

Notes

1,1'-Diisocyanoferrrocene and a Convenient Synthesis of Ferrocenylamine[†]

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Summary: The new ferrocene derivative 1,1'-diisocyanoferrrocene was prepared in 50% isolated yield from the reaction of 1,1'-diisocyanatoferrrocene with formic acid followed by thermal decarboxylation and reaction with POCl₃/NH(*i*-Pr)₂. An improved synthesis route to ferrocenylamine involves lithiation of ferrocene with *t*-BuLi followed by reaction with α -azidostyrene and subsequent acidification.

Introduction

The ferrocenyl moiety has been playing a useful role as backbone or substituent in ancillary ligands,¹ as a donor moiety in metal–organic nonlinear optical materials,² and in polymers.³ This is due to both the specific geometries that the ferrocenyl moiety can enforce and its electronic (redox) properties. We have developed an interest in ligands and materials that incorporate ferrocenyl-isocyanide groups. In particular, 1,1'-diisocyanoferrrocene seems potentially interesting as a bridging ligand in redox-active coordination polymers. However, 1,1'-diisocyanoferrrocene has not yet been reported,⁴ although the corresponding mono-isocyanide, ferrocenylisocyanide, is known.⁵ The best synthesis route thus far for ferrocenylisocyanide proceeds through ferrocenylamine, a compound that is synthesized from ferrocene either directly in low (12–13%) isolated yield⁵ or

through a four-step procedure.⁶ The potential precursor for 1,1'-diisocyanoferrrocene, 1,1'-diaminoferrrocene, is a rather poorly described compound obtained in low yield and unspecified purity.⁷ Here we report the first synthesis of 1,1'-diisocyanoferrrocene, using a route that avoids the use of 1,1'-diaminoferrrocene, as well as an alternative, simplified synthesis of ferrocenylamine.

Results and Discussion

Synthesis of 1,1'-Diisocyanoferrrocene. The most convenient synthesis of ferrocenylisocyanide, CpFe(C₅H₄NC), reported thus far proceeds from ferrocenylamine CpFe(C₅H₄NH₂) through the formamide CpFe(C₅H₄NHCHO), which can then be converted into the isocyanide by reaction with POCl₃ in the presence of diisopropylamine.⁵ Looking for an alternative route to prepare 1,1'-diisocyanoferrrocene, avoiding the 1,1'-diaminoferrrocene, we found a suitable access through the known compound 1,1'-diisocyanatoferrrocene.⁸

The route is based on the reaction of isocyanates with carboxylic acids to give mixed carbamic carboxylic anhydrides.⁹ These can thermally eliminate CO₂ to yield formamides, and as mentioned above, formamidoferrrocenes can be converted to isocyanoferrrocenes. This thus obviates the need to use 1,1'-diaminoferrrocene as an intermediate in the synthesis of 1,1'-diisocyanoferrrocene.

The 1,1'-diisocyanatoferrrocene is synthesized from the corresponding dicarboxylic acid through the bis(acyl)-azide.⁸ It can be converted to the 1,1'-diformamidoferrrocene by reaction with formic acid in toluene at ambient temperature, to give the intermediate mixed carbamic carboxylic anhydride,¹⁰ followed by thermal decarboxylation by raising the temperature of the

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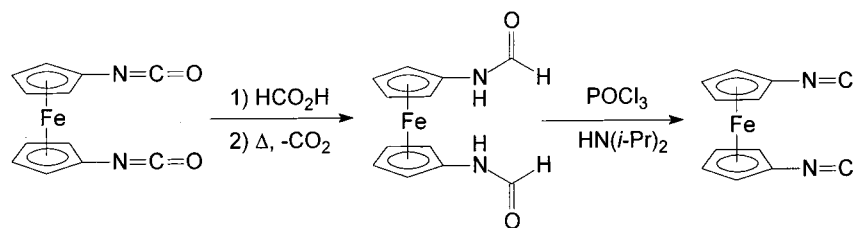
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(10) This intermediate can be observed as a precipitate in the reaction mixture. Decanting and rinsing with pentane gives a yellow solid with IR bands (Nujol mull) at ν 1779, 1743 cm⁻¹ (CO), 3305 cm⁻¹ (NH), consistent with a mixed carbamic carboxylic anhydride.

Scheme 1



reaction mixture to 110 °C (Scheme 1). The evolution of CO₂ sets in around 80 °C, and crude 1,1'-diformamidoferrrocene is obtained as a yellow solid after precipitation with light petroleum ether. The IR spectrum of the crude material shows a ν_{CO} vibration at 1680 cm⁻¹, comparable with that in formamidoferrrocene.⁵ This crude product was then converted to the 1,1'-diisocyanoferrrocene by subsequent reaction with POCl₃ in the presence of diisopropylamine base (Scheme 1). After column chromatography, 1,1'-diisocyanoferrrocene was obtained as a yellow crystalline solid in 50% yield based on the 1,1'-diisocyanoferrrocene.

The 1,1'-diisocyanoferrrocene was characterized by IR and NMR spectroscopy and elemental analysis. Its IR spectrum shows a ν_{NC} absorption at 2118 cm⁻¹ (2120 cm⁻¹ in ferrocenylisocyanide⁵). Its melting point (150 °C, with decomposition) is substantially higher than that of ferrocenylisocyanide (73–75 °C). In the ¹³C NMR spectrum the isocyanide carbon resonance is found at δ 162.3 ppm. (δ 163.9 ppm in ferrocenylisocyanide).

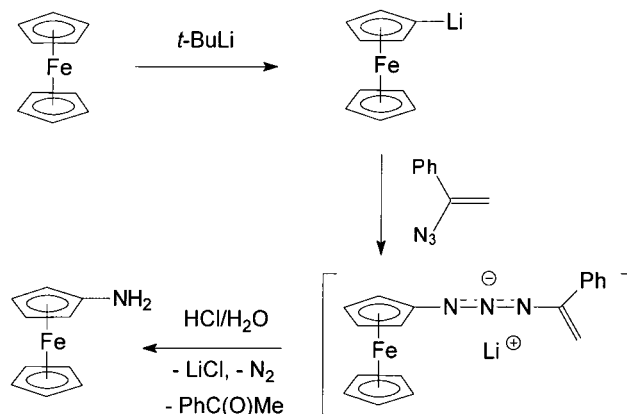
Synthesis of Ferrocenylamine. The most convenient direct route to ferrocenylamine reported thus far proceeds through lithiation of ferrocene with 2 equiv of *n*-BuLi and subsequent reaction with *O*-benzylhydroxylamine followed by acidification and basic extraction, in isolated yields of 12–13%.⁵ A recently optimized procedure for the route from ferrocene to ferrocenylamine in four steps via iodoferrocene and *N*-ferrocenyl phthalimide was reported with isolated yields around 50%.^{6a} In an attempt to devise a simplified but effective synthesis, we applied the method developed by Hassner et al. for the synthesis of anilines and heteroaromatic amines.¹¹ This procedure involves the reaction of aryllithium reagents with α -azidostyrene, a reagent that is readily available from styrene in three simple steps.¹²

Ferrocene was lithiated in THF solvent with 0.9 equiv of *t*-BuLi,¹³ and this was then reacted with α -azidostyrene at -70 °C. Acidification with HCl followed by extraction with water and precipitation with base afforded crude ferrocenylamine in 50% isolated yield, calculated on *t*-BuLi (Scheme 2). From this material *N*-ferrocenylformamide was obtained, following the published procedure,^{5a} in 52% isolated yield, with mp 96–97 °C (previously reported yield 46%, mp 86–87 °C). The crude ferrocenylamine can be purified by vacuum sublimation (72% yield).

Conclusions

The new ferrocene derivative 1,1'-diisocyanoferrrocene was obtained conveniently from the corresponding 1,1'-

Scheme 2



diisocyanoferrrocene. As the latter is easily prepared (in three high-yield steps) from ferrocene, the 1,1'-diisocyanoferrrocene should be an attractive redox-active linker for multimetallic ensembles and coordination polymers. The new preparation of ferrocenylamine makes this compound readily accessible in multigram quantities of good purity. We are presently exploring its use in the synthesis of new ancillary ligands for transition metal complexes and NLO chromophores.

Experimental Section

General Remarks. Where indicated, procedures were performed under nitrogen atmosphere using standard Schlenk techniques. THF was distilled under nitrogen from Na/K alloy before use. 1,1'-Ferrocenedicarboxylic acid¹⁴ and α -azidostyrene¹² were prepared following published procedures. **CAUTION:** Organic azides can decompose explosively and may be shock sensitive. α -Azidostyrene appears to be relatively stable and has been successfully molecularly distilled (not required for the present application), but caution remains required. 1,1'-Ferrocenediacyl azide decomposes smoothly in toluene solution under the conditions specified below. Ferrocene (Acros, 98%), POCl₃, diisopropylamine (Acros), and *t*-BuLi (1.5 M solution in pentane, Acros) were used as purchased. NMR spectra were recorded on a Varian VXR-300 spectrometer. IR spectra were recorded from Nujol mulls between KBr disks on a Mattson-4020 Galaxy FT-IR spectrometer. Elemental analyses were performed at the Microanalytical Department of the University of Groningen. The found values are the average of at least two independent determinations.

Preparation of 1,1'-Ferrocenediacyl Azide.⁸ At room temperature, oxalyl chloride (10.5 mL, 0.120 mol) and 5 drops of pyridine were added to a suspension of 1,1'-ferrocenedicarboxylic acid (6.84 g, 25 mmol) in 100 mL of dichloromethane. After stirring for 4 h, the mixture was heated to reflux overnight. Removal of the volatiles (solvent and excess oxalyl chloride) gave a solid residue that was dissolved in acetone

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(75 mL). A solution of sodium azide (4.0 g, 61 mmol) in 7 mL of water was added in one portion, giving a slightly exothermic reaction. After 25 min the mixture was poured into 700 mL of water, precipitating a red-brown solid. This was collected, rinsed with aqueous NaHCO₃ solution and with water, and dried to give 7.89 g (24.2 mmol, 97%) of the title compound (mp 117.5 °C, with decomposition). IR (Nujol mull): ν 2150 (N₃), 1689 and 1680 (C=O) cm⁻¹.

Preparation of 1,1'-Diisocyanatofercene.⁸ A solution of 1,1'-ferrocenediacyl azide (7.92 g, 24.4 mmol) in 100 mL of dry toluene was heated at 110 °C for 30 min, during which N₂ is evolved. The toluene was removed by distillation, and the residue was extracted with three portions of hexane (125 mL total). The combined extracts were filtered through Celite and cooled to -40 °C, yielding 5.27 g (19.5 mmol, 80%) of the title compound as golden yellow crystals (mp 79–91 °C). IR (Nujol mull): ν 2270 (N=C=O) cm⁻¹.

Preparation of 1,1'-Diisocyanatofercene. At room temperature, formic acid (0.385 mL, 10 mmol) was added to a stirred solution of 1,1'-diisocyanatofercene (1.34 g, 5.0 mmol) in 10 mL of toluene. A precipitate formed in the reaction mixture. After 15 min the temperature was raised to 110 °C (CO₂ evolution was observed from around 80 °C), and the mixture was kept at this temperature for 30 min. To precipitate the product, 20 mL of petroleum ether (bp 40–60 °C) was added. The solvent was decanted, and the sticky yellow solid residue was rinsed with petroleum ether (bp 40–60 °C, 2 × 10 mL) to give crude 1,1'-diformamidofercene. After addition of 50 mL of THF to this product, diisopropylamine (4.2 mL, 30 mmol) was added at 0 °C. After cooling to -20 °C POCl₃ (1.05 mL, 11 mmol) was slowly added and the mixture was stirred for 2 h at -10 to 0 °C. The mixture was poured into 400 mL of ice water, and the solid was collected, rinsed with water, and dried in vacuo over CaCl₂ to give 1.09 g of a brown powder. Column chromatography (Al₂O₃, activity II–III, ϕ = 3.5 cm, length = 4 cm, CH₂Cl₂ solvent) yielded 0.58 g (2.46 mmol, 50%) of yellow 1,1'-diisocyanatofercene as the first fraction. Analytically pure material was obtained from one crystallization from CH₂Cl₂ under N₂ atmosphere. Mp: 150

°C (with decomposition). IR (Nujol mull): ν 2118 cm⁻¹ (NC). ¹H NMR (300 MHz, 25 °C, CDCl₃): δ 4.27 (t, *J* = 2.0, CH), 4.64 (t, *J* = 2.0, CH). ¹³C(APT) NMR (75 MHz, 25 °C, CDCl₃): δ 162.3 (NC), 66.9 (Cp CH), 66.1 (Cp CH), Cp C not observed. Anal. Calcd for C₁₂H₈N₂Fe: C, 61.06; H, 3.42; N, 11.87; Fe, 23.66. Found: C, 61.02; H, 3.44; N, 11.73; Fe, 23.53.

Preparation of Ferrocenylamine. Under a nitrogen atmosphere, a suspension of ferrocene (17.6 g, 94 mmol) in 80 mL of THF was cooled to 0 °C, and 53.3 mL of a 1.5 M *t*-BuLi solution in pentane (80 mmol) was added. The mixture was allowed to warm to ambient temperature and stirred for 15 min. The mixture was then cooled to -70 °C, and α -azidostyrene (12 g, 83 mmol) was added. The dark mixture was allowed to warm to -10 °C, and 100 mL of a solution of 3 N hydrochloric acid was added slowly, during which nitrogen is evolved. In 30 min the mixture was allowed to warm to ambient temperature and then poured into 50 mL of water. This mixture was washed with ether (portions of 100, 50, and 50 mL). The water layer was cooled to 0 °C, and a solution of NaOH (16 g) in 50 mL of water was slowly added. After 10 min the precipitated solid was collected, rinsed with water, and dried to give 7.97 g (39.5 mmol, 50% calculated on *t*-BuLi) of crude ferrocenylamine with spectroscopic characteristics identical to those reported.^{5a} A portion of 2.50 g of this material was sublimed at 120 °C and 0.06 mmHg. The dark red sublimate (1.81 g, 72%) was collected and stored under nitrogen atmosphere. Mp: 155 °C (with decomposition). Anal. Calcd for C₁₀H₁₁NFe: C, 59.74; H, 5.51; N, 6.97; Fe, 27.78. Found: C, 60.55; H, 5.53; N, 7.02; Fe, 27.30.

Note Added in Proof. During the processing of this paper a report appeared describing an improved synthesis procedure for 1,1'-diaminofercene, making this compound available in multigram quantities.¹⁵

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