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The reaction of (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid with carbodiimide reagents: Characterisation of the acid anhydride and urea products

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ABSTRACT

Interaction of (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid [(S_p)-**1**] with *N*,*N*′-dicyclohexylcarbodiimide (DCC) and *N*-ethyl-*N*′-[3-(dimethylamino)propyl]carbodiimide (EDC) have been investigated in order to study the reacting system itself and to characterise side-products typically arising during the diimide-promoted condensation of acid (S_p)-**1** with nucleophiles. The reaction between (S_p)-**1** and DCC was found to give preferentially the respective urea derivative in the absence of a base, and (S_p)-2-(diphenylphosphino)ferrocenecarboxylic anhydride [(S_p,S_p)-**3**] when the same reaction was performed in the presence of 4-(dimethylamino)pyridine (DMAP). With EDC, the preference for a reaction pathway was less pronounced: whereas the reaction without the base afforded exclusively the corresponding urea, that in the presence of DMAP yielded a mixture of the urea and anhydride (S_p,S_p)-**3**.

1. Introduction

The research into ferrocene ligands represents an active research area, which is continually stimulated by numerous practical applications [1]. Aiming at new phosphinocarboxylic donors [2,3], we [4] and others [5] have previously reported about the preparation of (S_p)-2-(diphenylphosphino)ferrocenecarboxylic acid, (S_p)-**1**, via hydrolysis of the corresponding chiral oxazoline. Later, Breit and Breuninger devised a practical synthesis of both enantiomers of this acid based on *ortho*-directed lithiation of ferrocenecarboxylic acid and subsequent resolution of racemic **1** via diastereoisomeric esters with D-glucose diacetonide [6]. Acid **1** has already found manifold use in enantioselective catalysis: it was applied directly as a catalyst component [7], and also utilised as a chiral building block in the preparation of chiral amidophosphine ligands [5a,5b,7b,8] and an efficient chiral auxiliary [9].

In view of our continuing interest in the preparation of new amide derivatives from (S_p)-**1** [7b] as well as some related ferrocene phosphinocarboxylic acids [2] via diimide-promoted amide coupling [10], we decided to optimise the amidation procedure and possibly characterise any reaction by-products. In the present study, we report the reactivity of the commonly used diimides, *N*,*N*′-dicyclohexylcarbodiimide (DCC) and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC), with (S_p)-**1** both in the presence and the absence of a base.

2. Results

2.1. Reactivity studies

In order to study the reaction of acid (S_p)-**1** with diimides we performed a series of experiments with DCC and EDC in the presence and the absence of 4-(dimethylamino)pyridine (DMAP) as a base. The reactions were performed similarly as described in Ref. [6] – but without any nucleophile (alcohol or amine) added, and proceeded reproducibly as indicated by repeated runs. Representative experiments are described in Section 4.

The reaction of (S_p)-**1** with an excess of DCC (1.25 equiv.) afforded *N*,*N*′-dicyclohexyl-*N*-[(S_p)-2-(diphenylphosphino)ferrocenecarbonyl]urea [(S_p)-**2a**], slightly contaminated with anhydride (S_p,S_p)-**3** (ca. 5 mol.-% according to NMR spectra). The amount of isolated (S_p)-**2a** corresponded to 87% yield. A similar reaction performed in the presence of one molar equivalent of DMAP yielded (S_p,S_p)-**3** as the vastly dominating component in the product mixture (94 mol.-%); the only other detectable product was (S_p)-**2a**. A subsequent crystallisation of the mixture from ethyl acetate-pentane removed the urea derivative, affording analytically pure (S_p,S_p)-**3** as an orange microcrystalline solid (see Scheme 1).

Replacing DCC with EDC did not basically change the reaction course. First, the reaction between (S_p)-**1** and EDC (2 molar equiv.) gave exclusively *N*-[3-(dimethylamino)propyl]-*N*′-ethyl-*N*-[(S_p)-2-(diphenylphosphino)ferrocenecarbonyl]urea [(S_p)-**2b**] in 91% isolated yield. The isomeric product, *N*-[3-(dimethylamino)propyl]-*N*′-ethyl-*N*′-[(S_p)-2-(diphenylphosphino)ferrocenecarbonyl]urea

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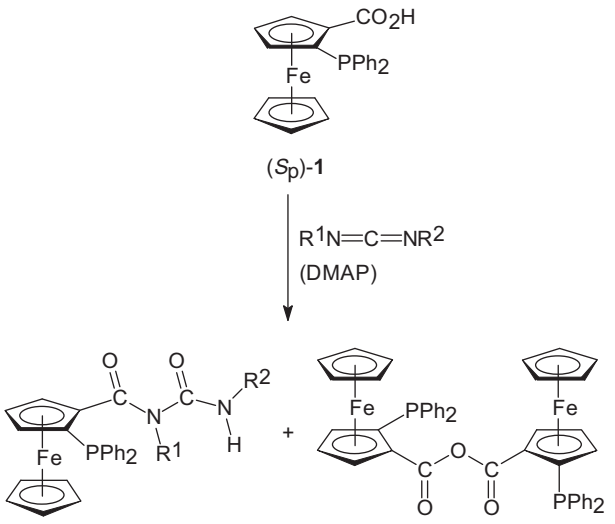


	R^1	R^2
(S_p)-**2a**	Cy	Cy
(S_p)-**2b**	$(CH_2)_3NMe_2$	Et
(S_p)-**2b'**	Et	$(CH_2)_3NMe_2$

Scheme 1. The reaction of (S_p)-**1** with diimides (DCC: R^1/R^2 = Cy/Cy, EDC: R^1/R^2 = Et/$(CH_2)_3NMe_2$; Cy = cyclohexyl).

[(S_p)-**2b**′], was not detected in the crude product. Second, the same reaction of (S_p)-**1** performed in the presence of DMAP afforded a mixture whose subsequent chromatographic purification allowed for isolation of anhydride (S_p,S_p)-**3** contaminated by minor amounts of its methanolysis product, methyl (S_p)-2-(diphenylphosphino)ferrocenecarboxylate (S_p)-**4** as the less polar components, and the more polar (S_p)-**2b** as the major product (55% isolated yield). Similarly to the previous case, the isomeric urea (S_p)-**2b**′ was not detected.

2.2. Characterisation of the products

Urea (S_p)-**2a** displays two strong carbonyl stretching bands at 1698 and 1521 cm^{-1} in its IR spectrum, while the ^1H NMR spectrum comprises a complex multiplet due to cyclohexyl (Cy) groups, signals attributable to 2-(diphenylphosphino)ferrocenyl group, and a CH-coupled doublet due to the amide proton at δ_H 6.05 ($^3J_{HH}$ = 7.7 Hz). Likewise, the $^{13}C\{^1H\}$ NMR spectra of (S_p)-**2a** combine two sets of Cy signals (five diastereotopic CH_2 and one CH per the ring) with the signals due to the phosphinoferrocenyl and urea moieties. The C=O carbons resonate at δ_C 154.70 (NC(O)N) and 171.24 (C(O)N), the latter as a doublet due to scalar coupling with the proximal phosphorus atom ($^3J_{PC}$ = 2 Hz). The observed chemical shifts compare favourably with those reported for FcC(O)N(Cy)C(O)NHCy (Fc = ferrocenyl) [11]. The $^{31}P\{^1H\}$ NMR spectrum of (S_p)-**2a** displays a single resonance at δ_P −20.0, indicating the presence of an unchanged diphenylphosphino group [4].

The spectral data provide also an insight into the nature of 'molecular' interactions of (S_p)-**2a**. For instance, the formation of N–H···acceptor hydrogen bonds is already indicated by IR spectra that display a broad asymmetric ν_{NH} band at ca. 3270 cm^{-1} in Nujol and at ca. 3425 cm^{-1} when recorded on a 0.01 M solution in $CHCl_3$. In ^1H NMR spectra, the position of the amide proton resonance changes with the sample temperature [12], the parameters showing a good linear correlation (Fig. 1):

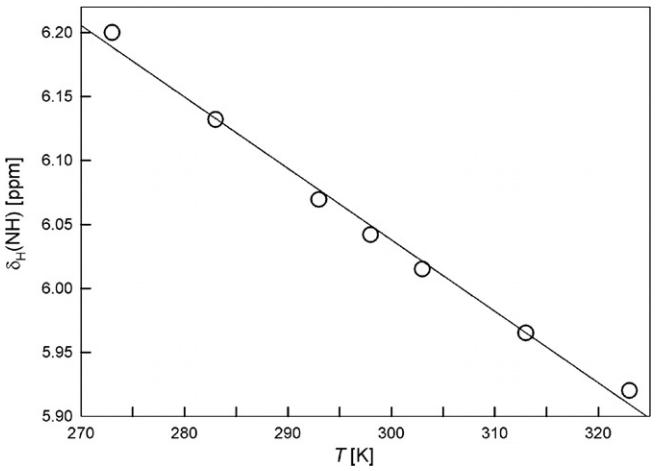
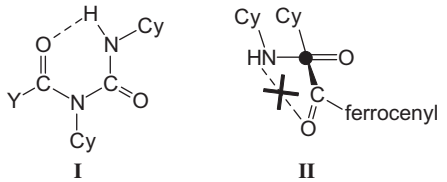


Fig. 1. Temperature dependence of amide proton chemical shift for urea (S_p)-**2a**. The spectra were recorded on a 0.01 M $CDCl_3$ solution and are referenced to tetramethylsilane. Solid line shows least-square linear fit of the data.

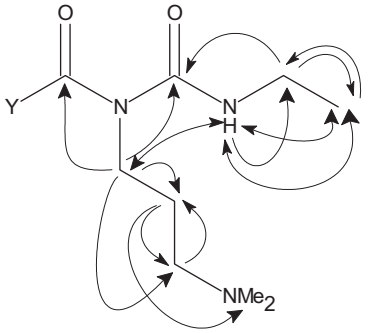
$$\delta_H(NH) = -0.0056(2)T + 7.71(6) \quad (r^2 = 0.993).$$

The negative temperature coefficient, $\Delta\delta/\Delta T$ = 5.6(2) ppb K^{-1} indicates that the NH groups experience less hydrogen-bonding at elevated temperatures while the magnitude of $\Delta\delta/\Delta T$ could be regarded as indicative of preferred formation of inter- rather than intramolecular hydrogen bonds [13].

In summary, the spectral data implicate that in $CHCl_3$ and $CDCl_3$ as poorly hydrogen-bonding solvents, *inter*molecular N–H···O=C hydrogen bonds are most probably the dominant interactions between the molecules of (S_p)-**2a**. This conclusion is in line with the fact that all structurally characterised mono-acyl *N,N*′-dicyclohexyl ureas [14] possess conformations unsuitable for the formation of *intra*molecular N–H···O hydrogen bonds. Formation of an intramolecularly stabilised structure such as **I** (Scheme 2) would require a favourable donor–acceptor distance and orientation of the NH and its more distant C=O bonds. Although the basic geometric parameters are not strikingly unfavourable [15], none of the structurally characterised compounds forms an intramolecular O···HN hydrogen bond in the solid state due to mutual rotation of the {CON} planes forming the acyl-urea moiety. Such twisting is typical also for ferrocenyl-substituted *N,N*′-dicyclohexyl ureas (**II** in Scheme 2). The dihedral angles of the {CON} planes in (ferrocenecarbonyl)ureas are as high as 86.3(3)° and 89(1)° in *N*-ferrocenecarbonyl-*N,N*′-dicyclohexylurea (**III**; refcode OBAYIZ [16]) and 1,1′-bis[(*N,N*′-dicyclohexylureido)carbonyl]ferrocene (**IV**; refcode EBIXUJ [17]), respectively, whilst the 1′-functionalised analogues show lower rotations [cf. 61.1(3)° for *N*-[1′-(*N*-cyclohexylcarbamoyl)ferrocenecarbonyl]-*N,N*′-dicyclohexylurea (**V**; refcode CAPJAF [18]), and 39.6(3)° for *N*-[1′-(acetylamino)ferrocenyl]-*N,N*′-dicyclohexylurea (**VI**; refcode DADFAQ [19])].



Scheme 2. A hypothetic planar, hydrogen-bonded conformation (**I**) and the conformation typically encountered in the crystal structures of compounds featuring C(ferrocenyl)C(O)N^ACyC^B(O)NHCy moiety (Cy = cyclohexyl) (**II**). For **II**, a projection along the $N^A\cdots C^B$ line is shown.



Scheme 3. Selected ^{13}C gHMBC (H → C) and NOESY (H ↔ H) correlations observed in the NMR spectra of (S_p)-**2b** (Y stands for the (S_p)-2-(diphenylphosphino)ferrocenyl group).

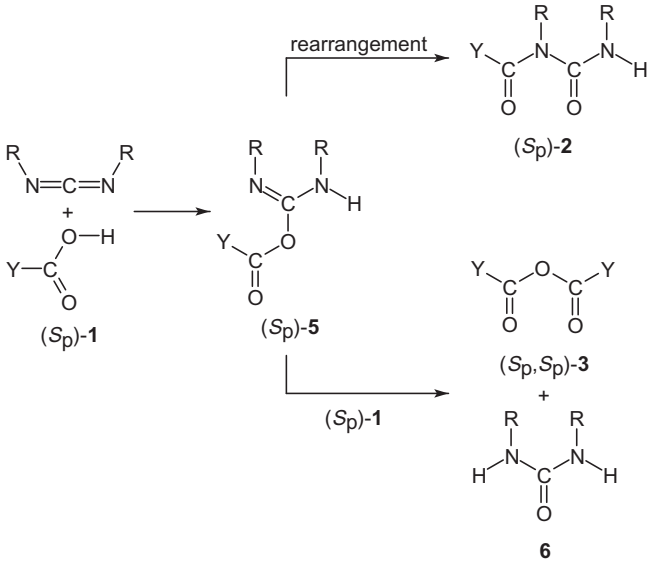
Urea (S_p)-**2b** was isolated as a non-crystallising amorphous solid, possessing a strong tendency to retain the reaction solvents. In IR spectra, it exerts characteristic $\nu_{C=O}$ bands (1706 and 1526 cm^{-1}) while its ^1H NMR spectrum shows characteristic multiplets attributable to both aliphatic pendants and to the 1,2-disubstituted ferrocene framework. The ^{13}C NMR spectrum of (S_p)-**2b** is also consistent with the formulation. The C=O signals are observed with the characteristic values, shifted to lower-fields than for (S_p)-**2a** [δ_C 156.12 (NC(O)N), 173.33 (d, $^3J_{PC}$ = 3 Hz, CC(O)N)]. Finally, the position of the $^{31}P\{^1H\}$ NMR resonance (δ_P −19.6) again indicates that phosphine group remains unaffected during the reaction. When combined with correlated 2D experiments, the NMR spectra allowed to clearly distinguish between the two possible isomeric forms [(S_p)-**2b** and (S_p)-**2b′**], the long-range H–C correlation (^{13}C gHMBC, Scheme 3) between the amide proton and the methylene carbon of the ethyl group being of particular diagnostic importance.

At first sight, the ^1H NMR spectra of anhydride (S_p,S_p)-**3** do not differ much from those of the parent acid (S_p)-**1** (cf. $\Delta\delta_H(C_5H_5)$ = 0.08 ppm, $\Delta\delta_H(C_5H_3) \leqslant 0.05$ ppm) [4]. The differences in the ^{13}C NMR spectrum are more pronounced. Most significantly, the C=O resonance of (S_p,S_p)-**3** is observed as a phosphorus-coupled doublet at δ_C 167.04, i.e. shifted by ca. 10 pm to higher field as compared to the acid. In IR spectra, the presence of the carboxanhydride moiety is reflected by a pair of strong bands attributable to coupled C=O stretching vibrations at 1767 and 1713 cm^{-1}. Position of these bands corresponds with that reported for ferrocenecarboxylic anhydride [20].

3. Discussion

On the whole, the observed reactivity in the (S_p)-**1**–carbodiimide systems is in accordance with the previous reports describing the preparation of *N,N′*-diorganyl ureas from simple [11,16,17,20a,20b] and functionalised [19,16] ferrocenecarboxylic acids and *N,N′*-disubstituted carbodiimides. However, the exact product distribution (anhydride/urea) differs for a particular acid–diimide combination.

A tentative reaction sequence leading to (S_p)-**2** is depicted in Scheme 4 [21]. The reaction is probably initiated with addition of the carboxylic acid across the diimide to give an *O*-acyl-urea (S_p)-**5**. In the absence of a nucleophile (e.g., alcohol or amine), (S_p)-**5** can only rearrange to give unreactive *N*-acyl-urea or react with another molecule of the acid to give anhydride (S_p)-**2** and urea **6**. Added DMAP (base) can change the reaction course (or at least favour one of the reaction pathways) via "activation" of the intermediate for the subsequent reaction yielding the anhydride, acting probably as an acyl transfer agent [22]. The preferential formation of (S_p)-**2b** over the isomeric product (S_p)-**2b′** remains yet unclear.



Scheme 4. Schematic depiction of the plausible reaction sequence (Y denotes the (S_p)-2-(diphenylphosphino)ferrocenyl group).

However, the tautomerism of cyclic forms of EDC [11,23] or a preferred configuration of the *O*-acyl-urea intermediate may play some role.

Finally, it is worth pointing out that the formation of the urea derivatives (S_p)-**2a/2b** represents a competitive, non-productive pathway in the synthesis of esters or amides from acid (S_p)-**1**. Fortunately, it can be suppressed by a proper choice of the coupling agent (diimide) and, particularly, by the presence of a nucleophilic reaction partner, which usually reacts preferentially. The latter was already demonstrated with the amidation of (S_p)-**1** [7b] in case of which no (S_p)-**2b** was detected in the reaction mixture.

4. Experimental

4.1. General considerations

All syntheses were performed under an argon atmosphere and with exclusion of direct daylight. Dichloromethane was dried over anhydrous potassium carbonate and distilled from CaH_2. Acid (S_p)-**1** was synthesised by the literature procedure [4]. Other chemicals and solvents were used as received from commercial sources (Fluka, Aldrich; solvents from Penta).

NMR spectra were measured on a Varian UNITY Inova 400 spectrometer at 25 °C. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^1H and ^{13}C) or to an external 85% aqueous H_3PO_4 (^{31}P), all set to 0 ppm. Detailed assignment of the NMR signals is based on COSY, NOESY, ^{13}C gHSQC, and ^{13}C gHMBC two-dimensional spectra. IR spectra were recorded on an FT IR Nicolet Magna 760 instrument in the range of 400–4000 cm^{-1}. Electrospray (ESI) mass spectra were recorded with a Waters Q-Tof Micromass or a Thermo Scientific LTQ Orbitrap XL hybrid FT MS spectrometer on methanol or methanol/$CHCl_3$ solutions. Optical rotations were determined with an automatic polarimeter Autopol III (Rudolph Research) at room temperature.

4.2. The reaction of (S_p)-**1** with DCC in the absence of a base

DCC (31 mg, 0.15 mmol) was added to a solution of (S_p)-**1** (50 mg, 0.12 mmol) in dry dichloromethane (5 mL). The resulting solution was stirred at room temperature overnight (20 h), filtered (PTFE syringe filter, 0.45 μm pore size) and evaporated under

vacuum. Column chromatography on silica gel (hexane–diethyl ether 1:1) afforded the product (S_p)-**2a** (65 mg) contaminated with a small amount of anhydride (S_p,S_p)-**3** (ca. 5 mol.-% according to NMR analysis).

4.3. The reaction of (S_p)-*1* with DCC in the presence of a base

The reaction was performed as above except that DMAP was added to the reaction mixture. Thus, DCC (31 mg, 0.15 mmol) was added to a solution of (S_p)-**1** (50 mg, 0.12 mmol) and DMAP (15 mg, 0.12 mmol) in dry dichloromethane (5 mL). After the reaction mixture had been stirred at room temperature overnight (20 h), it was filtered (PTFE syringe filter, 0.45 μm pore size) and evaporated under vacuum. Subsequent column chromatography (silica gel, hexane–diethyl ether 1:1) and evaporation gave the product (47 mg) which, according to NMR spectra, consisted of anhydride (S_p,S_p)-**3** (94 mol.-%) and a minor amount of (S_p)-**2a**. Crystallisation of this mixture from ethyl acetate-pentane at +4 °C afforded analytically pure (S_p,S_p)-**3**.

4.4. The reaction of (S_p)-*1* with EDC in the absence of a base

EDC (31 mg, 0.2 mmol) was added to a solution of (S_p)-**1** (41 mg, 0.1 mmol) in dry dichloromethane (4 mL). The resulting solution was stirred at room temperature overnight (20 h) and then evaporated under vacuum. The residue was purified by column chromatography (silica gel, dichloromethane–methanol 10:1, gradually increased to 5:1). Removal of the solvents under reduced pressure gave pure urea (S_p)-**2b**. Yield: 52 mg (91%).

4.5. The reaction of (S_p)-*1* with EDC in the presence of a base

EDC (78 mg, 0.50 mmol) was added to a solution of (S_p)-**1** (104 mg, 0.25 mmol) and DMAP (30 mg, 0.25 mmol) in dry dichloromethane (8 mL) and the resulting solution was stirred at room temperature overnight (20 h). Then, the reaction mixture was washed twice with saturated aqueous NaCl solution, the organic layer was dried over $MgSO_4$ and evaporated under vacuum. A subsequent purification by column chromatography (silica gel, dichloromethane–methanol 20:1, gradually increased to 5:1) afforded two major bands. The first fraction (32 mg after evaporation) contained mostly anhydride (S_p,S_p)-**3** accompanied with a small amount of methyl ester (S_p)-**4** resulting by methanolysis of the anhydride. Evaporation of the second band afforded urea (S_p)-**2b** as a red oil, which solidifies when stored at 4 °C. Yield: 78 mg (55%).

4.6. Analytical data for (S_p)-*2a*

^{1}H NMR ($CDCl_3$): δ 0.82–2.00 (m, 20H, Cy CH_2), 3.53 (m, 1H, NHCy C*H*), 3.89 (m, 1H, C_5H_3), 3.95 (tt, J = 3.6, 11.9 Hz, 1H, NCy C*H*), 4.22 (s, 5H, C_5H_5), 4.33 (apparent t, J = 2.6 Hz, 1H, C_5H_3), 4.73 (m, 1H, C_5H_3), 6.05 (d, $^3J_{HH}$ = 7.7 Hz, 1H, NH), 7.26–7.56 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 24.96 (2 C), 25.30, 25.55, 26.23, 26.43, 30.09, 31.51, 32.52, 33.16 (10× CH_2 of Cy); 49.89, 57.79 (2× CH of Cy); 69.72 (CH of C_5H_3), 70.00 (CH of C_5H_3), 71.58 (C_5H_5), 73.61 (d, J_{PC} = 4 Hz, CH of C_5H_3), 82.40 (d, J_{PC} = 16 Hz, C_{ipso} of C_5H_3), 83.89 (d, J_{PC} = 15 Hz, C_{ipso} of C_5H_3), 128.25, 128.31 (2× d, $^3J_{PC}$ = 5 Hz, CH_m of PPh_2); 128.52, 128.91 (2× s, CH_p of PPh_2); 133.04, 134.47 (2× d, $^2J_{PC}$ = 21 Hz, CH_o of PPh_2); 138.05, 139.91 (2× d, $^1J_{PC}$ = 15 Hz, C_{ipso} of PPh_2); 154.70 (NC(O)N), 171.24 (d, $^3J_{PC}$ = 2 Hz, C(O)N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −20.0 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3270 (br w), 1698 (vs), 1640 (w), 1521 (s), 1418 (m), 1342 (m), 1320 (m), 1279 (w), 1244 (w), 1177 (m), 821 (m), 766 (m), 748 (s), 701 (s), 497 (m). HR MS (ESI+) calcd. for $C_{36}H_{41}N_2O_2P^{56}Fe$ ($[M+H]^+$) 621.2325, found 621.2331.

4.7. Analytical data for (S_p)-*2b*

^{1}H NMR ($CDCl_3$): δ 1.14 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_2CH_3), 1.60–1.80 (m, 2H, $CH_2CH_2CH_2$), 2.23 (s, 3H, NMe_2), 2.20–2.40 (m, 2H, CH_2NMe_2), 3.21 (m, 2H, $NHCH_2CH_3$), 3.48 (dt, $^3J_{HH}$ = 7.6 Hz, $^2J_{HH}$ = 14.2 Hz, 1H, NCH_2CH_2), 3.75 (ddd, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.0 Hz, $^2J_{HH}$ = 14.1 Hz, 1H, NCH_2CH_2), 3.92 (m, 1H, C_5H_3), 4.18 (s, 5H, C_5H_5), 4.39 (apparent t, J = 2.6 Hz, 1H, C_5H_3), 4.67 (m, 1H, C_5H_3), 7.22–7.58 (m, 10H, PPh_2), 8.94 (t, $^3J_{HH}$ = 5.3 Hz, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.78 (CH_2CH_3), 26.24 ($CH_2CH_2CH_2$), 35.30 ($NHCH_2CH_3$), 44.73 (NMe_2 and NCH_2CH_2), 55.98 (CH_2NMe_2), 70.34 (CH of C_5H_3), 70.52 (d, J_{PC} = 2.5 Hz, CH of C_5H_3), 71.39 (C_5H_5), 73.38 (d, J_{PC} = 4 Hz, CH of C_5H_3), 80.90 (d, J_{PC} = 16 Hz, C_{ipso} of C_5H_3), 85.20 (d, J_{PC} = 17 Hz, C_{ipso} of C_5H_3), 128.12, 128.20 (2× d, $^3J_{PC}$ = 7 Hz, CH_m of PPh_2); 128.23, 129.02 (2× s, CH_p of PPh_2); 132.72, 134.80 (2× d, $^2J_{PC}$ = 21 Hz, CH_o of PPh_2); 138.23, 139.09 (2× d, $^1J_{PC}$ = 13 Hz, C_{ipso} of PPh_2); 156.12 (NC(O)N), 173.33 (d, $^3J_{PC}$ = 2.5 Hz, C(O)N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.6 (s). IR (RAS): $\tilde{\nu}$/cm^{-1} 3289, 3203 (m), 1706 (vs), 1570 (m), 1526 (s), 1435 (s), 1242 (s), 1202 (m), 1136 (s), 1002 (m), 963 (w), 823 (s), 761 (vs), 700 (vs). MS (ESI+): *m/z* 570 ($[M+H]^+$), 499 ($[M+H-EtNCO]^+$), 397 ($[(C_5H_5)Fe(C_5H_3)(PPh_2)CO]^+$). HR MS (ESI+) calcd. for $C_{31}H_{36}N_3O_2P^{56}Fe$ (M^+) 569.1895, found 569.1902. $[\alpha]_D$ = −109° (c = 1.0, $CHCl_3$).

4.8. Analytical data for (S_p,S_p)-*3*

^{1}H NMR ($CDCl_3$): δ 3.84 (m, 1H, C_5H_3), 4.32 (s, 5H, C_5H_5), 4.49 (apparent t, J = 2.6 Hz, 1H, C_5H_3), 5.03 (m, 1H, C_5H_3), 7.15–7.55 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 71.46 (C_5H_5), 72.78 (CH of C_5H_3), 73.58 (d, J_{PC} = 15 Hz, C_{ipso} of C_5H_3), 74.99 (CH of C_5H_3), 76.50 (d, J_{PC} = 5 Hz, CH of C_5H_3), 80.60 (d, J_{PC} = 18 Hz, C_{ipso} of C_5H_3), 128.10, 128.23 (2× d, $^3J_{PC}$ = 6 Hz, CH_m of PPh_2); 128.33, 129.19 (2× s, CH_p of PPh_2); 132.19, 135.11 (2× d, $^2J_{PC}$ = 21 Hz, CH_o of PPh_2); 137.98, 139.06 (2× d, $^1J_{PC}$ = 13 Hz, C_{ipso} of PPh_2); 167.04 (d, $^3J_{PC}$ = 4 Hz, C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.8 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1767 (s), 1713 (m), 1435 (s), 1417 (w), 1317 (w), 1238 (s), 1166 (w), 1090 (s), 1042 (m), 1021 (vs), 956 (m), 742 (s), 697 (s), 501 (m). HR MS (ESI+) calcd. for $C_{46}H_{36}NaO_3P_2{}^{56}Fe_2$ ($[M+Na]^+$) 833.0736, found 833.0728. $[\alpha]_D$ = −76° (c = 1.0, $CHCl_3$).

4.9. Analytical data for (S_p)-*4*

^{1}H NMR ($CDCl_3$): δ 3.69 (s, 3H, OCH_3), 3.72 (m, 1H, C_5H_3), 4.21 (s, 5H, C_5H_5), 4.44 (m, 1H, C_5H_3), 5.05 (m, 1H, C_5H_3), 7.15–7.55 (m, 10H, PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.4 (s). HR MS (ESI+) calcd. for $C_{24}H_{21}O_2P^{56}Fe$ (i.e., $[M+H]^+$) 429.0707, found 429.0726. NMR data are in agreement with those reported in Ref. [24].

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