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Synthesis and structural characterization of ferrocene phosphines modified with polar pendants and their palladium(II) complexes. Part I: *N*-aminocarbonyl and *N*-acyl phosphinoferrocene carboxamides

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Dedicated to Professor Heinrich Lang on the occasion of his 60th birthday.

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A B S T R A C T

Acylation of 1′-(diphenylphosphino)-1-(aminocarbonyl)ferrocene, $Ph_2PfcCONH_2$ (**1**; fc = ferrocene-1,1′-diyl), afforded a series of acyl-ureas including $Ph_2PfcCONHCONHEt$ (**1a**), $Ph_2PfcCONHCONHPh$ (**1b**), and $Ph_2PfcCONHCONMe_2$ (**1c**) as well as the acetyl derivative $Ph_2PfcCONHAc$ (**1d**). Compounds **1a-d** were converted to the corresponding phosphine oxides (**2a-d**) and further examined as ligands in Pd(II) complexes. The reactions of **1a-d** with $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) at a 2:1 ligand-to-metal ratio gave the bis(phosphine) complexes $[PdCl_2(L\text{-}\kappa P)_2]$ (**3a-d**; L = **1a-d**), whereas the reactions with $[Pd(L^{NC})Cl]_2$ (L^{NC} = [2-(dimethylamino-κ*N*)methyl]phenyl-κC^1) produced the bridge-cleavage products, $[PdCl(L^{NC})(L\text{-}\kappa P)]$ (**4a-d**). Removal of the Pd-bound halide from **4a-d** with $Ag[SbF_6]$ furnished the corresponding cationic bis-chelate complexes $[Pd(L^{NC})(L\text{-}\kappa^2 O,P)][SbF_6]$ (**5a-d**). All compounds were characterized by NMR and IR spectroscopy, electrospray ionization mass spectrometry, and elemental analysis. The crystal structures of **1a**, **2a-c**, **3a**·$2CHCl_3$, **3b**·$2CHCl_3$, **3d**·$2CHCl_3$, **4a**·$3CHCl_3$, **4b**·$2.5CHCl_3$, **5a**·$CHCl_3$, **5b**·$2CH_2Cl_2$, and **5d** were determined by single-crystal X-ray diffraction analysis, which revealed that the hydrogen-bonded arrays formed in the crystals of free ligands are often preserved in the structures of their complexes.

1. Introduction

Phosphinocarboxylic amides are attractive ligands for coordination chemistry and catalysis [1]. Although a vast number of these specific hybrid phosphines [2] differing in both the phosphine and amide parts of their molecules has been reported and utilized in various fields [1], little attention has been given to compounds with extended amide pendants. For instance, donors whose amide moieties are expanded to acylurea groups by an attached aminocarbonyl substituent typically comprise cyclic acylurea units such in 6-(diphenylphosphino)uracil (**A** in Scheme 1) [3]. Other examples include phosphine-tagged uracil nucleosides and oligonucleotides [4] and a phosphine-modified barbiturate employed in self-assembled catalysts for Rh-catalyzed hydroacylation and hydroarylation of terminal olefins (**B** in Scheme 1) [5].

Given our continuing interest in the coordination and catalytic chemistry of phosphinoferrocene carboxamides [6] and particularly in view of the favorable catalytic properties of phosphinoferrocene amido-ureas (**C** in Scheme 2) [7] and phosphinoferrocene ureas (**D** in Scheme 2) [8], we have decided to prepare and study phosphinoferrocene amides bearing aminocarbonyl groups at the amide nitrogen (Scheme 2, bottom). It should be noted that acylureas without phosphine substituents are not unprecedented in ferrocene chemistry. A series of ferrocenecarbonyl ureas of the type FcCONHCONHAr (Fc = ferrocenyl) has been prepared by the reaction of ferrocene carboxamide ($FcCONH_2$) with isocyanates ArNCO [9], and compounds of the type FcCON*R*CONHR were typically isolated from the conventional reactions of ferrocenecarboxylic acid with carbodiimides (RN = C = NR) [10], which also led to phosphine-substituted derivatives from ferrocene phosphinocarboxylic acids [11]. In addition, several structurally related compounds were recently obtained by the acylation of uracil, thymine, and 5-fluorouracil with FcCOCl or FcCOOCOOEt [12].

This contribution describes the synthesis and characterization

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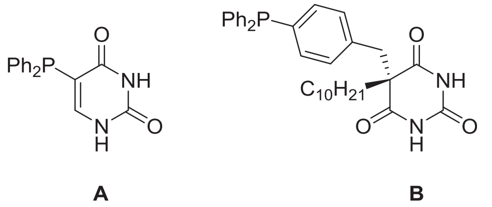
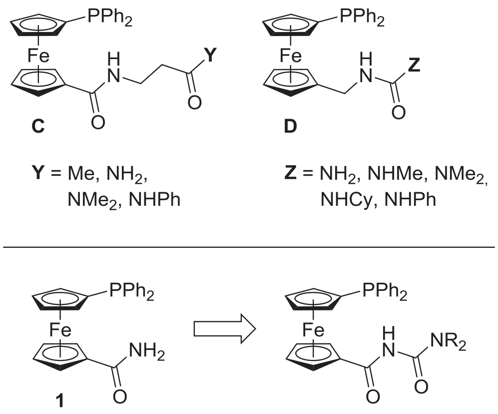


Scheme 1. Examples of phosphines possessing cyclic acyl-urea substituents.



Scheme 2.

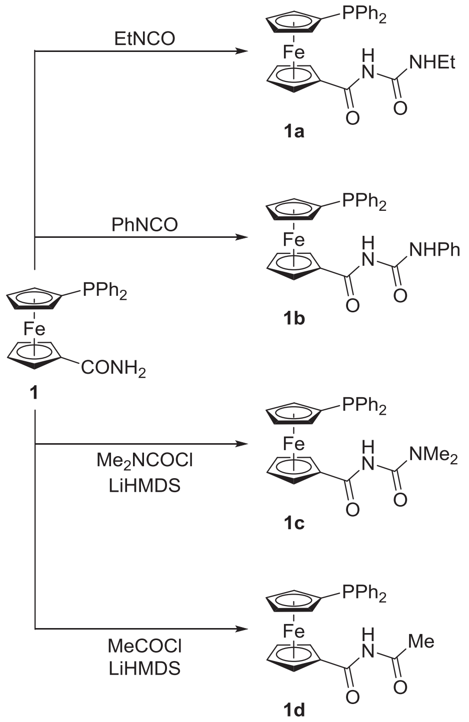
of phosphinoferrocene donors bearing (aminocarbonyl)amide substituents in the 1′ position of the ferrocene unit [13] that are accessible from phosphinoferrocene amide **1** [14], and their palladium(II) complexes. Particular attention is being paid to the crystal structures of these compounds because they possess extended polar moieties suitable for the formation of solid-state assemblies via hydrogen bonding interactions.

2. Results and discussion

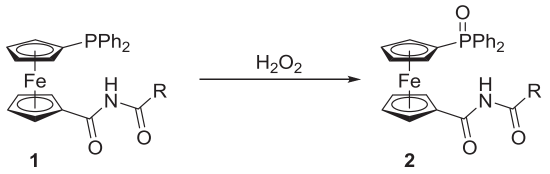
*2.1. Synthesis of phosphines **1a-d** and their corresponding phosphine oxides*

Compounds **1a-d** were obtained via extensions of the amide moiety in the parent compound **1** [14] as shown in Scheme 3. The acylureas **1a** and **1b** resulted from the reactions of **1** with the respective isocyanates (*N.B.* the reaction with EtNCO required the presence of LiHMDS), whereas the tertiary urea derivative **1c**, which is an isomer of **1a**, was prepared by the reaction of *in situ* deprotonated **1** with *N,N*-dimethylcarbamoyl chloride. An analogous reaction exploiting acetyl chloride as the acylating agent was used to prepare the diacyl derivative **1d**, which was included in the series of prospective ligands for the sake of comparison.

Compounds **1a-d** were isolated in moderate to good yields as orange amorphous solids that tenaciously retain traces of organic solvents used during column chromatography and were characterized by spectroscopic methods and elemental analysis. In their electrospray ionization (ESI) mass spectra, compounds **1a-d** display peaks of the pseudomolecular ions ($[M + Na/K]^+$ or $[M - H]^-$). The ^{1}H and ^{13}C NMR spectra of **1a-d** exhibit characteristic signals of the phosphinoferrocene moiety and the attached polar pendants [the signals of the C═O groups are observed at δ_C 152–154 (urea) and 169–172 (amide) in $CDCl_3$], whereas the ^{31}P NMR signals of **1a-d** are observed at $\delta_P \approx -17.5$ ppm, similar to that of the parent amide **1** [14].



Scheme 3. Synthesis of compounds **1a-d** from amide 1 (LiHMDS = $LiN(SiMe_3)_2$).



R = NHEt (**a**), NHPh (**b**), Me (**d**).

Compound **2c** (R = NMe_2) was isolated as a byproduct during the preparation of **1c**.

Scheme 4. Preparation of phosphine oxides **2** by oxidation of **1**.

Phosphines **1a-d** were further converted to the more easily crystallizable phosphine oxides **2a-c** by oxidation with hydrogen peroxide in acetone (Scheme 4; Note: compound **2c** was isolated as a byproduct during the synthesis of **1c**). The oxidation is nicely manifested by shifts of the ^{31}P NMR signals to lower fields (δ_P in the range ca. 29–31 ppm) and also results in characteristic shifts of the signals due to carbons within the phosphorus-substituted aromatic rings and in an increase in the J_{PC} coupling constants in the ^{13}C NMR spectra [15]. In contrast, the signals of the polar pendants remain practically unaffected by the oxidation of the phosphine moiety (cf. δ_C 151–155 and 169–172 for the urea and carboxamide C═O groups, respectively, in $CDCl_3$).

*2.2. The crystal structures of **1a**, **2a**, **2b**, and **2c***

The central ferrocene moieties in the structures of **1a**, **2a**, **2b**, and **2c** (Figs. 1–3 and Table 1) adopt their regular geometry with marginal variation in the individual Fe–C distances (up to ca. 0.05 Å for the ten Fe–C distances in one compound) and, consequently, minor tilting of their cyclopentadienyl rings (maximum 4.35(8)° for **1a**). Geometric parameters describing the attached functional groups do not depart from the usual ranges [16] and compare well

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