



Synthesis and structural characterization of a sterically encumbered ferrocenecarboxamido diphosphine and its platinum(II) complex



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ARTICLE INFO

Article history:

Received 25 November 2013

Received in revised form

2 January 2014

Accepted 4 January 2014

Keywords:

Ferrocene ligands

Phosphino-amides

Platinum complexes

Structure elucidation

ABSTRACT

{[Bis(2-(diphenylphosphino)ethyl)amino]carbonyl}ferrocene (**3**), a bulky ferrocenecarboxamido-diphosphine, was prepared in a good yield by the reaction of pentafluorophenyl ferrocenecarboxylate (**2**) with bis[2-(diphenylphosphino)ethyl]amine. The NMR data (¹H VT NMR study in particular) indicated a limited molecular mobility of amide **3** that presumably results from a hindered rotation around the amide C–N bond leading to a non-equivalency of the substituents attached to the amide nitrogen. Compound **3** was further converted to the corresponding diphosphine disulfide **4** and reacted with [PtCl₂(cod)] (cod = η²:η²-cycloocta-1,5-diene) to give the symmetric, ligand-bridged diplatinum complex [(μ-**3**)PtCl₂]₂ (**5**) having *cis* square-planar geometry around the Pt(II) centers. The molecular structures of **4** and **5** were determined by single-crystal X-ray diffraction analysis.

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1. Introduction

Phosphines modified with carboxamide functional substituents have found numerous applications in coordination chemistry, catalysis and biomedical research [1]. The majority of phosphino-carboxylic amides comprising ferrocene scaffold, which were reported to date, was obtained via conventional amidation of phosphinoferrocenecarboxylic acids with amines [1]. In contrast, there have been reported only a few compounds of this type resulting from conjugation of simple ferrocenecarboxylic acids and phosphinoamines.

For instance, compounds **A** and **B** (Scheme 1) derived from ferrocene-1,1'-dicarboxylic acid have been studied by Laguna et al. [2] and by Beer et al. [3]. In 1999, the latter group reported on the coordination properties and anion sensing ability of compound **B** in its free and coordinated form. Compound **A**, described ten years later, was utilized as a ligand in Group 11 metal complexes. The structurally related, chiral phosphinoamide obtained from ferrocenecarboxylic acid and a proline-based phosphinoamine (**C** in Scheme 1) was reported by Wang and coworkers. This compound was employed as a chiral donor in copper-catalyzed asymmetric conjugate addition of diethylzinc to imines [4]. Only a handful of other compounds resulting via reactions of ferrocene amines with carboxylic acids (or derivatives) have been designed and studied as molecular or immobilized chiral phosphinoferrocene ligands [5].

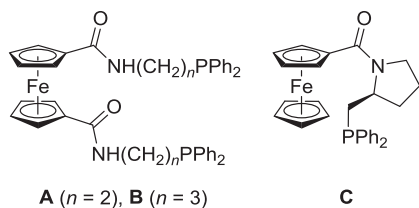
As a part of our ongoing studies focusing on the coordination behavior and catalytic properties of ferrocene phosphino-carboxamides [6], we decided to prepare {[bis(2-(diphenylphosphino)ethyl)amino]carbonyl}ferrocene (**3**) as a congener of donor **A** bearing two 2-(diphenylphosphino)ethyl pendants at one amide nitrogen (see Scheme 2 below). During the course of our studies, Gimeno et al. [7] reported the preparation of this compound and its gold(I) complexes, which were evaluated for their anticancer activity. With this contribution we describe an alternative synthesis of this bulky amidophosphine ligand, and the preparation and crystal structures of the corresponding diphosphine disulfide and the ligand-bridged platinum(II) complex [(μ-**3**)PtCl₂]₂.

2. Results and discussion

Unlike the previous synthesis based on the direct amidation of ferrocenecarbonyl chloride [7], compound **3** was obtained via active ester method (Scheme 2). In the first step, ferrocenecarboxylic acid (**1**) was reacted with pentafluorophenol and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDC·HCl) in the presence of a catalytic amount of 4-(dimethylamino)pyridine to afford pentafluorophenyl ferrocenecarboxylate (**2**) [8]. This stable intermediate was in turn coupled with bis[2-(diphenylphosphino)ethyl]amine, which was generated *in situ* from the corresponding hydrochloride [9] and triethylamine. The amidation reaction, carried out in dry *N,N*-dimethylformamide in the presence of 4-(dimethylamino)pyridine as a base additive, and the following chromatographic purification afforded amide **3** as an amorphous, rusty brown amorphous solid in a 64% yield based on

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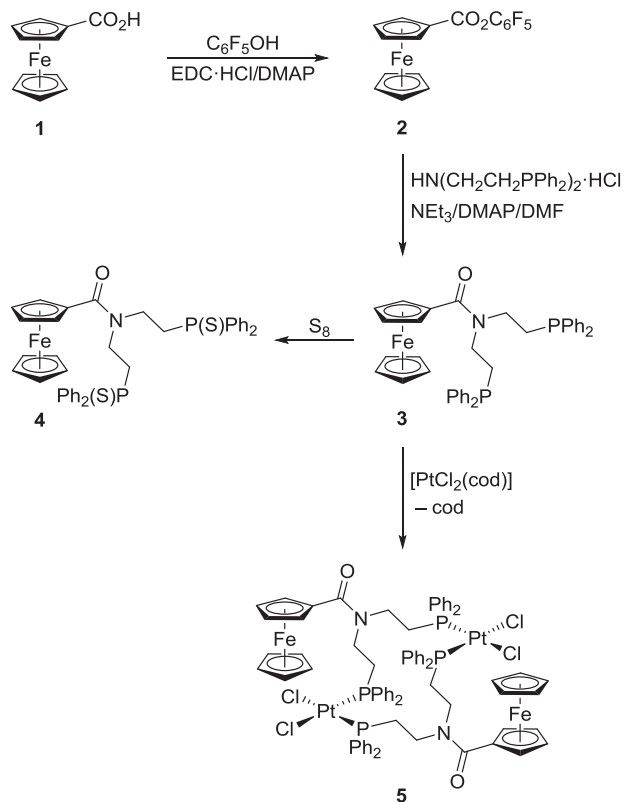
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Scheme 1.

ferrocenecarboxylic acid. In order to prepare a better crystallizing derivative, amide **3** was further converted to the corresponding phosphine sulfide **4** by reacting with elemental sulfur in toluene (Scheme 2).

Compounds **2–3** were characterized by multinuclear NMR spectroscopy, IR spectroscopy, ESI mass spectrometry and by elemental analysis. In addition, the molecular structure of the phosphine sulfide was determined by single-crystal X-ray diffraction analysis. Signals in the NMR spectra of phosphine **3** and the phosphine sulfide recorded at room temperature (25 °C) were markedly broad, suggesting some dynamic processes relatively slow at the NMR scale. A variable temperature (VT) ^1H NMR study performed for **3** (Fig. 1) confirmed this assumption. When the temperature of the measurement was lowered, the two broad signals attributed to the chemically non-equivalent CH_2 groups constituting the ethane-1,2-diyl linkers (i.e. CH_2P and CH_2N) split into a pair of signals, which gained fine structure due to scalar coupling upon further cooling. At higher temperatures, the spectra expectedly simplified due to a faster molecular motion and signal



Scheme 2. Preparation of amides **3** and **4**, and the diplatinum complex **5**. Legend: EDC·HCl = 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride, DMAP = 4-(dimethylamino)pyridine, DMF = *N,N*-dimethylformamide, cod = cycloocta-1,5-diene.

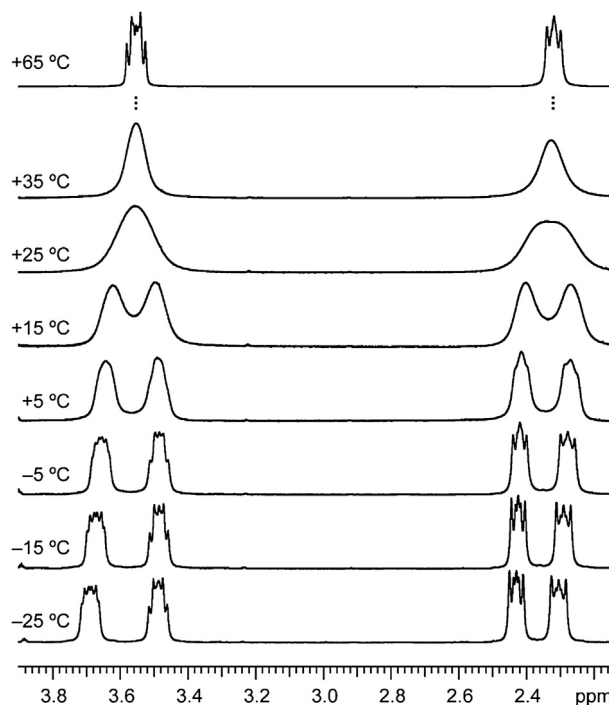


Fig. 1. ^1H VT NMR spectra of diphosphine **3** illustrating the changes occurring in the region of methylene protons. The spectra were recorded in CDCl_3 .

averaging, showing only one multiplet for each of the CH_2P and CH_2N moieties.

Signals of the benzene protons (PPh_2 groups) in **3** were observed as more or less resolved multiplets at ca. δ_{p} 7.30–7.50 ppm, while the signals of the ferrocene protons constituted the expected pattern consisting of a sharp singlet (C_5H_5) and a pair of virtual triplets (AA'BB' spin system of C_5H_4) that did not change with the temperature.

The spectra of **4** were rather similar, though only the low-field methylene signals were split (non-equivalent) and broadened at room temperature (δ_{H} 3.77 and 3.95 ppm) whereas the high-field resonance (δ_{H} 2.88 ppm, $2 \times \text{CH}_2$) was observed as a sharp multiplet. The protons of the PPh_2 groups gave rise to very broad signals centered at δ_{H} ca. 7.50 and 7.72 ppm in the intensity ratio 2:3. In the ^{31}P NMR spectrum, compound **4** displayed a pair of broad singlets (δ_{p} 37.9 and 41.3 ppm) shifted characteristically to lower fields as compared with the parent phosphine. The IR spectra of compounds **3** and **4** showed the characteristic, strong $\nu_{\text{C}=\text{O}}$ bands (amide I) at 1608 and 1605 cm^{-1} , respectively.

Recrystallization of **4** from ethyl acetate–hexane afforded single crystals of a stoichiometric solvate $4 \cdot \frac{1}{2}\text{CH}_3\text{CO}_2\text{Et}$. The compound was found to crystallize with two structurally independent molecules in the monoclinic unit cell (Fig. 2). These molecules are depicted in Fig. 2 while the selected geometric data are given in Table 1.

Interatomic distances and angles determined for the independent molecules of **4** in the structure of $4 \cdot \frac{1}{2}\text{CH}_3\text{CO}_2\text{Et}$ are quite similar, the molecules differing mainly by conformation of the C–C–P(S)Ph₂ moieties attached to the amide nitrogen (see overlap in Fig. 3). As the result, the non-bonding P···P distances in both molecules, which can be taken as a measure of conformational flexibility, differ by as much as ca. 1 Å.

Parameters describing the tertiary amide moiety, namely the C–O and C–N distances and the O=C–N angles determined for **4** do not depart from those reported for FcCONMe_2 [10] and $\text{FcCON}(\text{CH}_2\text{CH}_2\text{OH})_2$ [11] (Fc = ferrocenyl). The amide units in both

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