution of **3** (150 mg, 0.50 mmol) in diethyl ether (50 mL). The mixture was stirred for 0.5 h during which time the product precipitated. The yellow, microcrystalline solid was isolated by filtration, washed with diethyl ether (3 × 10 mL) and dried in vacuo. Yield 223 mg (100%). Anal. Calc. for $C_{20}H_{30}N_4FeS_2$ (446.5): C, 53.81; H, 6.77; N, 12.55. Found: C, 53.52; H, 6.76; N, 12.48%. ^{1}H NMR (CDCl$_3$): δ = 7.27 (br. s, 2H, NH), 4.60 (s, 4H, C_5H_4), 4.07 (s, 4H, C_5H_4), 3.73 (br. s, 8H, CH_2), 1.27 (br. s, 12H, Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 179.4, 98.4, 65.8, 65.0, 45.6, 12.8.

4.6. Synthesis of **9**

Diisopropylamine (102 mg, 1.01 mmol) was added to a solution of **3** (150 mg, 0.50 mmol) in diethyl ether (50 mL). The mixture was stirred for 4 h during which time the product precipitated. The yellow, microcrystalline solid was isolated by filtration, washed with diethyl ether (3 × 10 mL) and dried in vacuo. Yield 252 mg (100%). Anal. Calc. for $C_{24}H_{38}N_4FeS_2$ (502.6): C, 57.36; H, 7.62; N, 11.15. Found: C, 57.31; H, 7.79; N, 11.55%. ^{1}H NMR (CDCl$_3$): δ = 6.88 (br. s, 2H, NH), 4.82 (br. m, 4H, C*H*Me$_2$), 4.53 (s, 4H, C_5H_4), 4.14 (s, 4H, C_5H_4), 1.35 (d, J = 6.7 Hz, 24H, Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 182.1, 96.7, 67.7, 66.2, 49.3, 20.9.

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