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An investigation of the chemistry of ferrocenoyl derivatives. The synthesis and reactions of ferrocenoyl imidazolide and its derivatives

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Abstract

Ferrocenoyl imidazolide is synthesized readily from ferrocenecarboxylic acid in one step. It is a red crystalline compound that is stable at < 5 °C in the dark and it acts as an efficient ferrocenoyl equivalent. It reacts rapidly with alkoxides to give esters and with thiolates to give thioesters. Its reaction with Lawesson's reagent gave diferrocenoyl disulfide. Attempts to make diferrocenoyl peroxide by reacting ferrocenoyl imidazolide with hydrogen peroxide were unsuccessful. Ferrocenoyl imidazolide is converted into triferrocenylmethanol and diferrocenyl ketone in one step by reacting it with ferrocenyl-lithium. The X-ray crystal structures of ferrocenoyl phenyl sulfide and diferrocenoyl disulfide are described.

Keywords: Ferrocenoyl imidazolide; Ferrocenoyl equivalent; Triferrocenyl derivatives

1. Introduction

The discovery of ferrocene in 1951 heralded a new era in the realm of organometallic chemistry [1]. The discovery is not unlike some of the other ground breaking discoveries in chemistry because it provided a new direction in the subject. The events leading up to and shortly after the discovery of ferrocene make for interesting reading [2].

Amongst the first well documented reactions of ferrocene were the Friedel–Crafts acylation [3], the arylation using aryldiazonium salts [4] and metallation using *n*-butyl lithium [5]. In more recent times, there has been a renaissance in the chemistry of ferrocenes, particularly in the area of catalysis, organic synthesis and new materials [6].

The ferrocenoyl unit (**1**) has been incorporated in many ferrocenes synthesized recently for potential industrial application. Three examples are shown in Fig. 1. Compound **2** is a liquid crystal [7] whereas **3** and **4** are potential medicinal agents [8,9]. Two compounds of general structure **2** ($R = C_8H_{17}$ and $C_{10}H_{21}$) are historically important ferrocene derivatives since they represent the first examples of ferrocenyl-containing thermotropic liquid crystals (ferrocenomesogens) [7a]. They exhibit stable nematic liquid crystal phases. Compound **3** also holds a position of some importance in the applied chemistry of ferrocene materials since it is one of the few sandwich compounds to be used in a pharmaceutical treatment. It was patented in the USSR and marketed under the name of ferrocerone and has been used in the treatment of various conditions including iron deficiency anaemia, severe infection of the nasopharynx and others [8]. Finally, compound **4** is a ferrocenyl–penicillin molecule and this molecule displays antibacterial activity [9]. The ferrocenoyl unit has been established firmly in new molecules for use as novel electrochemical sensors [10] and Beer and coworkers have utilized ferrocenoyl derivatives for anion recognition [11].

The two common methods of introducing the ferrocenoyl unit into a molecule are either Friedel–Crafts acylation of ferrocene with acid halides and aluminium trichloride [3] or the reaction of ferrocenoyl chloride with nucleophilic reagents [12].

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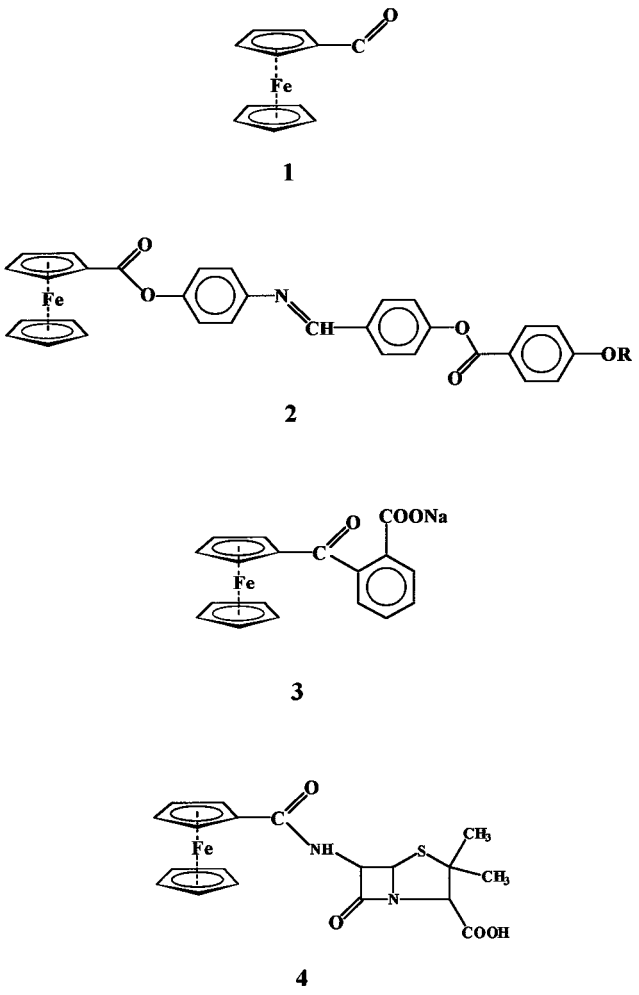


Fig. 1. The ferrocenoyl group and ferrocenoyl derivatives for applied chemistry.

The Friedel–Crafts acylation was one of the first well documented reactions in ferrocene chemistry and also one of the first to implicate the aromatic behaviour of the ferrocene molecule. The use of ferrocenoyl halides especially ferrocenoyl chloride as a ferrocenoyl equivalent has been widespread but it presents some major drawbacks. Firstly, ferrocenoyl chloride is moisture sensitive and should be used immediately after preparation; it also exhibits thermal and photochemical instability and is similar in behaviour to other ferrocenes carrying electron-withdrawing groups adjacent to the ferrocenyl group [13].

The preparation of ferrocenoyl chloride has been reported on a number of occasions using different reagents and reaction conditions [14]. A perhaps more useful ferrocenoyl equivalent is ferrocenoyl fluoride. Its synthesis and use have been described recently by Galow et al. [15]. It was synthesized by the reaction of ferrocenecarboxylic acid with cyanuric fluoride and pyridine. The compound is a stable orange solid at room temperature and provides exceptionally high yields of esters and amides in its reactions with alcohols and amines, respectively.

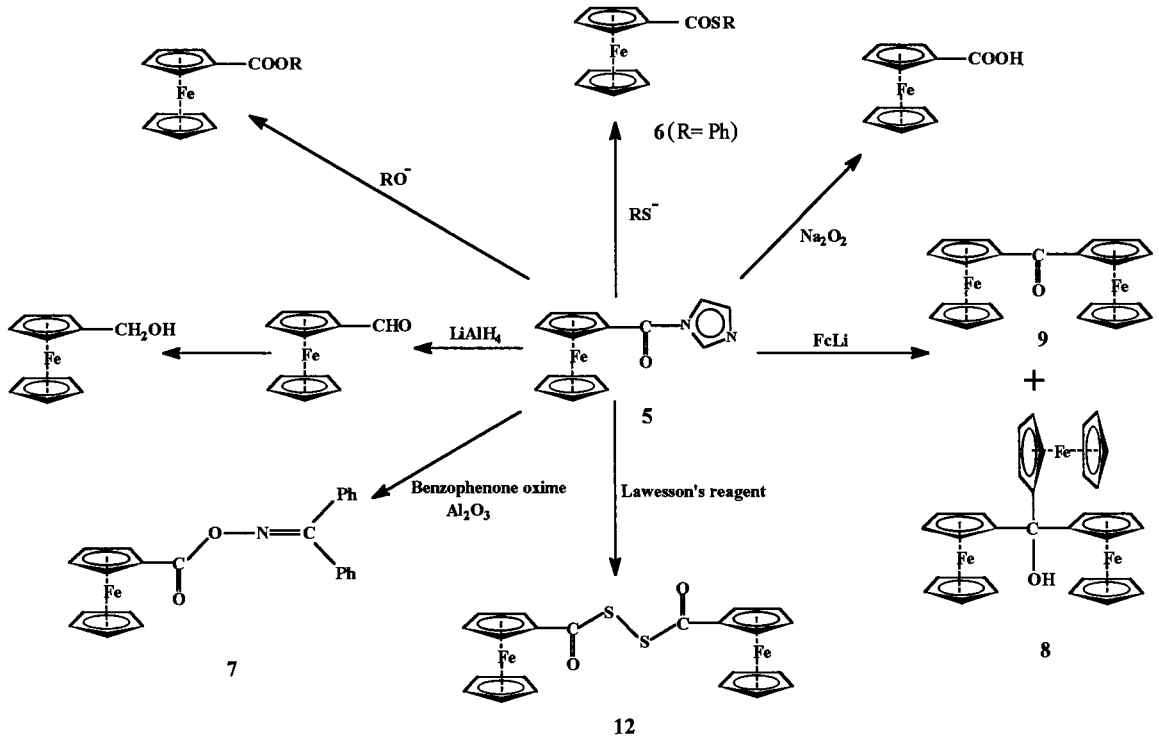
In 1962, Staab described the use of heterocyclic amides, commonly known as azolides, in organic synthesis [16]. The azolides were shown to be highly reactive in nucleophilic reactions and were used for the synthesis of a wide range of functionalities including esters, amides, peptides, hydrazides and hydroxamic acids. A recent monograph appeared on this subject providing an excellent overview of azolide chemistry [17]. The work herein describes the use of a ferrocenyl-containing azolide, ferrocenoyl imidazolide (**5**), in the synthesis of ferrocenoyl derivatives. Ferrocenoyl imidazolide is easy to store and handle and provides useful yields of ferrocenoyl derivatives at room temperature.

2. Results and discussion

2.1. Reactions of ferrocenoyl imidazolide

Ferrocenoyl imidazolide (**5**) was prepared in one step from the reaction of ferrocenecarboxylic acid with *N*,*N*-dicarbonyldiimidazole in anhydrous THF. The reaction to give **5** was reproducible and consistently provided the imidazolide in yields greater than 60%. The imidazolide **5** was isolated easily as an air-stable red solid and was stored in a vacuum desiccator below 5 °C. Purification of **5** was achieved either by cold recrystallization or by using flash chromatography on silica gel. A summary of the reactions of **5** is shown in Scheme 1. Reaction of **5** with alcohols such as methanol and ethanol at room temperature led to a slow alcoholysis reaction to give the corresponding esters. Reaction of **5** with sodium alkoxides generated by the reaction of alcohols with sodium was spontaneous providing good yields of esters. Similar behaviour of **5** was observed in its reactions with thiolate ions. For example, a reaction between sodium thiophenolate and **5** provided an excellent yield of ferrocenoyl phenyl sulfide **6**. The X-ray crystal structure determination of **6** was performed. The molecular structure and numbering scheme for **6** are shown in Fig. 2. Selected bond distances and bond angles are provided in Table 1.

A ferrocenoyl derivative of interest to us a number of years ago for the generation of ferrocenoyloxyl radicals ($FcCOO^{\bullet}$) was benzophenone *O*-ferrocenylcarbonyloxime (**7**) [18]. During that study on the generation of ferrocenoyloxyl radicals, **7** was prepared by the reaction of benzophenone oxime and ferrocenoyl chloride. We have also prepared it using the DCC/DMAP esterification route from ferrocenecarboxylic acid and benzophenone oxime. In the initial reaction between **5** and benzophenone oxime, the reaction was performed at



Scheme 1. Summary of the reactions of ferrocenoyl imidazolide.

room temperature with equimolar amounts of **5** and benzophenone oxime. These conditions provided unreacted starting material. However, on addition of aluminium oxide to the same reaction, a modest yield of **7** was obtained. Photolysis of **7** in benzene provided ferrocenecarboxylic acid (presumably formed from Fc-COO•) and benzophenone and there was no evidence for the decarboxylation product, ferrocene.

The chemistry of triferrocenylmethyl-derivatives has, so far, been investigated little and this is most likely because of difficulties encountered in the synthesis of the triferrocenylmethyl unit. Triferrocenylmethanol (**8**) has been synthesized by Pauson and Watts [19] from the reaction of diferrocenyl ketone (**9**) and ferrocenyl–lithium. The stumbling block in this sequence is actually the availability of diferrocenyl ketone rather than its conversion to the triferrocenylmethanol. Diferrocenyl ketone has been synthesized previously by a number of methods. It has been prepared by Friedel–Crafts acylations [20], oxidation of diferrocenylcarbinol [21], by the reaction of bromoferrocene, *n*-butyllithium and *N*,*N*-dimethyl carbamylchloride [22] and perhaps the most cheap, convenient and efficient method by the reaction of ferrocene, triphosgene and aluminium trichloride [14f].

The reaction of **5** with ferrocenyl–lithium gave rise to the formation of a mixture of triferrocenylmethanol and diferrocenylketone in one step and this reaction presumably proceeds through the intermediacy of diferrocenyl ketone. The yields of **8** and **9** were very low and further studies are required in order to optimize these.

Another compound that was of interest to us in terms of the free radical chemistry of ferrocenes was diferrocenoyl peroxide (**10**). This should act as a source of ferrocenoyloxyl free radicals by either thermal or photodecomposition. Previous attempts by Lau and Hart [23] to synthesize **10** from ferrocenoyl chloride and sodium peroxide were unsuccessful. Staab has reported previously on the synthesis of diaroyl peroxides from imidazolides and hydrogen peroxide. However, the reaction of **5** with hydrogen peroxide (30%) gave a complex mixture of organic and inorganic products. Assuming **10** had formed, it is unlikely to withstand the oxidizing conditions. A further problem envisaged with **10** is that of autodecomposition. Peroxide decomposition is catalyzed by metal salts such as iron(II) and so the ferrocenyl group could interact with the peroxide linkage. The reaction of **5** with sodium peroxide in anhydrous ether gave a quantitative yield of sodium

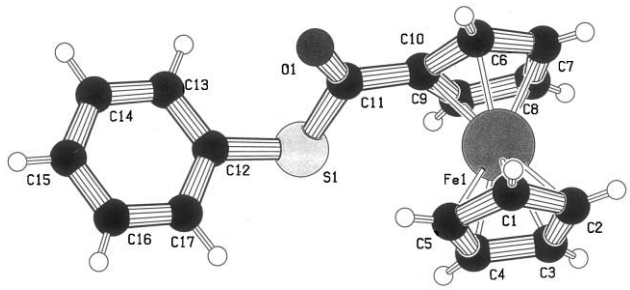


Fig. 2. Molecular structure of ferrocenoyl phenyl sulfide **6** with numbering scheme

Table 1
Bond lengths (Å) and selected bond angles (°) for **6**

Bond lengths			
Fe (1)–C(1)	2.028(5)	C(2)–C(3)	1.384(6)
Fe(1)–C(4)	2.029(4)	C(3)–C(4)	1.395(6)
Fe(1)–C(10)	2.030(4)	C(4)–C(5)	1.387(6)
Fe(1)–C(5)	2.031(4)	C(6)–C(7)	1.403(6)
Fe(1)–C(6)	2.036(4)	C(6)–C(10)	1.429(5)
Fe(1)–C(2)	2.038(5)	C(7)–C(8)	1.404(6)
Fe(1)–C(9)	2.041(4)	C(8)–C(9)	1.410(6)
Fe(1)–C(3)	2.044(4)	C(9)–C(10)	1.440(5)
Fe(1)–C(7)	2.053(4)	C(10)–C(11)	1.464(6)
Fe(1)–C(8)	2.057(4)	C(12)–C(13)	1.381(6)
S(1)–C(12)	1.771(4)	C(12)–C(17)	1.388(6)
S(1)–C(11)	1.788(4)	C(13)–C(14)	1.382(7)
O(1)–C(11)	1.206(4)	C(14)–C(15)	1.374(7)
C(1)–C(2)	1.396(7)	C(15)–C(16)	1.361(7)
C(1)–C(5)	1.402(7)	C(16)–C(17)	1.378(7)
Bond angles			
C(12)–S(1)–C(11)	103.59(19)	C(10)–C(11)–S(1)	112.5(3)
O(1)–C(11)–C(10)	124.2(4)	C(13)–C(12)–S(1)	122.7(3)
O(1)–C(11)–S(1)	123.3(3)	C(17)–C(12)–S(1)	117.7(3)

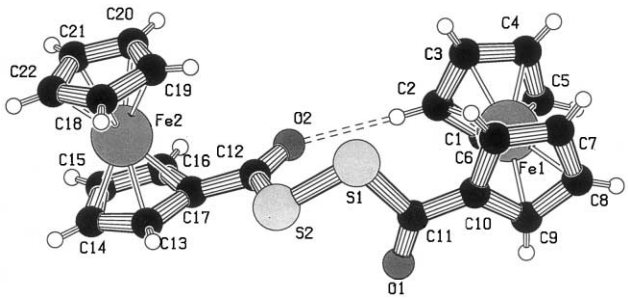
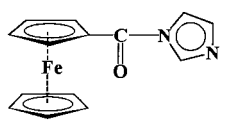


Fig. 3. Molecular structure of diferrocenoyl disulfide **12** with numbering scheme

ferrocenoate and ferrocenecarboxylic acid was recovered from this after acidification.



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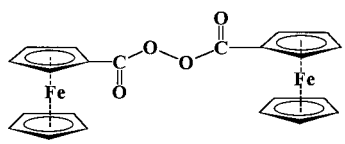

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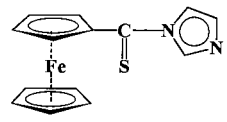

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Despite the widespread use of the thiocarbonyl functional group in organic chemistry especially in free radical chemistry, only a few ferrocenyl thiocarbonyl derivatives have been reported [24]. An attempt was therefore made to convert **5** into the thiocarbonylimidazole derivative (**11**) since such a compound should act as a precursor to a whole new range of ferrocenylthiocarbonyl compounds by nucleophilic displacement of the imidazole group. On adding Lawesson's reagent (a proven reagent for the conversion of carbonyl groups to thiocarbonyl groups) to a solution of **5** in anhydrous benzene, there was an almost immediate colour change of the solution from dull red to a bright red. TLC indicated the formation of a new ferrocene compound after only several hours and it was several days before this product intensified on the plate. The product was identified as diferrocenoyl disulfide (**12**), a compound that has been characterized partially before by Katada et al. [14d]. Dibenzoyl disulfide and similar compounds are reasonably well documented in the patent literature and have been used in rubber technology. They were made by reacting acid chlorides with sodium sulfide. However, the organic chemistry of the diacyl disulfide functional group is not extensive and further investigations of the new ferrocene compound may prove interesting.

The X-ray crystal structure determination of **12** was performed. The molecular structure and numbering scheme for **12** is shown in Fig. 3 and a packing diagram in Fig. 4. Selected bond distances and bond angles are provided in Table 2.

The reduction of **5** with lithium aluminium hydride provided an efficient method of reducing ferrocenecarboxylic acid to either ferrocenecarboxaldehyde or to ferrocenemethanol depending on the concentration of the reducing agent.

*2.2. Structural studies of the ferrocenoyl derivatives **6** and **12***

There is considerable interest in the role of hydrogen bonding and non-covalent interactions in designing supramolecular architectures [25]. This interest extends to hydrogen bonding effects in ferrocenes [26]. For this reason, the X-ray crystal structure of **12** will be discussed first since it exhibits some very interesting hydrogen bonding interactions. The unit cell of **12** is orthorhombic and the bond lengths fall within the expected limits (Table 2). The bond distance between S(1) and S(2) [2.022(2) Å] is close to that found in related compounds. For example, the S–S bond distance in dibenzoyl disulfide is 2.021(2) Å [27] and in bis(morpholinothiocarbonyl)disulfide is 2.009(5) Å [28]. The S–C bond distances in **12** [1.815(6) and 1.817(6) Å] are also similar to those in dibenzoyl disulfide [1.811(6)

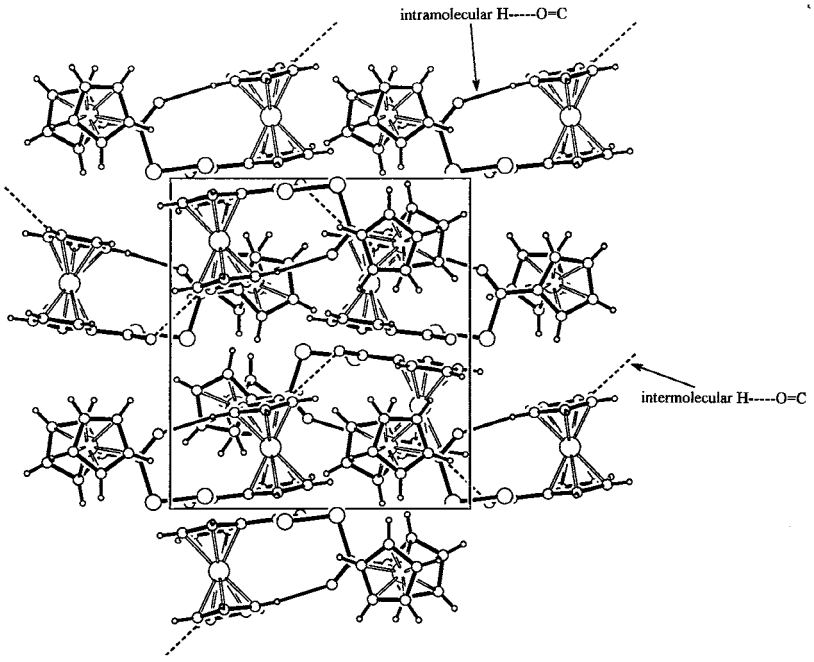

Fig. 4. Packing diagram for **12** with a view along the *c*-axis showing the intramolecular and intermolecular H···O=C interactions.

and 1.827(6) Å]. The two cyclopentadienyl rings in the ferrocenyl groups are more or less eclipsed and this is the normal behaviour of the majority of monosubstituted ferrocenyl derivatives [29]. The most interesting aspect of the crystal structure is highlighted in Fig. 4, which shows a packing diagram with a view down the *c*-axis. Looking down the *c*-axis, it is apparent that the conformation of a single molecule is such that there is a close intramolecular hydrogen bonding interaction between one of the cyclopentadienyl hydrogens and one of the carbonyl groups, for example between O(2) and C(2)–H. The intramolecular bond distance O(2)···H–C(2) is 2.467 Å and this is well within the range for hydrogen bonding. There is also a further hydrogen bonding interaction which is best observed by using the view down the *b*-axis. The second hydrogen bonding interaction is again between a cyclopentadienyl hydrogen atom and a carbonyl oxygen group but on this occasion, it is an intermolecular interaction. In this case, the intermolecular bond distance O···H–C is 2.542 Å. Intermolecular hydrogen bonding between the cyclopentadienyl protons in ferrocenyl molecules and electronegative atoms such as oxygen and nitrogen have been reported previously. For example, they are observed in the crystal structure of 4′-formyl-4-biphenylferrocene between the cyclopentadienyl hydrogen atoms and the aldehydic carbonyl group [30]. A similar interaction has been reported by Sato et al. for ferrocenecarboxaldehyde in an investigation of the plastic crystal phase of that molecule by X-ray diffraction [31]. Intramolecular hydrogen bonding interactions have also been observed for ferrocenyl derivatives. For example, when benzoylferrocene oxime is prepared by the reaction of benzoylferrocene and hydroxylamine hydrochloride, the red crystalline solid consists of a mixture of *syn*- and *anti*-isomers [32]. In the crystal, the molecules occur as a random distribution of *syn–syn* or *anti–anti* hydrogen bonded dimers. In the *syn*-isomer, there is evidence for an intramolecular hydrogen bonding interaction between the OH group and one of the cyclopentadienyl hydrogen atoms. The issue of whether a C–H group can form a hydrogen bond with an electronegative atom such as oxygen has been a controversial one [33] but was apparently settled by a landmark study that provided good evidence for the existence of C–

Table 2
Selected bond lengths (Å) and bond angles (°) for **12**

Bond lengths			
Fe(1)–C(10)	2.005(6)	Fe(1)–C(2)	2.043(8)
Fe(1)–C(1)	2.026(8)	Fe(1)–C(7)	2.051(7)
Fe(1)–C(9)	2.024(7)	C(1)–C(5)	1.412(10)
Fe(1)–C(6)	2.028(7)	C(1)–C(2)	1.409(10)
Fe(1)–C(3)	2.027(7)	S(1)–S(2)	2.022(2)
Fe(1)–C(4)	2.033(8)	0(1)–C(11)	1.193(6)
Fe(1)–C(5)	2.038(7)	S(2)–C(12)	1.817(6)
Fe(1)–C(8)	2.052(7)	O(2)–C(12)	1.204(7)
Bond angles			
C(11)–S(1)–S(2)	102.7(2)	O(1)–C(11)–C(10)	125.2(6)
C(5)–C(1)–C(2)	107.3(8)	O(1)–C(11)–S(1)	123.0(5)
C(12)–S(2)–S(1)	100.6(2)	C(10)–C(11)–S(1)	111.9(5)
C(3)–C(2)–C(1)	107.1(8)	O(2)–C(12)–C(17)	124.3(6)
C(9)–C(10)–C(11)	124.7(6)	O(2)–C(12)–S(2)	123.0(5)
C(6)–C(10)–C(11)	128.1(6)	C(17)–C(12)–S(2)	112.7(5)
C(13)–C(17)–C(12)	128.1(6)	C(16)–C(17)–C(12)	124.1(6)

H···O hydrogen bonding in crystals [34]. However, disagreement still continues as to whether a C–H···O interaction is a hydrogen bond or a van der Waals interaction [35].

The unit cell of compound **6** is monoclinic. The bond lengths for **6** fall within the expected limits (Table 1). The bond distances between S(1) and C(11) [1.788(4) Å] and S(1) and C(12) [1.771(4) Å] are similar to that found in a related compound, *S*-(2-nitrophenyl)-benzenecarbothiolate [1.788(12) and 1.767(5) Å] [36]. The two cyclopentadienyl rings in the ferrocenyl group are more or less eclipsed again. There are no significant short intermolecular bonding contacts between molecules.

3. Experimental

3.1. Purification and characterization of the materials

Reactions were carried out under nitrogen or argon. Silica gel or neutral aluminium oxide was used for column chromatography. Infrared spectra were recorded using a Perkin–Elmer 1600 series FT-IR spectrometer as KBr discs or in solution using chloroform. NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 200 MHz for ^{1}H-NMR or 50.1 MHz for ^{13}C-NMR as solutions in $CDCl_3$ unless otherwise stated. Melting points were determined using a Reichert hot stage microscope or using an Electrothermal IA 900 series digital melting point apparatus and are uncorrected. Mass spectra were recorded on either an AEI MS 902/MSS update (70 eV, direct insertion probe) or a VG70-SEQ/MSSMS2 spectrometer at the Cape Technikon. Microanalyses were performed using a Carlo-Erba MOD 1160 elemental analyser by the Council for Scientific and Industrial Research (CSIR), Pretoria. Crystal X-ray crystallography was performed on a Bruker/AXS SMART-CCD diffractometer at the Centre for Molecular Design, University of the Witwatersrand. Ferrocenecarboxylic acid and *N*,*N*-carbonyldiimidazole were purchased from the Aldrich Chemical company (USA) and were used without further purification.

3.2. Synthesis

3.2.1. Preparation of ferrocenoyl imidazolide (**5**)

A solution of ferrocenecarboxylic acid (0.5 g, 2.2 mmol) in anhydrous THF (40 cm^3) was added to a solution of *N*,*N*-carbonyldiimidazole (0.36 g, 2.2 mmol) in THF (10 cm^3). The mixture was stirred for 1 h at room temperature (r.t.) after which it was poured onto ice. Ether (50 cm^3) was added and the solution was washed with sodium hydrogen carbonate solution, water and was finally dried over anhydrous sodium sulphate. Evaporation of the solvent in vacuo afforded a dark red solid, identified as ferrocenoyl imidazolide (0.39 g, 63%), m.p. 121–122 °C; ν_{max} (KBr)/cm^{-1} 1670, 1430, 1370, 1300, 1000, 830; δ_H ($CDCl_3$) 7.15–8.45 (3H, m, imidazole), 4.90 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.50 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.28 (5H, s, C_5H_5); δ_c ($CDCl_3$)/ppm: 139.2, 132.2, 119.6, 74.9, 73.7, 72.7, 71.9; *m*/*z* 281 (18%), 280 ([M$^+$], 100%), 230 (18%), 213 (60%), 185 (57%), 138 (16%), 129 (31%), 121 (25%). Anal. Found: C, 59.7; H, 4.3; [M$^+$], 280.0287. Calc. for $C_{14}H_{12}FeN_2O$: C, 60.0; H, 4.3%; [M$^+$], 280.0295.

This reaction was repeated several times and proved to be reproducible. The product was purified by either cold recrystallization or was passed through a silica gel column. The compound was eluted successfully using diethyl ether under nitrogen without undue hydrolysis back to ferrocenecarboxylic acid.

3.2.2. Reaction of ferrocenoyl imidazolide with sodium methoxide

A solution of sodium methoxide was made up by dissolving sodium metal (0.5 g, 22 mmol) in methanol (5 cm^3). This solution was added to a solution of ferrocenoyl imidazolide (101 mg, 0.36 mmol) in methanol (10 cm^3). The colour of the reaction solution changed from red to yellow immediately. After 3 h, diethyl ether (50 cm^3) was added, the solution was filtered, washed with water, and dried over anhydrous sodium sulphate. After removing the solvent, the residue was passed through a short column of silica gel. A yellow band was removed with dichloromethane:petroleum ether (1:1). Removal of the solvent left yellow crystals of methyl ferrocenoate (55 mg, 63%), m.p. 64–66 °C, lit. [21], 70 °C; ν_{max} (KBr)/cm^{-1} 2956, 1712, 1460, 1284, 1142, 1030, 824; δ_H ($CDCl_3$) 4.80 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.39 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.20 (5H, s, C_5H_5), 3.82 (3H, s, CH_3); *m*/*z* 244 ([M$^+$], 100%), 213 (6%), 186 (2%), 185 (2%). Anal. Found: [M$^+$], 244.0181. Calc. for $C_{12}H_{12}O_2Fe$: [M$^+$], 244.0185.

3.2.3. Reaction of ferrocenoyl imidazolide with sodium ethoxide

The experimental procedure is similar to that described in Section 3.2.2 except that ethanol (5 cm^3) was used instead of methanol. The product was ethyl ferrocenoate (45 mg, 48%), m.p. 62–63 °C, lit. [23], 59–60 °C; ν_{max} (KBr)/cm^{-1} 2962, 1696, 1458, 1377, 1276, 1134, 1033, 826; δ_H ($CDCl_3$) 4.82 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.40 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.28 (2H, q, CH_2), 4.21 (5H, s, C_5H_5), 1.36 (3H, t, CH_3); δ_c ($CDCl_3$) 223.9, 73.2 (Fc), 72.1 (Fc), 71.7 (Fc), 62.1 (CH_2), 16.7; *m*/*z* 259 (18%), 258 ([M$^+$], 97%), 231 (16%), 230 (100%), 213 (20%), 186 (10%), 185 (15%), 149 (62%), 138 (43%), 136 (20%), 129 (29%), 121 (36%). Anal. Found: [M$^+$], 258.0328. Calc. for: $C_{13}H_{14}FeO_2$: [M$^+$], 258.0339.

3.2.4. Reaction of ferrocenoyl imidazolide with sodium propoxide

The experimental procedure is similar to that described in Section 3.2.2 except that propan-1-ol (5 cm^3) was used instead of methanol. The product was propyl ferrocenoate (58 mg, 59%); δ_H ($CDCl_3$) 4.82 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.40 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.21 (5H, s, C_5H_5), 4.18 (2H, t, CH_2), 1.75 (2H, m, CH_2), 1.04 (3H, t, CH_3); m/z 273 (21%), 272 ([M^+], 100%), 213 (9%). Anal. Found: [M^+], 272.0481. Calc. for $C_{14}H_{16}O_2Fe$: [M^+], 272.0499.

3.2.5. Reaction of ferrocenoyl imidazolide with sodium phenolate

A solution of sodium phenolate was prepared by treating phenol (38 mg, 0.40 mmol) with sodium hydride (12 mg, 0.50 mmol) in anhydrous dimethylformamide. This solution was added to a solution of ferrocenoyl imidazolide (101 mg, 0.36 mmol) in anhydrous DMF (5 cm^3). The reaction was stirred for 5 min at r.t. and was then poured into water. The aqueous solution was extracted with diethyl ether (3×50 cm^3), and the extracts were combined and dried over anhydrous sodium sulphate. The product was ferrocenyl benzoate (32 mg, 29%), m.p. 123 °C, lit. [37], 124–124.5 °C; ν_{max} (KBr)/cm^{-1} 1700, 1637, 1618, 1457, 1374, 1273, 1126, 1020, 830; δ_H ($CDCl_3$) 7.17–7.49 (5H, m, Ar), 4.98 (2H, t, $J = 2.1$ Hz, C_5H_4), 4.51 (2H, t, $J = 2.1$ Hz, C_5H_4), 4.32 (5H, s, C_5H_5); m/z 307 (21%), 306 ([M^+], 100%), 214 (51%), 213 (100%), 186 (19%), 185 (51%) 149 (10%), 129 (32%), 121 (29%). Anal. Found: [M^+], 306.0332. Calc. for $C_{17}H_{14}FeO_2$: [M^+], 306.0339.

3.2.6. Reaction of ferrocenoyl imidazolide with benzophenone oxime

Ferrocenoyl imidazolide (100 mg, 0.36 mmol) and benzophenone oxime (71 mg, 0.36 mmol) were added to anhydrous dichloromethane (40 cm^3). To this solution neutral aluminium oxide was added and the solution was stirred at r.t. for 12 h. The solution was then filtered and the solvent was removed in vacuo to leave an orange solid. This was passed through a column of neutral aluminium oxide and the yellow band removed from the column using dichloromethane gave the product, benzophenone *O*-ferrocenylcarbonyloxime (**7**) (50 mg, 34%), m.p. 130–131 °C; ν_{max} (KBr)/cm^{-1} 1730, 1440, 1370, 1320, 1255, 1090, 1020, 910; δ_H ($CDCl_3$) 7.40–7.70 (10H, m, Ar), 4.60 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.36 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.10 (5H, s, C_5H_5); δ_c ($CDCl_3$) 132.8, 131.5, 131.0, 130.7, 130.4, 130.2, 73.6 (Fc), 72.1 (Fc), 71.9 (Fc); m/z 409 ([M^+], 100%), 344 (88%), 300 (61%), 182 (68%). Anal. Found: C, 70.7; H, 5.0; [M^+], 409.080. Calc. for $C_{24}H_{19}FeNO_2$: C, 70.4; H, 4.7%; [M^+], 409.267.

3.2.7. Reaction of ferrocenoyl imidazolide with sodium thiophenolate

Thiophenol (4 cm^3) and sodium were stirred in a round-bottomed flask for 30 min. The resulting solution containing sodium thiophenolate was added to a solution of ferrocenoyl imidazolide (114 mg, 0.41 mmol) in methanol (5 cm^3). After leaving overnight at r.t., the solution was added to diethyl ether (50 cm^3), washed with dilute sodium hydroxide solution, water and finally dried over anhydrous sodium sulphate. After removal of the solvent, the residue was passed through a short column of silica gel using petroleum ether:dichloromethane (2:3) to elute an orange band. Removal of the solvent left an orange solid, identified as ferrocenoyl phenyl sulfide (75 mg, 64%), m.p. 108–109 °C; ν_{max} (KBr)/cm^{-1} 2950, 1664, 1614, 1438, 1239, 1044, 807; δ_H ($CDCl_3$) 7.46 (5H, m, Ar), 4.94 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.54 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.29 (5H, s, C_5H_5); δ_c ($CDCl_3$) 192.08, 135.43, 129.59, 129.52, 128.28, 79.21, 72.45, 71.12, 69.59; m/z 323 (17%), 322 ([M^+], 75%), 230 (49%), 214 (15%), 213 (100%), 186 (7%), 185 (47%), 129 (36%), 121 (23%). Anal. Found: C, 63.4; H, 4.3%; [M^+], 322.0117. Calc. for $C_{17}H_{14}FeOS$: C, 63.4; H, 4.4%; [M^+], 322.0111.

The reaction above was repeated on a larger scale using ferrocenoyl imidazolide (500 mg, 1.8 mmol), thiophenol (5 cm^3) and sodium (1 g, 43.5 mmol) to give the product ferrocenoyl phenyl sulfide (490 mg, 84%).

3.2.8. Reaction of ferrocenoyl imidazolide with lithium aluminium hydride

Ferrocenoyl imidazolide (200 mg, 0.71 mmol) was added to a solution of diethyl ether (50 cm^3) containing lithium aluminium hydride (20 mg, 0.53 mmol). The solution was stirred for 15 min at r.t. after which it was added to cold water containing ethyl acetate. The solution was extracted with diethyl ether (3×50 cm^3) and the combined ether extracts were dried over anhydrous sodium sulphate. The oil remaining after removal of the solvent was passed through a short column of aluminium oxide. A red band was removed from the column with petroleum ether (40–60 °C):diethyl ether (10:1) that on removing the solvent left a red solid, identified as ferrocenecarboxaldehyde (80 mg, 52%), m.p. 118 °C, lit. [38], 124–125 °C; ν_{max} (KBr) 1650, 1440, 1405, 1240, 1020, 1000, 810; δ_H 9.96 (1H, s, CHO), 4.80 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.61 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.28 (5H, s, C_5H_5); m/z 215 (14%), 214 (100%), 186 (66%), 184 (10%). Anal. Found: [M^+], 214.0073. Calc. for $C_{11}H_{10}FeO$: [M^+], 214.0080.

3.2.9. Reaction of ferrocenoyl imidazolide with an excess of lithium aluminium hydride

Ferrocenoyl imidazolide (200 mg, 0.71 mmol) was added to a solution of diethyl ether (50 cm^3) containing lithium aluminium hydride (100 mg, 2.6 mmol). The

solution was stirred for 3 h at r.t. after which it was added to cold water containing ethyl acetate. The solution was extracted with diethyl ether (3×50 cm^3) and the combined ether extracts were dried over anhydrous sodium sulphate. The yellow oil remaining on removing the solvent was passed through a short column of silica gel. A yellow band was removed from the column with diethyl ether that on removing the solvent left a yellow solid, identified as hydroxymethylferrocene (136 mg, 89%), m.p. 80–82 °C, lit. [39], 82 °C; δ_H ($CDCl_3$) 4.31 (2H, s, CH_2), 4.22 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.16 (5H, s, C_5H_5), 4.15 (2H, t, $J = 1.8$ Hz, C_5H_4), 2.04 (1H, s, OH); m/z 217 (13%), 216 ([M$^+$], 100%), 200 (8%), 186 (8%). Anal. Found: [M$^+$], 216.0229. Calc. for $C_{11}H_{12}OFe$: [M$^+$], 216.0237.

3.2.10. Reaction of ferrocenoyl imidazolide with ferrocenyl-lithium

n-Butyl-lithium (5 cm^3 of a 1.6 M solution) was added over a period of 10 min to a solution of ferrocene (1.0 g, 5.4 mmol) in anhydrous diethyl ether:THF (50 cm^3) (1:1). The solution was stirred at 0 °C for 5 h. A solution of ferrocenoyl imidazolide (200 mg, 0.7 mmol) in dry THF (10 cm^3) was added dropwise and the solution immediately took on a darker colour. After stirring overnight at r.t., the solution was added to cold water after which the layers were separated. The organic layer was washed with water several times and then dried over anhydrous sodium sulphate. Removal of the solvent left an orange oil that was placed on a column of neutral aluminium oxide. Elution with petroleum ether (40–60 °C) gave unreacted ferrocene (0.6 g, 60%); a second yellow band was eluted using petroleum ether:diethyl ether (9:1) followed finally by a red band removed using petroleum ether:diethyl ether (1:1). The second yellow band gave after evaporation of solvent a yellow solid identified as triferrocenylmethanol (**8**) (35 mg, 9%), m.p. 165–166 °C dec., lit. [21], 160–162 °C; ν_{max} (KBr) 3571, 3096, 2929, 2856, 1790–1570 (br), 1468, 1411, 1388, 1316, 1234, 1110, 1074, 1051, 1017, 1000, 823, 738, 647, 575, 478; δ_H ($CDCl_3$) 4.07 (15H, s, $3 \times C_5H_5$), 4.06 (6H, t, $J = 1.8$ Hz, $3 \times C_5H_4$), 3.99 (6H, t, $J = 1.8$ Hz, $3 \times C_5H_4$); δ_c ($CDCl_3$) 99.73, 69.21, 67.90, 67.14; m/z 585 (18%), 584 ([M$^+$], 45%), 568 (15%), 567 (5%), 447 (33%), 446 (100%), 444 (17%), 398 (12%), 278 (39%), 323 (22%), 260 (12%), 186 (17%). Anal. Found: [M$^+$], 584.0177. Calc. for $C_{31}H_{28}OFe_3$: [M$^+$], 584.0180. The red band gave diferrocenyl ketone (**9**) (30 mg, 11%); ν_{max} (KBr)/cm^{-1} 3208, 3125, 1610, 1467, 1380, 1295, 1203, 1109, 1056, 1030, 1012, 838, 820, 808, 772, 580, 479; δ_H ($CDCl_3$) 4.93 (4H, t, $J = 1.8$ Hz, C_5H_4), 4.46 (4H, t, $J = 1.8$ Hz, C_5H_4), 4.13 (10H, s, C_5H_5); δ_c ($CDCl_3$) 71.85, 71.01, 70.37; m/z 399 (27%), 398 ([M$^+$], 100%), 214 (10%), 199 (10%), 186 (24%).

3.2.11. Reaction of ferrocenoyl imidazolide with Lawesson's reagent

Ferrocenoyl imidazolide (200 mg, 0.71 mmol) was added to a solution of anhydrous benzene (20 cm^3) to which was added 2,4-bis (4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent) (287 mg, 0.71 mmol). The solution was stirred for ca. 20 days at r.t. until TLC indicated complete consumption of the starting material. The solvent was evaporated and the residue was extracted into ether. The ether extract was washed with water (3×50 cm^3) and was then dried over sodium sulphate. The final residue was passed through a column of aluminium oxide. A red band was removed using petroleum ether (40–60 °C)–dichloromethane which gave after removing the solvent diferrocenoyl disulfide as a red solid (90 mg, 52%), m.p. 182–184 °C dec.; ν_{max} (KBr)/cm^{-1} 1680, 1433, 1237, 1042, 1024, 792; δ_H ($CDCl_3$) 5.00 (4H, t, $J = 1.8$ Hz, $2 \times C_5H_4$), 4.60 (4H, t, $J = 1.8$ Hz, $2 \times C_5H_4$), 4.41 (10H, s, $2 \times C_5H_5$); m/z 492 (2%), 491 (4%), 490 ([M$^+$], 14%), 304 (3%), 288 (5%), 246 (27%), 214 (15%), 213 (100%), 187 (9%), 186 (6%), 185 (32%). Anal. Found: C, 53.6; H, 3.8; [M$^+$], 489.9440. Calc. for $C_{22}H_{18}Fe_2O_2S_2$: C, 53.9; H, 3.7%; [M$^+$], 489.9445.

3.2.12. Reaction of ferrocenoyl imidazolide with sodium peroxide

Ferrocenoyl imidazolide (100 mg, 0.36 mmol) was added to anhydrous diethyl ether (20 cm^3) to which was added sodium peroxide (48 mg, 0.63 mmol). The solution was stirred at room temperature until TLC indicated that all the starting material had reacted. The reaction mixture was then quenched in water and the aqueous solution was acidified with dilute hydrochloric acid. This solution was then extracted with ether and the ether extracts were washed with water and then dried. Removal of the ether left ferrocenecarboxylic acid (45 mg, 54%); ν_{max}/cm^{-1} 3500–2700, 1650, 1465, 1390, 1280, 1150, 1100, 1020, 820; δ_H ($CDCl_3$) 4.80 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.45 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.25 (5H, s, C_5H_5).

3.3. Preparation of benzophenone O-ferrocenylcarbonyloxime

Ferrocenecarboxylic acid (2.17 g, 9.43 mmol) was dissolved in anhydrous dichloromethane to which benzophenone oxime (1.67 g, 8.47 mmol), 4-dimethylaminopyridine (0.42 g, 3.44 mmol) and dicyclohexylcarbodiimide (3.16 g, 15.32 mmol) were added in succession. The solution was allowed to stir at r.t. overnight after which the solution was filtered and then the solvent removed under vacuum. The residue was analysed by TLC using dichloromethane as the

developer and the alumina plate showed two spots, $R_f = 0.01$ and 0.51. The residue was separated using column chromatography and dichloromethane eluted the first fraction. After removing the solvent, an orange solid was obtained, identified as benzophenone *O*-ferrocenylcarbonyloxime (1.07 g, 31%), m.p. 130–131 °C; ν_{max} (KBr)/cm^{-1} 1730, 1440, 1370, 1320, 1255, 1090, 1020, 910; δ_H ($CDCl_3$) 7.70–7.30 (10H, m, Ar), 4.60 (2H, t, $J = 1.8$ Hz, C_5H_4), 4.38 (2H, t, $J = 1.8$ Hz, C_5H_4) 4.11 (5H, s, C_5H_5); m/z 409 ([M$^+$], 100%), 344 (88%), 300 (61%), 182 (68%). Anal. Found: C, 70.7; H, 5.0; [M$^+$], 409.080. Calc. for $C_{24}H_{19}FeNO_2$: C, 70.4; H, 4.7%; [M$^+$], 409.267.

3.4. Crystal structure determination

3.4.1. Crystal data for **6**

$M_r = 322.19$ g mol^{-1}, dark red prism, size $0.36 \times 0.10 \times 0.08$ mm, monoclinic, space group $P2_1/n$, $a = 12.1267(9)$, $b = 10.2687(8)$, $c = 12.5496(9)$ Å, $V = 1434.01(19)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{calc} = 1.492$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.188 mm^{-1}, $F(000) = 664$, 8370 reflections in h (−12/16), k (−9/13), l (−15/16), measured in the range $1.98 \leq \Theta \leq 28.26°$, completeness $\Theta_{max} = 92.0\%$, 3192 independent reflections, $R_{int} = 0.0478$, 237 parameters, 0 restraints, $R1_{obs} = 0.0602$, $\omega R^2_{obs} = 0.1082$, $R1_{all} = 0.1129$, $\omega R^2_{all} = 0.1257$, goodness-of-fit = 1.057, largest difference peak and hole: 0.305/−0.429 e Å^{-3}.

3.4.2. Crystal data for **12**

$M_r = 490.18$ g mol^{-1}, yellow plate, size $0.34 \times 0.08 \times 0.07$ mm, orthorhombic, space group $P2_12_12_1$, $a = 11.5785(8)$, $b = 12.8171(9)$, $c = 13.3831(9)$ Å, $V = 1986.1(2)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{calc} = 1.639$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.686 mm^{-1}, $F(000) = 1000$, 10900 reflections in h (−14/14), k (−16/16), l (−17/14), measured in the range $2.20 \leq \Theta \leq 28.30°$, completeness $\Theta_{max} = 92.4\%$, 4166 independent reflections, $R_{int} = 0.0583$, 253 parameters, 0 restraints, $R1_{obs} = 0.0691$, $\omega R^2_{obs} = 0.0859$, $R1_{all} = 0.1203$, $\omega R^2_{all} = 0.0987$, goodness-of-fit = 1.115, largest difference peak and hole: 0.272/−0.302 e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153994 for compound **6** and CCDC no. 153995 for compound **12**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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