Asymmetric activation of the tropos biphenyldiamidophosphite moiety: Synthesis and complexation to rhodium of a deoxycholic acid derived diamidophosphite

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Abstract

A tropos deoxcholic acid derived diamidophosphite was synthesised starting from deoxycholic acid and N,N0-dimethyl-2,2'-diamino-1,1'biphenyl and its stereodinamic characteristics were assessed by VT-NMR spectroscopy. The capability of the diamidophosphite to act as Rh-ligand was investigated in the formation of ionic as well as covalent Rh-complexes. The stereodinamic properties of these complexes were studied by VT-NMR spectroscopy.

1. Introduction

Rh complexes of optically active monophosphorus ligands have received a great deal of attention as catalytic precursors in enantioselective hydrogenations [1] as well as in asymmetric CeC bond forming reactions [2]. The success of this approach lies in the easy achievement of the monodentate ligands with respect the bidentate ones, together with the good capability of asymmetric induction of their Rh-complexes. The easy preparation of enantiomerically pure monophosphorus ligands makes possible to check new and different structures aimed at reaching better results in asymmetric catalysis. Among the features making appealing a monophosphorus ligand, the presence of a chiral flexible moiety
represents an interesting structural motif, which, by means of asymmetric activation, permits to obtain chiral tropos ligands [3]. The asymmetric activation is realized by covalently linking the flexible moiety to a chiral framework possessing fixed stereogenic elements: in this way a new chiral compound that adopt a preferential diastereomeric conformation is obtained. The conformational preference will depend on the capability of the configurationally stable moiety to transfer the chiral information and can increase further after metal complexation [3]. By using a natural compound as configurationally stable subunit for the asymmetric activation of a biphenyl moiety, a chiral auxiliary possessing independent stereogenic elements can be obtained, without any step of enantiomeric resolution [4]. We have used this approach in the synthesis of bile acid derived tropos biphenylphosphites which have been successfully used as chiral ligands in different Rh-catalyzed asymmetric reactions [5]. Encouraged by these results, we decided to approach in the same way the achievement of monophosphorus ligands, possessing different electronic and steric features.

To this aim we turned our attention toward the synthesis of bile acid derived biphenyldiamidophosphites, where the phosphorus is linked to one oxygen and two nitrogen atoms, which can be obtained starting from N,N0-dimethylbiphenyl diamine and a bile acid
derivative possessing only one reactive hydroxyl group. Here we present the synthesis of the biphenyldiamidophosphite 1 (Fig.1) derived from deoxycholic acid and its stereochemical characterization by variable temperature NMR spectroscopy. The results concerning the formation of some Rh-complexes of 1 are also presented, together with their dynamic stereochemical characterization.

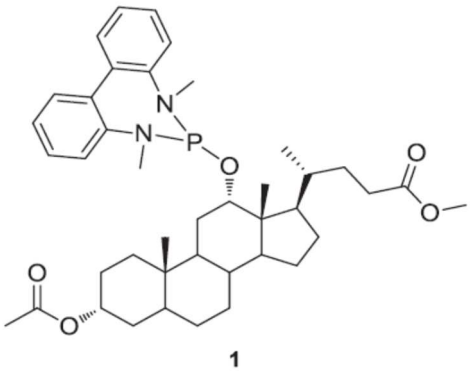

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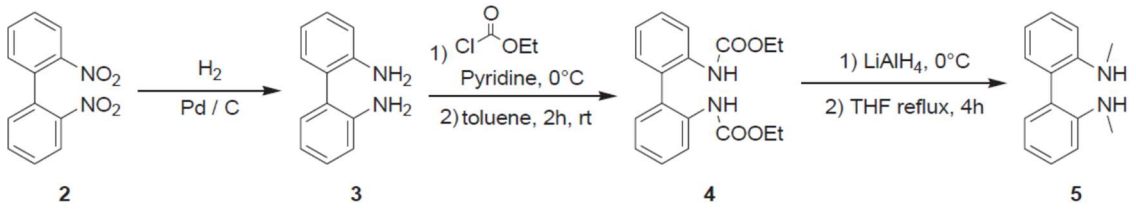
Fig. 1. Structure of the biphenyldiamidophosphite 1.

2. Results and discussion

*2.1. Synthesis and characterisation of diamidophosphite **1***

The N,N'-dimethyl-2,2'-diamino-1,1'-biphenyl **5** was prepared starting from the commercial 2,2'-dinitro-1,1'-biphenyl 2 according to Scheme 1.

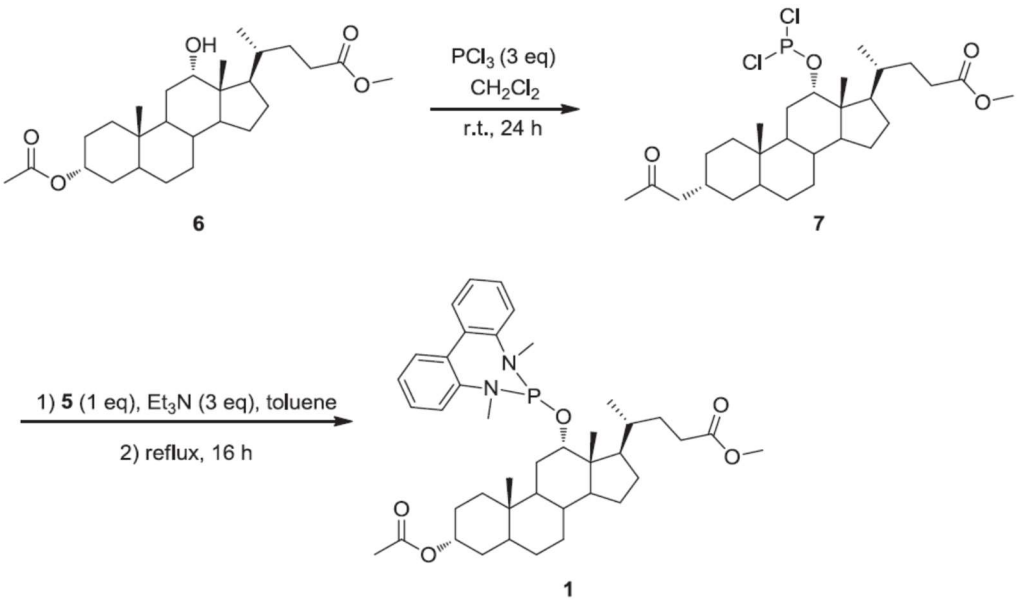


2 3 4 5

Scheme 1. Synthesis of N,N′-dimethyl-2,2′-diamino-1,1′-biphenyl diamine (5).

The catalytic hydrogenation [6] of **2** gave the diamine **3** in 70% yield, which was reacted with ethyl chloroformate [7] leading to the dicarbamoyl derivative **4** in 75% yield after recrystallization of the crude. Reduction of 4 by $LiAlH_4$ [7] afforded diamine **5** as chemically pure product in 75% yield.

The synthesis of diamidophosphite **1** was approached at first with the same procedure used for the synthesis of the analogous biphenylphosphite [5a], by preparing the chlorodiamidophosphite of **5**, then by reacting it with the appropriate deoxycholic acid derivative. Unfortunately in this way low conversion of the substrate was observed and a product in low yield and low chemical purity was isolated. Therefore we changed strategy and the synthesis was performed as summarised in Scheme 2.



Scheme 2. Synthesis of diammidophosphite 1 starting from deoxycholic acid derivative 6.

The deoxycholic acid derivative **6**, prepared as previously described [5a], was reacted with an excess of phosphorus trichloride until complete conversion of the substrate was detected by TLC. The resulting chlorophosphite **7** was not isolated but directly used for the next step, by reacting it with diamine **5** in the presence of triethylamine at the reflux of toluene, until complete conversion of the diaminewas detected by TLC. The pure product was obtained in 50% yield after filtration on a pad of neutral alumina under nitrogen atmosphere. The chemical identity of diamidophosphite **1** was assessed by NMR spectroscopy (^{1}H, 13C, 31P) and NMR-COSY (see supplementary data) and its dynamic stereochemical properties by variable temperature 31P NMR spectroscopy. In fact the presence of the flexible chiral biphenyl moiety can give rise to the formation of two diastereoisomers of **1**, which will be in slow or fast equilibrium between themselves, depending on the activation energy to the interconversion of the M and P forms (Fig. 2).

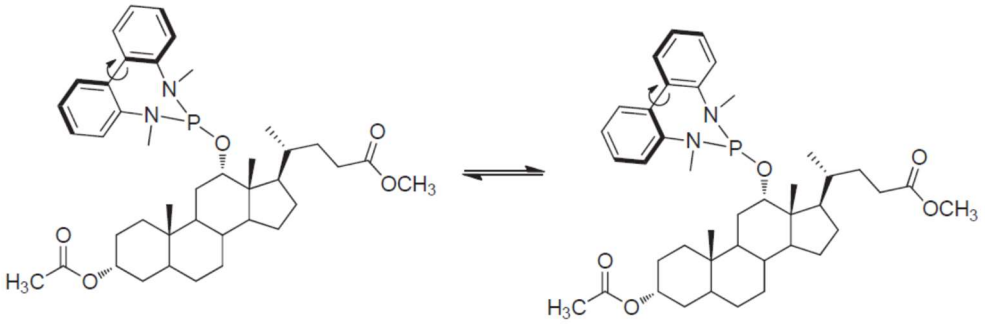


Fig. 2. Interconversion between the diastereomeric M and P forms of diammidophosphite **1**.

To check the dynamic stereochemical nature (labile or stable) of 1 and to assess its diastereomeric composition, VT 31P NMR spectroscopy measurements were used. The 31P NMR spectrum recorded at 298 K in toluene-d8 as a solvent shows a sharp signal at 168.2 ppm that, on lowering the temperature, undergoes a progressive broadening and splits in two broad signals at 233 K (Fig. 3).

The splitting is maximum at 223 K where two sharp and very well distinguishable signals are found at 164.6 and 169.0 ppm. This behaviour suggests that 1 exists as a mixture of diastereoisomers fast interconverting at 298 K; the equilibrium between the two diastereomeric species slows down at lower temperatures and the signals of the M and P forms are well separated at 223 K. The value of the integrated areas of the signals at this temperature

gives a diasteromeric ratio of 53:47. These results point out the tropos nature of the diamidophosphite 1, which exists in solution as a mixture of fast interconverting M-P diastereoisomers, whose the activation energy for the interconversion process has been evaluated, on the basis of the variable temperature NMR parameters [8], as 10.3 kcal/mol.

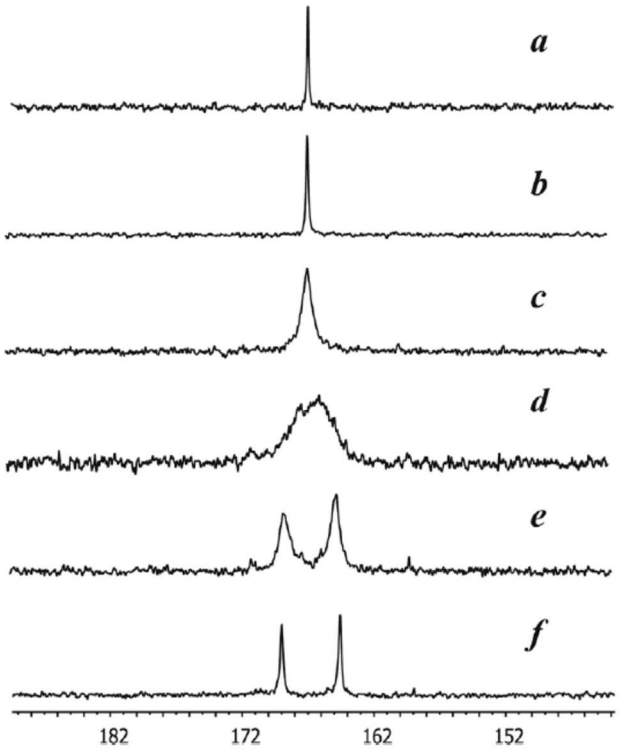


Fig. 3. ^{31}P NMR spectra (80 MHz, toluene-d_8) of **1** at: (a) 298 K, (b) 273 K, (c) 253 K, (d) 243 K, (e) 233 K, (f) 223 K.

2.2. Characterisation of the Rh-complexes of 1

To check the capability of diamidophosphite 1 to act as ligand, its cationic and neutral Rh-complexes, which can be used as catalytic precursors in different asymmetric reactions [1,2], were analyzed by 31P NMR spectroscopy.
The cationic Rh-complex was prepared by stirring a solution of 1 and Rh(cod)2BF4, at P:Rh ¼ 2 M ratio, in deuterated dichloromethane as a solvent for 30 min. The 31P NMR spectrum (Fig. 4) recorded at 298 K on the solution, shows the presence of a doublet signal at 135.9 ppm (J ¼ 211 Hz) and, very close to this, at lower chemical shifts, a broad low signal, whereas the signal allied to the free ligand at 168.3 ppm is absent.

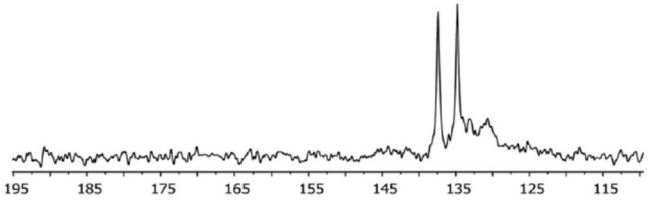
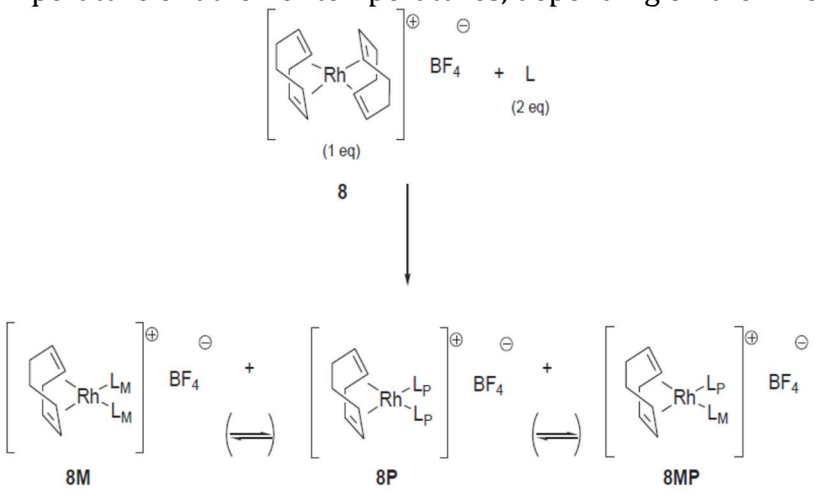


Fig. 4. ^{31}P NMR spectrum (80 MHz, CD_2Cl_2) at 298 K of the mixture $Rh(cod)_2BF_4$:**1** = 1:2.

The lack of the signal of the free ligand and the presence of a doublet signal with a typical P-Rh coupling constant suggests the complete coordination of 1 to Rh, which gives rise to the formation of a disubstituted complex. Given the tropos nature of the ligand, this complex can be constituted, in principle, by three species (Scheme 3), which can be in equilibrium among

themselves: 8M and 8P will give rise in the spectrum to a couple of doublets, distinguishable at room temperature if the equilibrium is slow, or at lower temperature if the equilibrium is fast; whereas 8MP, where the two P atoms are unequivalents, will produce two double doublets at room temperature or at lower temperatures, depending on the kinetic of the equilibrium.



Scheme 3. Equilibrium among the three species 8M, 8P and 8MP.

The nature of the complex and its composition in terms of diastereomeric species can be analyzed by VT 31P NMR spectroscopy. Lowering of the temperature until 223 K (decoalescence temperature for the signals of the free ligand) guarantees that also the decoalescence point of the signals of the complexes has been reached: in fact, it is known that the activation energy to the M-P interconversion rises after coordination to a metallic centre [3a]. The variable temperature 31P NMR profile (Fig. 5) shows no significant changes as far as the doublet signal is concerned, which does not undergo broadening, splitting or even shift in the range 298e223 K. By contrast, the less intense broad signal gives several small signals, already resolved at 253 K and partially superimposed to the more intense doublet.

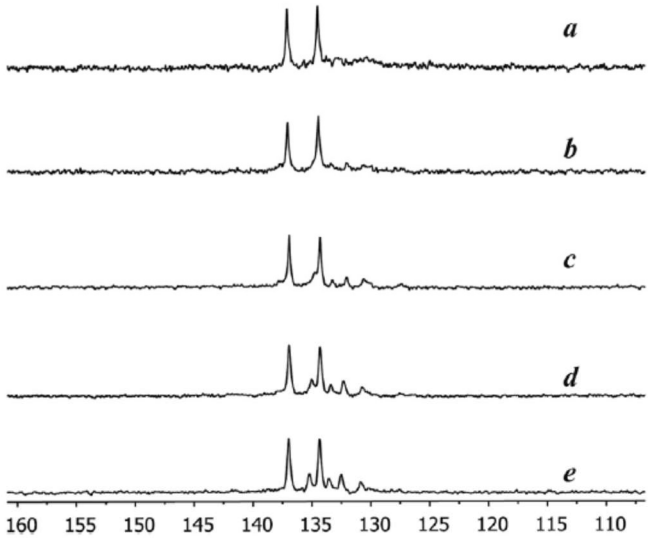


Fig. 5. ^{31}P NMR spectra (80 MHz, CD_2Cl_2) of the mixture $Rh(cod)_2BF_4$:**1** = 1:2 at: (a) 298 K, (b) 273 K, (c) 253 K, (d) 233 K, (e) 223 K.

The observed trend suggests that the doublet signal is attributable to one of the diastereomeric forms 8M or 8P, in which the P atoms are magnetically equivalent, taking into consideration that it does not undergo changes with the temperature. In addition, since only one doublet is visible, there is likely a very large prevalence of one diastereoisomer, the other one being under the detection limit of the NMR technique. This was confirmed by Circular Dichroism (CD)

measurements: as a matter of fact the CD spectrum of the complex (see supplementary data) is much more intense with respect to the CD spectrum of the free ligand (see supplementary data), suggesting a very high prevalence of one the two diastereomeric forms in the complex [5b]. The less intense broad signal, which undergoes resolution on lowering the temperature, can be attributable to the presence of a small percentage of a complex, originated from a different coordination mode of the ligand (may be involving also the nitrogen atom). This complex must be flexible and the diastereomeric species are in fast equilibrium at room temperature and are distinguishable only at lower temperatures: however, the structure of this minor species cannot be inferred on the basis of these data.

The mononuclear covalent Rh-complex was prepared by stirring a solution of 1 and Rh(C2H4)2acac] in toluene-d8 at P:Rh = 2 M ratio for 30 min. The 31P NMR spectrum, recorded on the solution at 298 K (Fig. 6), shows the presence of two doublet signals, at 151.4 ppm (J = 260 Hz) and at 149.9 ppm (J = 256 Hz), together with the signal at 168.3 due to the resonance of the free ligand.

The 31P NMR spectrum, recorded after 24 h, showed the same signals at the same frequencies, suggesting that the ligand does not coordinate totally to the metallic centre, even prolonging the reaction time.

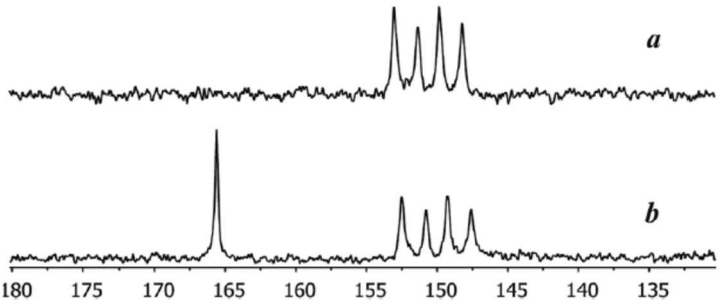


Fig. 6. ^{31}P NMR spectra (80 MHz, toluene-d_8) at 298 K of the mixture: (a) [$Rh(C_2H_4)_2$acac]: **1** = 1:1; (b) [$Rh(C_2H_4)_2$acac]: 1 = 1:2.

Taking into account the complexation behaviour of the parent phosphite [4c], we hypothesized that the lack of complete coordination of 1 could be attributable to the bulkiness of the ligand, which prevents the formation of a disubstituted complex. To confirm this hypothesis a solution of 1 and [Rh(C2H4)2acac] in toluene at P:Rh = 1 M ratio was stirred for 30 min and analyzed by 31P NMR. Much to our delight, the 31P NMR spectrum (Fig. 6) showed the same two doublets, at 151.4 ppm (J ¼ 260 Hz) and at 149.9 ppm (J ¼ 256 Hz), but no signal of the free ligand was detectable. On the basis of these results we can reasonably assume the formation of a monosubstituted complex in both cases, the bulkiness of 1 preventing the coordination of two ligands to the Rh centre also at P:Rh ¼ 2Mratio. The presence of a couple of doublets suggests that two diastereoisomers of the complex are formed, due to the differentMor P screwsense assumed by the biphenyl moiety of the coordinated diamidophosphite. The VT 31P NMR analysis on both samples confirm this hypothesis. In fact, on lowering the temperature until 233 K the signals remain unchanged (Fig. 7), whereas on rising the temperature, the two doublets coalesce at 313 K, and at 343 K a well defined doublet appears at 150.1 ppm (J =258.4 Hz).

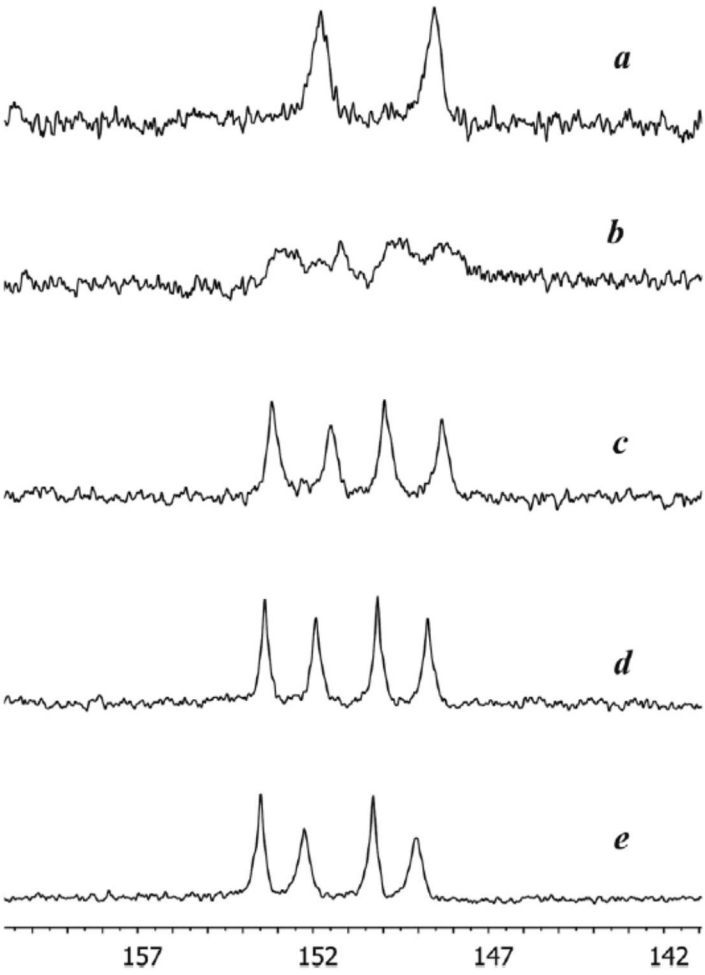


Fig. 7. ^{31}P NMR spectra (80 MHz, toluene-d_8) of the mixture [$Rh(C_2H_4)_2acac$]: **1** = 1:1 at: (a) 343 K, (b) 313 K, (c) 298 K, (d) 273 K, (e) 233 K.

Therefore, the coordination of 1 to [Rh(C2H4)2acac] gives two diastereomeric complexes in slow equilibrium at room temperature and fast interconverting at 343 K, where the two species give only one doublet signal. The integrated areas of the two signals at 233 K gives a diastereomeric ratio of 60:40.

A covalent dinuclear Rh-complex of 1 can be obtained by reacting the ligand with [Rh(C2H4)2Cl]2. Since, also in this case the formation of both mono and disubstituted complexes is possible in principle, [Rh(C2H4)2Cl]2 was reacted with different amounts of 1 in toluene-d8 and the resulting solutions were analyzed by 31P NMR spectroscopy. The 31P NMR spectra of both samples at P:Rh = 1 and at P:Rh = 2 M ratio recorded at 298 K after 30 min (Fig. 8) show no presence of the signal of the free ligand, suggesting that in both cases all the ligand is coordinated to the metallic centre. A doublet signal at 144.2 (J = 178.0 Hz) is present in both spectra; in addition, the spectrum of the sample at P:Rh = 1Mratio shows also a less intense doublet signal at 142.5 ppm (J = 259 Hz). A different situation is found in the 31P NMR spectrum of the sample at P:Rh = 1 M ratio recorded after 16 h (Fig. 8c), where the doublet at 144.2 is absent and only the doublet at 142.5 is clearly visible.

Since in the 31P NMR spectrum of the sample at P:Rh ¼ 2Mratio the signal of the free ligand is absent it is conceivable to deduce that a disubstituted complex is formed. The same complex is also present in the sample at P:Rh ¼ 1Mratio, considering that there is the same signal in the spectrum recorded after 30 min. The less intense signal, which become the only one present in the spectrum recorded after 16 h, can be attributed to a monosubstituted complex, already present in small amount in the just prepared sample, which is the only species after 16 h. This

trend reflects the behaviour observed for the complexation of the parent phosphite [4c]: the formation of a disubstituted complex is preferred for kinetic reasons, but a monosubstituted complex is thermodynamically favourite because of the bulkiness of the ligand. Therefore on the basis of the P:Rh molar ratio and the reaction time it is possible to obtain dinuclear Rh-complexes having different composition. Both mono and disubstituted complexes can be present as diastereomeric mixtures, due to the M-P interconversion and, since at room temperature for both species only one signal is visible, these can be detectable only at lower temperatures. In particular the disubstituted complex can exist as mixtures of three diastereomeric species: two in which the biphenyl groups of the two ligands coordinated at the same metallic centre assume the same screw sense (MM and PP) and the other one where the two ligands have biphenyl groups with opposite screw sense (MP). The VT 31P NMR profile of the disubstituted complex (see supplementary data) shows no changes until 223 K: the doublet signal neither splits nor shifts, suggesting that only one diasereoisomeric complex in which the biphenyl groups of all the ligands assume the same screw sense is formed after coordination.

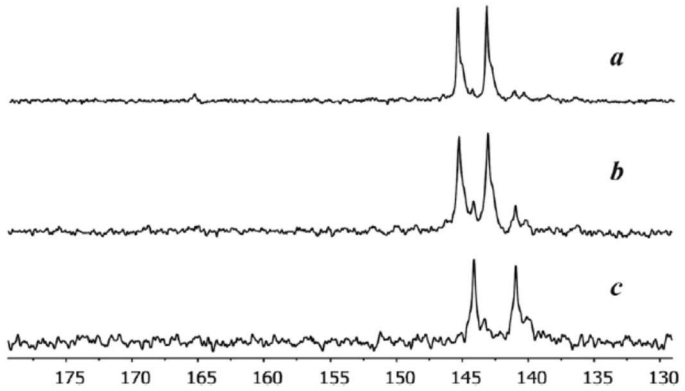


Fig. 8. ^{31}P NMR spectra (80 MHz, toluene-d_8) of the samples: (a) P: Rh = 2 M ratio at room temperature, (b) P: Rh = 1 M ratio at room temperature after 30 min, (c) P: Rh = 1 M ratio after 16 h.

The same trend is observed in the case of the monosubstituted complex: no changes are observed in the 31P NMR spectra recorded at lower temperatures (see supplementary data), suggesting that also in this case a highly prevalent diastereoisomer is formed.

3. Conclusions

The diamidophosphite 1 is able to work as Rh-ligand both for the preparation of ionic and covalent complexes. The reaction with Rh(cod)2BF4 afforded a ionic complex with very high diastereoselectivity, whereas the reaction with [Rh(C2H4)2acac] gave a monosubstituted complex constituted by a mixture of diastereoisomers in slow equilibrium at room temperature and fast interconverting at 343 K. The reaction with the dinuclear covalent complex [Rh(C2H4)2Cl]2 afforded different complexes depending on the P:Rh molar ratio and the reaction time: both monosubstituted and disubstituted complexes with very high diastereoselectivity have been obtained under suitable reaction conditions. On the basis of these results the ionic and the dinuclear covalent complexes can be used as catalytic precursors in asymmetric Rh-catalyzed reactions, such as asymmetric hydrogenations and enantioselective C-C bond formations: these results will be discussed in due course.

4. Experimental section

4.1. General methods and materials

TLC analyses were performed on Merck 60 F254 plates (0.2 mm) and chromatography purifications were carried out with MachereyeNagel silica gel (230e400 mesh) or with Sigma Aldrich neutral alumina (Brockmann I). All the reactions involving sensitive compounds were

carried out under dry N2, in flame-dried glassware. Toluene was refluxed over sodium-benzophenone and distilled before the use. THF was refluxed over potassium benzophenone and distilled before the use. Dichlorometane, triethylamine and pyridine were refluxed over CaH2 and distilled before the use. The hexane was refluxed over Na/K and distilled before the use. PCl3 and 1,5-cyclooctadiene were distilled before the use. Unless otherwise specified, the other compounds were commercially available and used as received. Bile acid derivative 6 was obtained as described previously [5a].
1H NMR spectra were recorded in CDCl3, benezene-d6, toluene-d8 or CD2Cl2 on a 200 MHz NMR spectrometer; the following abbreviations are used: singlet (s), doublet (d), double doublet (dd), triple doublet (td), triplet (t), multiplet (m), broad (br). 13C NMR spectra were recorded in CDCl3 or benezene-d6 at 50 MHz. The temperature was controlled to ±0,1 _C. 1H and 13C NMR chemical shifts (ppm) are referred to TMS as external standard. 31P NMR spectra were recorded in benzene-d6, toluene-d8 or CD2Cl2 at 80 MHz; chemical shifts (ppm) are referred to H3PO4 as external standard.
Circular dichroic (CD) spectra were obtained using a 0.01 or 0.05 cm path length cell and spectropolarimetric grade acetonitrile and CH2Cl2 solvents, at 25 °C. Sample concentrations for CD analyses were in the range from 10^4 to 10^3 M.

4.2. 2,2'-diamino-1,1'-biphenyl, 3

2,2'-dinitro-1,1'-biphenyl 2 (16,7 g, 68 mmol) and 10% Pd/C (2,8 g) were combined with 45 ml of AcOEt in a hydrogen vessel. The vessel was pressurized to 6 atm H2 for 72 h. The slurry was filtered through a plug of celite. Rotary evaporation followed by drying on a vacuum line gave pure product as a light yellow/orange solid (8.81 g, 70%).
1H NMR (CDCl3, 200 MHz, d): 2.12 (br, 4H), 6.83 (dd, 3J ¼ 8.0 Hz, 4J ¼ 1.1 Hz, 2H), 6,87 (td, 3J ¼ 7.4 Hz, 4J ¼ 1.2 Hz, 2H), 7.15 (dd, 3J = 7.5 Hz, 4J = 1.5 Hz, 2H), 7.23 (dd, 3J = 7.8 Hz, 4J = 1.5 Hz, 2H). 13C NMR (CDCl3, 50 MHz, d): 115.8, 119.1, 124.9, 129.1, 131.4, 144.4.

4.3. Diethyl-1,1'- biphenyl-2,2'-diyldicarbamate, 4

To a solution of diamine 3 (8.17 g, 44 mmol) in toluene (225 ml) and pyridine (32.6 ml) under N2, cooled to 0 _C, was added a solution of ethyl chloroformate (10.8 ml, 113 mmol) in oluene (25 ml). The reaction mixture was warmed to room temperature and stirred overnight. The reaction was subsequently quenched by addition of 2 N KOH (300 ml), the organic layer was separated and washed with 10% HCl (3x 30 ml) and the aqueous layer was extracted with toluene (3 x 80 ml). The organic layers were combined and dried over anhydrous Na2SO4. After removing the solvent in vacuo and recrystallization from CH2Cl2/hexane, pure 4 was obtained as a white solid (10.9 g, 75%).
1H NMR (CDCl3, 200 MHz, d): 1.26 (t, J ¼ 7.10 Hz, 6H), 4.16 (q, J ¼ 7.16 Hz, 4H), 6.34 (br, 2H), 7.14e7.23 (m, 4H), 7.39e7.53 (m, 2H), 8.23 (d, 3J ¼ 8.1 Hz, 2H).

4.4. N,N'-dimethyl-2,'diamino-1,10-biphenyl, 5

To a stirred suspension of LiAlH4 (8 g, 211 mmol) in THF (200 ml) under N2, cooled to 0 °C, the dicarbamate 4 (10.9 g, 33 mmol) in THF solution (50 ml) was slowly added via dropping funnel. The reaction mixture was subsequently refluxed for 4 h, then, was cooled to 0 °C and the excess of LiAlH4 was quenched with water. The grey precipitate was filtered off and washed with diethyl ether (3 x50 ml). The filtrate and washings were combined and dried over anhydrous Na2SO4. The solvent was removed at reduce pressure obtaining the diamine 5 (5.3 g, 75%) as a white solid.
1H NMR (CDCl3, 200 MHz, d): 2.22 (s, 6H), 3.56 (br, 2H), 6.55 (dd, 3J = 8.1 Hz, 4J = 0.7 Hz, 2H), 6.79 (td, 3J = 7.4 Hz, 4J =1.2 Hz, 2H), 7.11-7.31 (m, 4H).

13C NMR (CDCl3, 50 MHz, d): 30.2, 109.8, 117.1, 124.3, 129.3, 131.1, 147.2.

4.5. Diamidophosphite 1

To a solution of bile acid derivative 6 (0.5 g, 1.11 mmol) in dry dichlorometane (6 ml), under N2, was added PCl3 (0.29 ml, 3.34 mmol). The reaction mixturewas subsequently stirred at room temperature for 24 h. After removing the solvent at reduced pressure, the crude product was dissolved in dry toluene (2.5 ml) and a solution of 5 (197 mg, 0.93 mmol) and triethylamine (0.47 ml, 3.34 mmol) in dry toluene (3 ml) was added dropwise under N2.

The reaction mixture was subsequently refluxed for 16 h, then the suspension was cooled to room temperature and dry hexane was added (5 ml). The reaction mixture was filtered under N2 and the solvent removed under reduced pressure. The crude product was dissolved in dry dichlorometane and was purified by filtration under N2 on a pad of neutral alumina (3 g, Brockmann I), obtaining pure diamidophosphite 1 (0.316 g, 50%) as a white solid.

1H NMR (benzene-d6, 600 MHz, d): 0.54 (s, 18-CH3, 3H), 0.74 (s, 19-CH3, 3H), 0.96 (d, 21-CH3, 3H), 1.03-1.92 (m, 24H), 1.65 (s, OC(O) CH3, 3H), 2.09-2.29 (m, 2H), 2.76 (d, 3J = 12.0 Hz, -NCH3, 3H), 2.83 (d, 3J = 11.6 Hz, -NCH3, 3H), 3.33 (s, -OCH3, 3H), 4.25 (m,12-CH, 1H),
4.77 (m, 3-CH, 1H), 6.99 (dd, 3J = 7.32 Hz, 4J = 1.25 Hz, 2H), 7.08-7.16 (m, 4H), 7.22 (dd, 3J = 7.60 Hz, 4J = 1.45 Hz, 1H), 7.26 (dd, 3J = 7.60 Hz, 4J = 1.45 Hz, 1H).

13C NMR (50 MHz, benzene-d6) δ ppm: 12.8, 18.1, 18.2, 21.1, 23.2, 24.3, 26.7, 27.0, 27.1, 27.4, 27.5; 28.1, 31.3, 31.4, 32.6, 33.9, 34.6, 35.4, 36.1, 36.3, 37.3 (d, J = 5.2 Hz), 38.0 (d, J = 6.3 Hz), 42.1, 46.4, 47.5, 47.6, 48.2, 51.0, 74.0, 77.5 (d, J = 11.7 Hz),123.6 (d, J = 16.0 Hz), 124.5 (d, J = 15.8 Hz), 130.3, 130.5, 137.9, 169.6, 173.7.

31P NMR (80 MHz, benzene-d6, δ ppm: 168.2.

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