Reactivity and Structure of Diferrocenylamine and N,N-Diferrocenylcarbamoylchloride

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Z. Naturforsch. 54b, 1450–1456 (1999); received June 29, 1999

Ferrocene, Diferrocenylamine, Carbamoylchloride, X-Ray Data

The reactivity of diferrocenylamine has been investigated aiming at the preparation of novel diferrocenylamino compounds, including nitrenium salts, amino radicals, transition metal amides, carbamato ligands, and others. However, diferrocenylamine is unexpectedly difficult to derivatize: only simple metalation by butyl lithium, alkylation by iodomethane, and chloroformylation by phosgene were possible. X-ray crystal structures are reported for the starting diferrocenylamine, and for the derivatives diferrocenylmethylamine and N,N-diferrocenylcarbamoylchloride.

Introduction

The chemistry of amines with N-bonded ferrocenyl substituents has been investigated in some detail with main emphasis on the reactivity and derivatives of ferrocenylamine FeNH₂ [1]. Somewhat surprisingly, almost nothing is known about derivatives of diferrocenylamine (Fc)₂NH; only the tertiary amines triferrocenylamine (Fc)₃N and phenylferrocenylamine (Fc)₂(C₆H₅)N have been prepared therefrom [2, 3]. We have been interested in the use of diferrocenylamine as a promising starting material for a number of possible novel target compounds, including (i) transition metal amides [(Fc)₂N]ₓM; (ii) nitrenium salts (Fc)₂N⁺X⁻; amino radicals (Fc)₂N•; (iii) carbamato and dithiocarbamato ligands (Fc)₂NCO₂⁻ and (Fc)₂NCS₂⁻; and (iv) isocyanatium salts [(Fc)₂N=C=O]⁺X⁻. In all these compounds, the combination of the steric bulk of the two N-bonded ferrocenyl substituents and the known stabilization of adjacent electron deficient centers by ferrocenyl groups [4] should (in principle) facilitate the synthesis and isolation of the products, as opposed to otherwise analogous but non-ferrocenylated compounds where no such effects can be envisaged. Here we summarize our synthetic efforts to synthesize molecules of the type (i) to (iv) with diferrocenylamine (Fc)₂NH as the key starting material. As will be seen in the following, diferrocenylamine is unexpectedly difficult to derivatize in general, and some of the successfully prepared intermediates show quite unique chemical reactivities, either unanticipated low stability or exceptional inertness, respectively.

Results and Discussion

Diferrocenylamine (Fc)₂NH 1 was synthesized from acetamide by sequential Cu-mediated ferrocenylation with bromoferrocene and subsequent alkaline hydrolysis according to the procedure developed by M. Herberhold and coworkers [3]. For comparison with the structures of derivatives, a single crystal structure analysis of 1 was performed. In Fig. 1 the steric bulk of the two N-bonded ferrocenyl groups is clearly evident. The structural features of the metalloccenyl groups are in accord with expected values. Similarly as in triferrocenylamine [2], the N(1)/C(10)/C(10a)/H(1) pyramid is distorted toward a planar structure as can be seen from the bond distances and angles listed in Table I.

Deprotonation of 1 with butyl lithium afforded the corresponding alkali metal amide 2. Its formation in THF solution was clearly indicated by a color change from yellow to red. 2 was prepared only in situ and reacted further according to Scheme 1:

Alkylation with methyl iodide gave access to the tertiary amine diferrocenylmethylamine 3 in 97% yield.
isolated yield. The NMR spectral properties of 3 are similar to those of other ferrocenyl derivatives. A single crystal structure analysis of 3 gave further proof of the identity of 3 (Fig. 2). In accord with the NMR spectral properties, the solid state structure also shows regular and undistorted metallo-ceny groups. The most notable feature of the molecular structure of 3 is the less marked planarity of the N(1)/C(1)/C(10)/C(20) pyramid (compare structural parameters listed in Table I), in comparison to 1 and triferrocenylamine [2].

The synthesis of diferrocenylmethylamine 3 was mainly performed as a test reaction in terms of establishing the degree of metalation of diferrocenylamine 1 by butyl lithium. The obtained yield of 97% of 3 (after isolation) indicates that essentially a quantitative metalation of 1 is possible, analogous to cases of other purely organic secondary amines. Therefore, we were quite confident that 2 could be silylated with trimethylchlorosilane. However, no diferrocenyltrimethylsilylamine 4 could be obtained from this reaction as indicated in Scheme 1. Obviously, severe steric hindrance prevents the formation of a diferrocenylamine with a third tertiary substituent. Although this negative result is somewhat disappointing, on the other hand this steric hindrance by the two ferro-

![Fig. 1. Molecular structure of 1, showing the atom-numbering scheme. Cyclopentadienyl carbon atoms of ferrocene 1 are numbered C(10)–C(19).](image1)

![Fig. 2. Molecular structure of 3, showing the atom-numbering scheme. Cyclopentadienyl carbon atoms of ferrocene 1 are C(10)–C(19), and of ferrocene 2 C(20)–C(29), respectively.](image2)

**Table I. Selected structural properties of 1, 3, 9.**

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<tr>
<th></th>
<th>(Fc)₂NH 1</th>
<th>(Fc)₂NCH₃ 3</th>
<th>(Fc)₂NCOCl 9</th>
<th>(Fc)₂N [2]</th>
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<td>N(1)–C(1) [pm]</td>
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<tr>
<td>C(10)–N(1)–C(20) [°]</td>
<td>126.5(2) b</td>
<td>118.7(2)</td>
<td>120.2(6)</td>
<td>119.8 a</td>
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<tr>
<td>C(10)–N(1)–C(1) [°]</td>
<td>–</td>
<td>116.2(2)</td>
<td>118.7(6)</td>
<td>119.8 a</td>
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<tr>
<td>C(20)–N(1)–C(1) [°]</td>
<td>–</td>
<td>117.2(2)</td>
<td>121.1(6)</td>
<td>119.8 a</td>
</tr>
<tr>
<td>C(10)–N(1)–H(1) [°]</td>
<td>114(6)</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>h [pm] c</td>
<td>9.2(3.1)</td>
<td>23.2(3)</td>
<td>2.2(7)</td>
<td>6</td>
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</table>

a Mean value of all three N–C distances or C–N–C angles, respectively [2];
b for 1 this angle is C(10)–N(1)–C(10a) due to the symmetry-related ferrocenyl groups;
c h (height) is defined as the distance of N(1) from the plane of the three N–bonded atoms.
cycly moieties might prove useful in terms of steric protection of other functional derivatives of diferrocenylamine 1.

Accordingly, we attempted the synthesis of diferrocenylnitrenium tetrafluoroborate 5. In fact, this goal was the main objective in the beginning of this work. Nitrenium salts have been shown to be only transient species in general [5-7] and it was only recently that a nitrenium salt has been isolated [8]. The anticipated higher stability of a diferrocenylnitrenium ion versus purely organic diarylnitrenium species [5-7] is related to the established capacity of ferrocenyl groups to effectively stabilize an adjacent electron-deficient center [4] as is exemplified by the existence of the isoelectronic very stable diferrocenylearbenium [9, 10] and diferrocenylphosphonium [11] salts. On reaction of diferrocenylamine 1 at -80 °C with trityl [12] or trialkyloxonium tetrafluoroborate as hydride abstracting reagents dark brown solutions were obtained, and, most importantly, no green-blue ionic ferrocenium species was observed, indicating that no competing Fe(II)–Fe(III) oxidation [13] by the trityl reagent had occurred. Besides the brown main product, a blue less polar compound was formed in low yield, which decomposed to the starting diferrocenylamine 1 within one minute on exposure to air. This blue product could be either the desired nitrenium salt 5 or — according to its non-ionic character — a diferrocenylamino radical 6 formed by oxidation of 1. It is common knowledge that organic diarylamines can be oxidized to the corresponding aminyl species which are usually in equilibrium with their dimers, tetraarylhydrazines [14]. At this point it is interesting to mention that tetraferrocenylhydrazine (Fc)2 N–N (Fc)2 is one of the “missing” homolectic ferroceny derivatives of the elements, as noted recently by Herberhold [15]. However, all attempts to synthesize 6 in better yield by oxidation with other reagents (PbO2, Ag2O [16], BaMnO4) which are commonly used [14] for the synthesis of organic tetrasubstituted hydrazines or amino radicals, respectively, met with failure. Another approach to nitrenium salt 5 was attempted by first converting the lithium diferrocenylamide 2 to the N-chlorodiferrocenylamine 7 using hexachloroethane as a mild chlorination agent, followed by removal of the N-chlorine with silver tetrafluoroborate. However, the N-chlorination of 2 to 7 did not proceed as anticipated.

Furthermore, transmetalation of the lithium amide 2 with halides of Cu(I), Fe(II), and Hg(II) resulted in brown very polar solids which had none of the expected properties of transition metal amides [17]; according to FAB mass spectrometry no
simple molecular compounds were formed in these reactions. The main reason for attempting the synthesis of \((\text{Fc})_2\text{N–Cu}^\text{I}_\text{N} 8\text{a}\) was its anticipated use in Ullman-type cross-coupling reactions [18], while \((\text{Fc})_2\text{N–Hg–N(Fc)}_2 8\text{c}\) was thought to be a convenient stable precursor from which the diferrocenylamino radical 6 or its dimer tetrarrocenylhydrazine, respectively, could be cleanly prepared by thermolysis. We have no simple explanation for the obvious inaccessibility of such transition metal diferrocenylamides.

In contrast to these unsuccessful reactions, the chloroformylation of diferrocenylamine 1 with bis(trichloromethyl)carbonate – “triphosgene” [19, 20] – afforded the expected N,N-diferrocenylcarbamoylchloride 9 in 65% yield. The NMR and other spectral properties of 9 (compare Experimental Section) are in line with the expectations. In addition, suitable X-ray quality single crystals could be obtained and the solid state structure of 9 is shown in Fig. 3.

The two ferrocenyl groups effectively shield the nitrogen atom of the carbamoyl group and in contrast to the two structures of 1 and 3 (where distorted pyramidal nitrogen atoms were observed) the nitrogen atom N(1) is planar with bond angles close to 120 degrees, as expected for an amide derivative. Relevant bond distances and angles are listed in Table I for comparison with the structural features of amines 1 and 3.

Carbamoylchloride 9 was synthesized as a potential progenitor of novel N,N-diferrocenylisocyanatium salts 10 which have not been reported in the literature but which were anticipated to be accessible due to the cation-stabilizing property of the ferrocenyl substituents [4]. However, no halide abstraction proved possible with various silver salts of non-coordinating anions, e.g. silver trifluoromethanesulfonate, as depicted in Scheme 1. It soon became evident that 9 is an extremely unreactive acid chloride: no hydrolysis of 9 with H₂O or with saturated KOH/EtOH solution (!) was possible, preventing the formation of N,N-diferrocenylcarbamate 11 which would be an interesting new chelating ligand. Similarly, no tetraferrocenyleurea could be obtained from the interaction of 9 with diferrocenylamine 1 or diferrocenylamide 2. Such reactions are quite common for organic carbamoylchlorides [21, 22]. In addition, no reaction was observed with elemental Mg or with Zn/tri-methylchlorosilane [23] as reducing agents. Finally we note that the potential ligand diferrocenylthiocarbamate 12 cannot be obtained from nucleophilic addition of the diferrocenylamide 2 to carbon disulfide.

**Summary**

A detailed investigation of the reactivity of diferrocenylamine has been carried out with the aim of synthesizing novel ferrocenyl-containing compounds, including nitrenium salts, amino radicals, transition metal amides, carbamato ligands, and isocyanatium compounds. In general, these objectives could not be fulfilled; only metalation of diferrocenylamine to give the corresponding lithium amide, alkylation with methyl iodide (but not silylation with trimethylchlorosilane), and chloroformylation to yield an unusually unreactive carbamoylchloride were possible. Obviously steric and electronic effects contribute to the observed low reactivity of diferrocenylamine and its derivatives, preventing in most cases access to further functionalized diferrocenylamino compounds.

**Experimental Section**

All synthetic operations were performed using standard Schlenk techniques with protection from air using Ar as inert atmosphere. Solvents were purified, deoxygenated, and dried prior to use. Instrumentation and standard methods have been published previously [24].
Diferrocenylamine 1 was prepared according to the literature [3].

X-ray structure determinations of 1, 3, and 9

X-ray crystallographic data (Table II) were collected by a Siemens P4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 71.073 pm). The unit cell parameters were determined from 25 randomly selected reflections, obtained by P4 automatic routines. Data were measured via ω-scan and corrected for Lorentz and polarisation effects, an empirical absorption correction, based on ψ-scans, was applied. The structures were solved by direct methods (SHELXS-86) [25] and refined by a full matrix least-squares procedure using $F^2$ (SHELXL-93) [26]. The function minimized was $\sum w(F_o^2 - F_c^2)^2$ with the weight defined as $w^{-1} = [\sigma(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located by difference Fourier methods, but in the refinement the ferrocenyl hydrogen atoms were included in calculated positions and refined with isotropic displacement parameters 1.2 times higher than $U(\text{eq})$ of the attached atoms. The hydrogen atom at N(1) of compound 1 is disordered and lies nearby a twofold rotation axis. It was refined with 0.5 occupancy (the distance to the symmetry equivalent hydrogen atom is 0.42 Å). Further details of the crystal structure investigations of compounds 1, 3, 9 are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

Table II. Crystal data and structure refinement for 1, 3, 9.

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Lithium diferrocenylamide 2 and diferrocenylmethylamine 3

A Schlenk vessel was charged with 90 mg (0.23 mmol) of diferrocenylamine 1 and 30 ml of THF. After cooling to -80 °C, 0.12 ml of a 2M solution of n-butyl lithium in pentane (0.23 mmol) was added. The stirred mixture changed its color gradually from yellow to red, indicating formation of lithium diferrocenylamide 2. After warming to room temperature, 0.5 ml (8 mmol) of iodomethane was added and the solution was stirred for further 15 min. Standard aqueous workup yielded 91 mg (23 mmol, 97%) 3: yellow solid, mp 127 °C.

IR (KBr): cm^-1 3110w, 3089w, 1499s, 1456m, 1382w, 1350w, 1263m, 1104s, 1050s, 1032m, 1001m, 934s, 816s, 804s, 486s, 469s. MS (EI, 70 eV): m/z 399 (100%, M^+), 384 (14%, M^+ – CH₃), 319 (11%, M^+ – C₅H₅), 304 (27%), 263 (42%, Fe–N–C₅H₅), 241 (33%), 212 (61%, Fe–N–CH₃), 200 (76%, Fe–N^+), 186 (66%, Fe^+), 121 (61%, FeCp^+).

1H–NMR (CDCl₃): ppm 3.08 (s, 3H, CH₃), 3.95 (pseudo-t, 4H, Cpsubst), 4.10 (pseudo-t, 4H, Cpsubst), 4.17 (s, 10H, Cpunsubst). 13C–NMR (CDCl₃): ppm 40.5 (CH₃), 58.8 (Cpsubst), 63.6 (Cpsubst), 68.1 (Cpunsubst), 110.3 (C(1) od Cpsubst).

Single crystal structure: Fig. 2, Table II.

C_{21}H_{21}Fe₂N (399.09)

Calcd C 63.20 H 5.30%,
Found C 63.41 H 5.33%.

N,N′-diferrocenylcarbamoyl chloride 9

A solution of 530 mg (13.8 mmol) of diferrocenylamine 1 in 10 ml of dichloromethane and 136 mg (4.6 mmol) of triphosgene was stirred over night at ambient temperature. Solvents and volatile materials were removed in vacuo, the residue was chromatographed (Al₂O₃, n-hexane/ether 9/1),
yielding 401 mg (0.9 mmol, 65%) \( \mathbf{9} \): yellow solid, mp 176 °C, dec. IR (KBr): cm\(^{-1} \) 3127w, 3098m, 2963w, 1728s (\( v_{C=O} \)), 1456s, 1410m, 1375w, 1291s, 1179s, 1105s, 1054m, 1022m, 1001s. MS (EI, 70 eV): \( \frac{m}{z} \) 447 (52%, \( M^+ \)), 384 (40%, (Fc)\(_2\)N\(^+ \)), 319 (12%, \( M^+ – COCICp \)), 304 (10%), 263 (100%, Fe–N–Cp\(^+ \)), 200 (44%, FeCn\(^+ \)), 186 (20%, Fe\(^+ \)), 121 (45%, FeCp\(^+ \)). \( ^{1}H \) NMR (CDCl\(_3\)): ppm 4.07 (s, 10H, C\(_{\text{unsubst}}\)), 4.14 (pseudo-t, 4H, C\(_{\text{subst}}\)), 4.46 (pseudo-t, 4H, C\(_{\text{subst}}\)). \( ^{13}C \) NMR (CDCl\(_3\)): ppm 64.7 (C\(_{\text{subst}}\)), 66.7 (C\(_{\text{subst}}\)), 69.7 (C\(_{\text{unsubst}}\)), 102.8 (C(1) od C\(_{\text{subst}}\)), not observed: COCl. Single crystal structure: Fig. 3, Table II.

\[ \text{C}_{21}\text{H}_{18}\text{ClFe}_{7}\text{NO} (447.52) \]
Calcld C 56.36 H 4.05%,
Found C 56.22 H 4.03%.