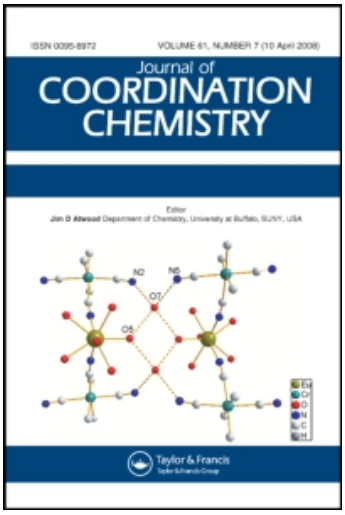

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Synthetic and spectroscopic characterization of Rh(I)-(S)-amino acid complexes with diphosphine and triphosphine ligands

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Synthetic and spectroscopic characterization of Rh(I)-(*S*)-amino acid complexes with diphosphine and triphosphine ligands

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Reaction of [Rh(η^4-cod)(*S*)-amino-acidato] ((*S*)-amino acidate = (*S*)-O_2C-CHR-NH_2; cod = cycloocta-1,5-diene) with 1,2-*bis*(diphenylphosphino)ethane (dppe) affords the ionic [Rh(dppe)$_2$]{(*S*)-O_2C-CHR-NH_2} (R = Me, **I**; Ph, **II**) complexes. Reactions with 1,3-*bis*(diphenylphosphino)propane (dppp) or 2,2,2-*tris*(diphenylphosphinomethyl)ethane (triphos) give the neutral [Rh(dppp){(*S*)-O_2C-CHR-NH_2}] (R = Me, **III**; Ph, **IV**) or [Rh(η^2-triphos){(*S*)-O_2C-CHR-NH_2}] (R = Me, **V**; Ph, **VI**) complexes. The complexes are characterized by elemental analysis, UV–Vis-, IR-, ^{1}H/^{31}P{^{1}H} NMR- and mass-spectroscopy. Two molecules of dppe coordinate to the Rh(I) symmetrically by replacing both cod and (*S*)-amino acidate to give **I**–**II**. Only one molecule of dppp (or triphos) coordinate to the Rh(I) asymmetrically by replacing only cod to give **III**–**VI**. Two diastereomeric Rh(I)-complexes are present in **V** and **VI**. The results further suggest that the ligands are arranged in a distorted square planar geometry around the Rh(I) centre. The use of triphos instead of dppe or dppp yields the same coordination sphere.

Keywords: Rh(η4-cod)-complexes; (*S*)-amino acids; Diphosphine and triphosphine; Diastereomers

1. Introduction

Metal complexes with amino acids or peptides have been extensively studied for their potential applications as *chiral* catalysts [1, 2]; synthesis and studies of Rh(I)-amino acids complexes have shown considerable interests along the line of *chiral* catalysis. Singh first reported the syntheses of Rh(I)-amino acids complexes containing CO, PPh_3 and $AsPh_3$ ligands [3]. Afterwards, Marko synthesised the [Rh(amino acidato)$(CO)_2$] complexes starting from the dimeric [Rh(η^4-cod)$(O_2CR)]_2$ *via* the formation of intermediate [Rh(η^4-cod)(amino acidato)] complexes [4]. Beck reported the synthesis and crystal structures of analogous [Rh(L)$(CO)_2$] (L = L-aziridin-2-carboxylato) [5] and [Ru(AA)(L)]$^+$ + (AA = amino acidato; L = 2,7-dimethylocta-2,6-dien-1,8-diyl) [6] complexes. Few efforts to synthesise the Rh(I)-amino acids complexes containing the

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phosphorous atoms as donor ligands were reported. In fact, Beck first reported the synthesis, spectroscopy and crystal structures of Rh(I)-(*S*/*R*)-amino acids complexes with phosphine, [Rh(AA)(CO)(PPh_3)] [7]. However, the synthesis of Rh(I)-diphosphine complexes containing dines, (*Z*)-α- acetamidocinnamic acid and its ester derivatives, dehydrodipeptides, etc. as co-ligands have drawn much attention for their potential applications as *chiral* catalysts in several asymmetric hydrogenation reactions [8–12].

Recently, we focused our attention on Rh(η^4-cod)-complexes with *chiral*-amino acids and *chiral*-amino alcohols as co-ligands starting from the dinuclear [Rh(η^4-cod)(O_2CMe)]$_2$ [13]. We reported the synthesis, spectroscoy and crystal structures of monomeric Rh(η^4-cod)-complexes with *chiral*-amino acids or *chiral*-amino alcohols, [Rh(η^4-cod)(AA)] (AA = (*S*)-amino acidato = L-alaninato, *S*-2-amino-2-phenylacetato, *N*-methylglycinato, *N*-phenylglycinato) or [Rh(η^4-cod){(*S*)-amino alcohols)}](O_2CMe) [13a]. Similarly, the enantiopure Schiff bases, (*R*)-*N*-(X)ethylsalicylaldimine, readily react with [Rh(η^4-cod)(O_2CMe)]$_2$ to afford the monomeric [Rh(η^4-cod){(*R*)-*N*-(X)ethylsalicylaldiminato}] complexes [14]. These complexes are particularly useful as precursors due to the possibility to substitute the (cod) with phosphorus donor ligands such as diphosphine (diphos) and triphosphine (triphos) to form neutral complexes of the type, [Rh(diphos/triphos){(*S*)-amino acidato)}] or [Rh(diphos/triphos){(*R*)-*N*-(X)ethylsalicylaldiminato}]; or, if possible, to displace both cod and (*S*)-amino acidate or (*R*)-*N*-(X)ethylsalicylaldiminate ligands to form the cationic [Rh(diphos/triphos$)_2$](X) complexes. Thus, we attempted to synthesise the analogous Rh(I)-(S)-amino acids complexes containing diphos and triphos as co-ligands [15]. Such ligands, exercise strong influences on the stereochemistry as well as the reactivity of Rh(I)-complexes, especially for their uses as *chiral* catalysts in asymmetric hydrogenation reactions.

The complexes have been synthesised from the reaction of [Rh(η4-cod)(AA)] (AA = (*S*)-amino acidato = O_2C-CHR-NH_2) with 1,2-*bis*(diphenylphosphino)ethane (dppe), 1,3-*bis*(diphenylphosphino)propane (dppp) and 2,2,2-*tris*(diphenylphosphinomethyl)ethane (triphos), respectively. The present paper reports results of synthetic and spectroscopic studies of [Rh(dppe$)_2$]{(S)-O_2C-CHR-NH_2} (R = Me, **I**; Ph, **II**), [Rh(dppp){(*S*)-O_2C-CHR-NH_2}] (R = Me, **III**; Ph, **IV**) and [Rh(η^2-triphos){(*S*)-O_2C-CHR-NH_2}] (R = Me, **V**; Ph, **VI**) complexes.

2. Experimental

2.1. *Materials and methods*

All reactions were carried out under an atmosphere of nitrogen using Schlenk techniques. The solvents (toluene and petroleum ether, 40/60) used were purified and distilled over Na under nitrogen. The 1,2-*bis*(diphenylphosphino)ethane (dppe) and 1,3-*bis*(diphenylphosphino)propane (dppp) were used as received from Lancaster. The compounds $RhCl_3 \cdot 3H_2O$ (Wako), 1,5-cyclooctadiene (Wako), (*S*)-amino acids such as L-alanine and (*S*)-2-amino-2-phenylacetic acids (L-Phenylglycine) (Lancaster) were used as received. The 2,2,2-*tris*(diphenylphosphinomethyl)ethane (triphos) was synthesised according to literature [16]. The starting mononuclear [Rh(η^4-cod){(*S*)-O_2C-CHR-NH_2}] (R = Me and Ph) complexes were synthesised according to our previous literature [13].

UV–Vis spectra of the complexes were recorded with a Shimadzu UV 3150 spectrophotometer in CH_2Cl_2 at room temperature. IR-spectra were recorded as KBr disks and in Nujol on a Bruker IFS 66 FT-IR Spectrometer at ambient temperature. NMR-spectra were run on a Bruker AC DPX 200 spectrometer operating at 200 MHz (^{1}H) and 81 MHz (^{31}P{^{1}H}) at 25°C. NMR grade solvents CD_2Cl_2 and toluene-$d_8$8 were used as internal standards and deoxygenated prior to use. ^{1}H NMR chemical shifts are expressed in ppm relative to $SiMe_4$ ($\delta = 0$) and ^{31}P{^{1}H} NMR to 85% H_3PO_4 (^{31}P $\delta = 0$). FAB-MS (positive mode): Finnigan MAT 8400 with data system SS 300, matrix: *m*-nitrobenzyl alcohol (NBA), ionisation temperature 150°C. Though several attempts were made to grow single crystals of the complexes for X-ray measurements, unfortunately none succeeded.

2.2. *Syntheses of the complexes*

[Rh(dppe)$_2$]{(*S*)-O$_2$C-CHMe-NH$_2$} (I) and [Rh(dppe)$_2$]{(*S*)-O$_2$C-CHPh-NH$_2$} (II). 1,2-*bis*(diphenylphosphino)ethane (dppe) (167 mg, 0.42 mmol) was dissolved in 5 mL toluene and the solution was poured into the yellowish suspension of [Rh(η^4-cod){(*S*)-O$_2$C-CHMe-NH$_2$}] (62.2 mg, 0.21 mmol) in 10 mL toluene. Stirring the solution for 4–5 h at room temperature, yellow precipitate was formed. The precipitate was filtered off and washed twice with petroleum ether (5 mL in each). The products were dried in *vacuo* (0.01–0.02 mbar) at 40°C giving the yellow complex **I**. The same procedure was followed for **II** by using [Rh(η^4-cod){(*S*)-O$_2$C-CHPh-NH$_2$}].

Complex I. Yield 152 mg (74% w. r. t. [Rh(η^4-cod){(*S*)-O$_2$C-CHMe-NH$_2$}]). Anal. Calcd for $C_{55}H_{56}P_4NO_2Rh$ (987.22): C, 66.85; H, 5.51; N, 1.42. Found: C, 68.42; H, 5.38; N, 1.23%. UV–Vis (2.20×10^{-4} mol dm^{-3}, CH_2Cl_2): λ_{max} (ε_{max}) = 401 nm (4032 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (200 MHz, CD_2Cl_2) (ppm) δ: 1.79 (d, $J = 7$ Hz, 3H, C*H*$_3$); 2.13 (m, 8H, CH_2P); 2.44 (m, 2H, N*H*, C*H*); 2.63 (m, 1H, N*H*); 7.20–7.60 (m, 40H, *H*-Ph). MS (FAB, Pos) [*m*/*z* (%)]: 915 (8) [Rh(dppe)$_2$ + O]$^+$, 899 (100) [Rh(dppe)$_2$]$^+$, 822 (5) [Rh(dppe)$_2$ − Ph]$^+$, 501 (25) [Rh(dppe)]$^+$, 395 (10) [dppe − H$_2$]$^+$ and 317 (18) [dppe − Ph − H$_2$ − H]$^+$.

Complex II. dppe (172 mg, 0.43 mmol), [Rh(η^4-cod){(*S*)-O$_2$C-CHPh-NH$_2$}] (76 mg, 0.21 mmol), yield 155 mg (70% w. r. t. [Rh(η^4-cod){(*S*)-O$_2$C-CHPh-NH$_2$}]). Anal. Calcd for $C_{60}H_{56}P_4NO_2Rh$ (1049.91): C, 68.64; H, 5.38; N, 1.33. Found: C, 68.11; H, 5.52; N, 1.94%. UV–Vis (2.31×10^{-4} mol dm^{-3}, CH_2Cl_2): λ_{max} (ε_{max}) = 408 nm (4112 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (200 MHz, CD_2Cl_2)(ppm) δ: 2.13 (s, 8H, C*H*$_2$P); 2.41 (m, 2H, N*H* and C*H*); 2.65 (m, 1H, N*H*); 7.20–7.66 (m, 45H, *H*-Ph). MS (FAB, Pos) [*m*/*z* (%)]: 915 (5) [Rh(dppe)$_2$ + O]$^+$, 899 (100) [Rh(dppe)$_2$]$^+$, 822 (5) [Rh(dppe)$_2$ − Ph]$^+$, 501 (23) [Rh(dppe)]$^+$, 395 (10) [dppe − H$_2$]$^+$ and 317 (25) [dppe − Ph − H$_2$ − H]$^+$.

[Rh(dppp){(*S*)-O$_2$C-CHMe-NH$_2$}] (III) and [Rh(dppp){(*S*)-O$_2$C-CHPh-NH$_2$}] (IV). 1,3-*bis*(Diphenylphosphino)propane (dppp) (208 mg, 0.50 mmol) was dissolved in 10 mL toluene and the solution was poured into the yellowish suspension of [Rt(η^4-cod){(*S*)-O$_2$C-CHMe-NH$_2$}] (150 mg, 0.50 mmol) in 15 mL toluene. The suspension was stirred for 3–4 h at room temperature, changing to a bright yellow clear solution. The solution was filtered and dried in vacuo (0.01–0.02 mbar) at 40°C giving the bright yellow complex **III**. The same procedure was followed for **IV** by using [Rh(η^4-cod){(*S*)-O$_2$C-CHPh-NH$_2$}]. The complexes are very sensitive to air and readily oxidatize.

Complex III. Yield 220 mg (73%). Anal. Calcd for $C_{30}H_{32}P_2NO_2Rh$ (603.09): C, 59.69; H, 5.35; N, 2.32. Found: C, 59.21; H, 5.25; N 2.12%. UV-Vis. (2.50×10^{-4} mol dm^{-3}, CH_2Cl_2): λ_{max} (ε_{max}) = 398 nm (4157 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (200 MHz, CD_2Cl_2) (ppm) δ: 1.31 (d, J = 7 Hz, 3H, C*H*$_3$); 1.74 (m, 2H, C*H*$_2$); 2.33 (m, 5H, N*H*, C*H*$_2$P); 2.51 (m, 1H, NH); 3.31 (m, 1H, C*H*); 7.17–7.69 (m, 20H, *H*-Ph). MS (FAB, Pos) [*m*/*z* (%)]: 1046 (5) [Rh(dppp + O)$_2$(AA) − H]$^+$, 958 (25) [Rh(dppp + O)$_2$ − H$_2$]$^+$, 942 (10) [Rh(dppp)$_2$ + O − H$_2$]$^+$, 638 (15) [M + (H$_2$O)$_2$]$^+$, 618 (15) [M + O]$^+$, 603 (25) [M + H]$^+$, 602 (25) [M]$^+$, 531 (24) [Rh(dppp) + O]$^+$, 515 (100) [Rh(dppp)]$^+$, 445 (20) [dppp + O$_2$ + H]$^+$, 438 (25) [Rh(dppp) − Ph]$^+$, 412 (15) [dppp + H]$^+$, 411 (6) [dppp]$^+$, 334 (12) [dppp − Ph]$^+$, 318 (20) [dppp + O − PPh − H]$^+$ and 303 (10) [dppp − PPh]$^+$ (M$^+$ = [Rh(dppp)(AA)]$^+$; AA = (S)-O$_2$C-CHCH$_3$-NH$_2$).

Complex IV. dppp (210 mg, 0.51 mmol), [Rh(η^4-cod){(S)-O$_2$C-CHPh-NH$_2$}] (185 mg, 0.51 mmol), yield 252 mg (72%). Anal. Calcd for $C_{35}H_{34}P_2NO_2Rh \cdot H_2O$ (683.12): C, 61.48; H, 5.31; N, 2.05. Found: C, 61.26; H, 5.75; N 1.71%. UV–Vis (2.33×10^{-4} mol dm^{-3}, CH_2Cl_2): λ_{max} (ε_{max}) = 403 nm (4178 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (200 MHz, CD_2Cl_2) (ppm) δ 1.62 (m, 2H, C*H*$_2$); 2.36 (m, 4H, CH$_2$P); 2.89 (m, 1H, N*H*); 3.85 (m, 1H, C*H*); 4.35 (m, 1H, N*H*); 7.16–7.73 (m, 25H, *H*-Ph). MS (FAB, Pos) [*m*/*z* (%)]: 958 (15) [Rh(dppp + O)$_2$ − H$_2$]$^+$, 944 (5) [Rh(dppp)$_2$ + O]$^+$, 680 (10) [M + O]$^+$, 665 (12) [M + H]$^+$, 664 (10) [M]$^+$, 638 (18) [M + H$_2$ − CO]$^+$, 620 (20) [M − CO$_2$]$^+$, 531 (50) [Rh(dppp) + O]$^+$, 515 (100) [Rh(dppp)]$^+$, 445 (70) [dppp + O$_2$ + H]$^+$, 438 (22) [Rh(dppp) − Ph]$^+$, 412 (30) [dppp + H]$^+$, 411 (10) [dppp]$^+$, 335 (22) [dppp − Ph + H]$^+$, 318 (33) [dppp + O − PPh − H]$^+$ and 303 (30) [dppp − PPh]$^+$ (M$^+$ = [Rh(dppp)(AA)]$^+$; AA = (*S*)-O$_2$C-CHPh-NH$_2$).

[Rh(η^2-triphos){(*S*)-O$_2$C-CHMe-NH$_2$}] (V) and [Rh(η^2-triphos){(*S*)-O$_2$C-CHPh-NH$_2$}] (VI). 2,2,2-*tris*(diphenylphosphinomethyl)ethane (triphos) (189 mg, 0.30 mmol) was dissolved in 10 mL toluene and the solution was poured into the yellowish suspension of [Rh(η^4-cod){(*S*)-O$_2$C-CHMe-NH$_2$}] (90 mg, 0.30 mmol) in 15 mL toluene. The suspension was stirred for 3–4 h at room temperature changing to a bright yellow clear solution. The solution was filtered and dried in vacuo at 45°C. The product was then washed twice with petroleum ether (5 mL), dried again in vacuo (0.01–0.02 mbar) at 45°C obtaining the bright yellow complex **V**. The same procedure was followed for **VI** by using [Rh(η^4-cod){(*S*)-O$_2$C-CHPh-NH$_2$}]. The complexes are very sensitive to air, readily oxidatizing.

Complex V. Yield 185 mg (75%). Anal. Calcd for $C_{44}H_{45}P_3NO_2Rh$ (815.17): C, 64.77; H, 5.56; N 1.72. Found: C, 64.34; H, 5.28; N, 1.43%. UV–Vis. (2.13×10^{-4} mol dm^{-3}, CH_2Cl_2): λ_{max} (ε_{max}) = 410 nm (4231 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (200 MHz, CD_2Cl_2) (ppm) δ 1.37 (d, *J* = 7 Hz, 3H, CH$_3$); 1.67 (d, *J* = 8 Hz, 3H, C*H*$_3$triphos); 2.24 (s, 4H, C*H*$_2$PRh); 2.60 (s, 2H, C*H*$_2$P); 2.90 (m, 2H, N*H*, C*H*); 3.29 (m, 1H, N*H*); 7.20–7.61 (m, 30H, *H*-Ph). MS (FAB, Pos) [*m*/*z* (%)]: 865 (30) [M + H$_2$O + O$_2$ + H]$^+$, 847 (35) [M + O$_2$ + H]$^+$, 831 (40) [M + O + H]$^+$, 815 (50) [M + H]$^+$, 741 (100) [Rh(η^2-triphos) + O − H$_2$]$^+$, 727 (60) [Rh(η^2-triphos)]$^+$, 649 (50) [Rh(η^2-triphos)-Ph-H]$^+$, 619 (20) [(triphos)-2H$_2$]$^+$, 541 (15) [(triphos)-Ph-2H$_2$-H]$^+$ and 459 (60) [(triphos)-Ph$_2$-5H$_2$]$^+$ (M$^+$ = [Rh(η^2-triphos)(AA)]$^+$; AA = (*S*)-O$_2$C-CHMe-NH$_2$).

Complex VI. triphos (210 mg, 0.34 mmol), [Rh(η^4-cod){(*S*)-O$_2$C-CHPh-NH$_2$}] (122 mg, 0.34 mmol), yield 210 mg (71%). Anal. Calcd for $C_{49}H_{47}P_3NO_2Rh$ (877.19): C, 67.03; H, 5.40; N 1.60. Found: C, 68.04; H, 5.88; N, 1.53%. UV–Vis

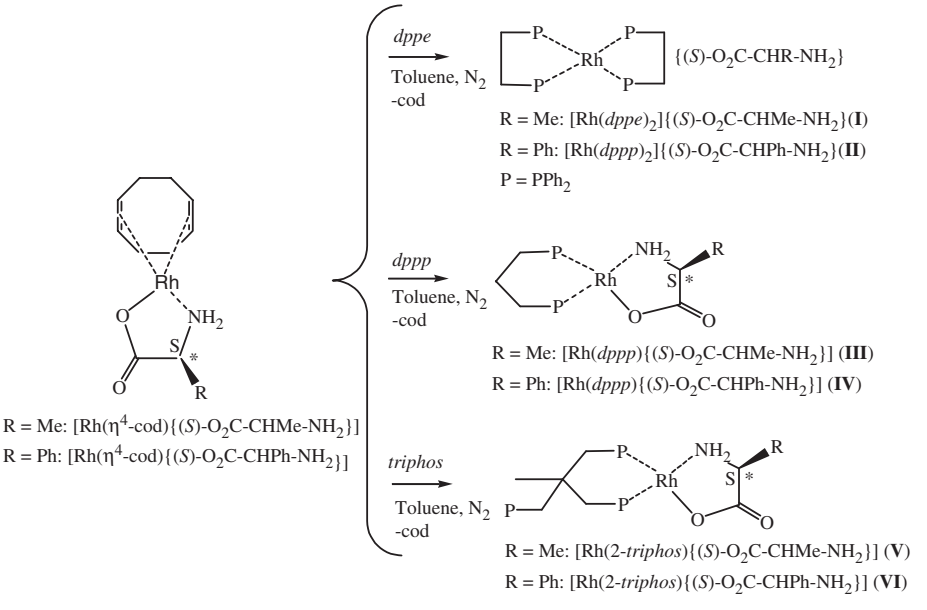
(2.33×10^{-4} mol dm^{-3}, CH_2Cl_2): λ_{max} (ε_{max}) = 414 nm (4271 dm^3 mol^{-1} cm^{-1}). ^{1}H NMR (200 MHz, CD_2Cl_2) (ppm) δ: 1.64 (d, 3H, J = 8 Hz, CH_3triphos); 2.28 (d, 4H, J = 7 Hz, CH_2PRh); 2.55 (m, 2H, CH_2P); 2.86 (m, 2H, NH and CH); 4.33 (m, 1H, NH); 7.32–7.61 (m, 35H, H-Ph). MS (FAB, Pos) [m/z (%)]: 894 (20) $[M + H_2O]^+$, 892 (15) $[M + O]^+$, 876 (35) $[M]^+$, 875 (60) $[M - H]^+$, 743 (65) [Rh(η^2-triphos) + O]$^+$ 727 (100) [Rh(η^2-triphos)]$^+$, 665 (30) [Rh(η^2-triphos) + O-Ph-H]$^+$, 650 (20) [Rh(η^2-triphos)-Ph]$^+$, 541 (55) [(triphos)-Ph-2H$_2$-H]$^+$, 465 (60) [(triphos)-Ph$_2$-2H$_2$]$^+$, 395 (40) [(triphos)-Ph$_3$ + H$_2$]$^+$, 392 (22) [(triphos)-Ph$_3$]$^+$ and 317 (65) [(triphos) − Ph$_4$ + H$_2$]$^+$ (M^+ = [Rh(dppp)(AA)]$^+$; AA = (S)-O$_2$C-CHPh-NH$_2$).

3. Results and discussion

Reaction of [Rh(η^4-cod){(S)-O$_2$C-CHR-NH$_2$}] (cod = cycloocta-1,5-diene) with 1,2-*bis*(diphenylphosphino)ethane (dppe) affords the ionic [Rh(dppe)$_2$]{(S)-O$_2$C-CHR-NH$_2$} (R = Me, **I**; Ph, **II**) complexes in toluene under nitrogen. Reactions with 1,3-*bis*(diphenylphosphino)propane (dppp) or 2,2,2-*tris*(diphenylphosphinomethyl) ethane (triphos) give neutral [Rh(dppp){(S)-O$_2$C-CHR-NH$_2$}] (R = Me, **III**; Ph, **IV**) or [Rh(η^2-triphos){(S)-O$_2$C-CHR-NH$_2$}] (R = Me, **V**; Ph, **VI**) complexes (scheme 1). Mass spectra are dominated by the parent ion peak including the main peak for [Rh(dppe/dppp/η^2-triphos)]$^+$ species and peaks for several oxidative adducts.

3.1. *UV–Vis spectroscopy*

Electronic spectra of the complexes show a very strong band at <350 nm, associated to the intraligand $\pi \rightarrow \pi^*$ transitions, and a strong broad band at 350–500 nm



Scheme 1. Synthetic route to and formula of the complexes **I**–**VI**.

with absorbtion maxima at $\lambda_{max} = 398–414\,nm$ ($\varepsilon_{max} = 4032–4271\,dm^3 \cdot mol^{-1}\,cm^{-1}$). The latter are assigned to the metal-to-ligand charge transfer (*mlct*) transition based on the formation of [Rh(dppe/dppp/η^2-triphos)]$^+$ and [Rh{(*S*)-O_2C-CHR-NH_2}] [13, 15, 17, 18].

3.2. *IR spectroscopy*

The characteristic IR-bands of the complexes are summarized in table 1; assignments were made based on the literature [3–7, 13, 15]. The strong carbonyl band ($^{\nu}C{=}O_{asy}$) of free amino acid (usually observed at 1615–1620 cm^{-1}) shifts to higher frequencies upon coordination to Rh(I), and observed at 1630–1650 cm^{-1} (table 1) in **III–VI**. The same band is found at 1620–1625 cm^{-1} in the starting complexes, [Rh(η^4-cod)(AA)] (AA = L-alaninato, *S*-2-amino-2-phenylacetato, *N*-methylglycinato, *N*-phenylglycinato) [13]. Further, these complexes show two kinds of $^{\nu}$N–H stretching bands at the range of 3260–3200 cm^{-1} (asymmetric) and 3140–3100 cm^{-1} (symmetric). These bands shift to higher frequencies upon coordination of dppp/triphos to the [Rh-{(*S*)-amino acidato)}] by replacing cod, observed at 3340–3310 cm^{-1} and 3270–3210 cm^{-1} in **III–VI** (table 1). However, **I–II** show the $^{\nu}C{=}O_{asy}$ and $^{\nu}$N-H bands at 1627–1625 cm^{-1} and 3150–3141 cm^{-1} (table 1), respectively. The $^{\nu}$C–H and $^{\delta}$N–H (deformation) vibrations appear as strong bands at 3052–3058 cm^{-1} and 1578–1600 cm^{-1}. The vibrational results strongly suggest that the (*S*)-amino acidates are bound to [Rh(dppp/η^2-triphos)]$^+$ by nitrogen and oxygen atoms as a *N*,*O*-chelate in **III–VI**, as depicted in the scheme 1, while remaining as counter anion in **I–II**.

3.3. *NMR-spectroscopy*

^{1}H NMR spectra of **I** and **II** show the proton signals associated to dppe as well as the (*S*)-amino acidates (see experimental section) [12, 13, 15, 18]. No proton signals associated to the [Rh(η^4-cod)]$^+$ moiety are observed, as found in the starting complexes, indicating the replacement of the cod by the dppe in the complexes. $^{31}P\{^1H\}$ NMR spectra of **I** and **II** are identical and show a doublet at 57.7 ppm (see table 2 and figure 1), indicating that the P atoms are coordinated and coupled to the Rh(I) symmetrically. The relatively larger downfield shift of P signals, in comparison to other complexes ($\delta < 45$ ppm), is typical of dppe chelation in the cationic [Rh(dppe)$_2$](X) systems [12, 17, 18]. The four equivalent P atoms from two molecules of dppe are coordinated to the Rh(I) from both sides in a distorted square planar geometry,

Table 1. IR data (cm^{-1}, KBr*) of the complexes at ambient temperature.

Complexes	$^{\nu}$N–H	$^{\nu}$C–H	$^{\nu}$C = 0	$^{\delta}$N–H
I	3150m	3056s	1625vs	1585sh
II	3141m	3054s	1627vs	1588sh
III	3330m, 3210w (3326m, 3206w)	3052s (3048s)	1637vs (1635 vs)	1585sh (1590sh)
IV	3326m, 3242w (3313m, 3206w)	3055s (3052s)	1643vs (1647vs)	1590sh (1600s)
V	3336m, 3266w	3054s	1637vs	1586sh
VI	3332m, 3263w	3053s	1649vs	1589sh

*Values in parentheses are taken in Nujol; vs: very strong, s: strong, m: medium, w: weak, sh: shoulder.

Table 2. $^{31}P\{^1H\}$ NMR data for the complexes.

Complexes	$\delta^{31}P\{^1H\}$ (ppm)	References
$[Rh(dppe)_2]\{(S)\text{-}O_2C\text{-}CHMe\text{-}NH_2\}$ (**I**)[a]	57.7 ($J_{P-Rh} = 133$ Hz)	This work
$[Rh(dppe)_2]\{(S)\text{-}O_2C\text{-}CHPh\text{-}NH_2\}$ (**II**)[a]	57.7 ($J_{P-Rh} = 133$ Hz)	This work
$[Rh(dppe)_2]\{(S)$-N-acetylphenylalanate$\}$	56.3 ($J_{P-Rh} = 133$ Hz)	[12]
$[Rh(dppe)_2](Q)$	58.2 ($J_{P-Rh} = 132$Hz)	[18]
$[Rh(dppp)\{(S)\text{-}O_2C\text{-}CHMe\text{-}NH_2\}]$ (**III**)[b]	31.1 ($J_{P-RhN} = 170$ Hz, $J_{P-P} = 70$ Hz); 43.9 ($J_{P-RhO} = 173$ Hz, $J_{P-P} = 70$ Hz)	This work
$[Rh(dppp)\{(S)\text{-}O_2C\text{-}CHPh\text{-}NH_2\}]$ (**IV**)[b]	30.7 ($J_{P-RhN} = 169$ Hz, $J_{P-P} = 70$ Hz); 43.0 ($J_{P-RhO} = 172$ Hz) ($J_{P-P} = 70$ Hz)	This work
[Rh(dppp)(Q)]	36.3 ($J_{P-Rh} = 186$ Hz, $J_{P-P} = 76$ Hz); 41.3 ($J_{P-Rh} = 185$ Hz, $J_{P-P} = 76$ Hz)	[18]
$[Rh(\eta^2\text{-[triphos)}\ \{(S)\text{-}O_2C\text{-}CHMe\text{-}NH_2\}]$ (**V**)[a]	−28.4, 29.8, 30.0 ($J_{P-RhN} = 172$ Hz, $J_{P-P} = 70$ Hz); 44.7, 45.0 ($J_{P-RhO} = 172$ Hz, $J_{P-P} = 70$ Hz)	This work
$[Rh(\eta^2\text{-triphos})\{(S)\text{-}O_2C\text{-}CHPh\text{-}NH_2\}]$ (**VI**)[a]	− 28.3, 31.0, 31.1 ($J_{P-RhN} = 171$ Hz, $J_{P-P} = 70$ Hz); 44.5, 44.8 ($J_{P-RhO} = 172$ Hz, $J_{P-P} = 70$ Hz)	This work
$[Rh(dppp)(L)](BF_4)$	17.5, 18.2 ($J_{P-RhN} = 131$ Hz, $J_{P-P} = 48$ Hz); 34.1, 34.3 ($J_{P-RhN} = 145$ Hz, $J_{P-P} = 51$ Hz)	[10]
$[Rh(dppp\text{-}AE)(L)](BF_4)$	22.5, 22.7 ($J_{P-RhN} = 132$ Hz, $J_{P-P} = 49$ Hz); 37.0, 37.1 ($J_{P-RhN} = 144$ Hz, $J_{P-P} = 49$ Hz)	[10]

[a]In CD_2Cl_2; [b]in toluene-d_8.
Q = 1-Phenyl-3-methyl-4-(2-furanoyl)-pyrazolonate-5-one L = *R*-(*Z*)-α-acetamidocinnamic acid.

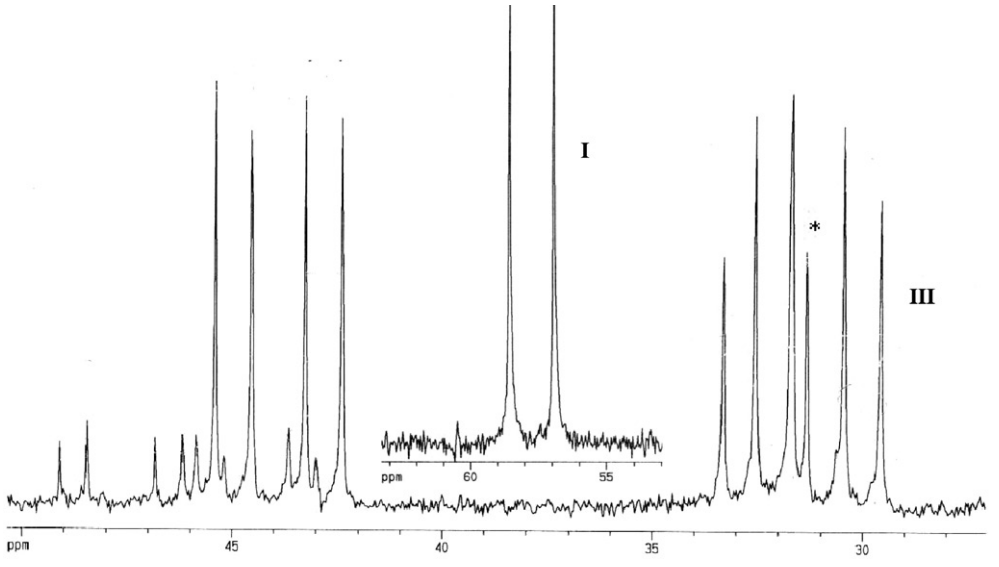


Figure 1. Typical $^{31}P\{^1H\}$ NMR spectra of **I** and **III**. The asterisked signal due to oxidative adduct of dppp and minor resonance due to $[\{O{=}P(Ph_2)(CH_2)_3P(Ph_2)\}_2Rh\{(S)\text{-}O_2C\text{-}CHMe\text{-}NH_2\}]$ in case of **III**.

as reported from the crystal structure determination of the related $[Rh(dppe)_2](X)$ complexes [12, 17–20]. These results indicate dppe completely replaced the cod and (*S*)-amino acidate forming the cationic $[Rh(dppe)_2]^+$ with the counter anion (*S*)-amino acidate. Addition of equimolar dppe to $[Rh(\eta^4\text{-cod})$(S-amino acidato)] solution

gives the same results. Similar results were reported from reaction of dppe with [Rh(Q)(1,5-cod)] (Q = 1-phenyl-3-methyl-4-(2-furanoyl)-pyrazolonato-5-one) in a ratio of 2 : 1 in benzene, giving [Rh(dppe)$_2$](Q) with a doublet at 58.2 ppm for ^{31}P [18]. Accordingly, reaction of dppe with [Rh(NBD){(*S*)-*N*-acetylphenylalanate}] in a ratio of 2 : 1 in methanol forms [Rh(dppe)$_2$]{(*S*)-*N*-acetylphenylalanate}, showing a doublet at 56.3 ppm [12].

Reactions of dppp or triphos with an equimolar amount of [Rh(η^4-cod)(*S*)-O$_2$C-CHR-NH$_2$}] in toluene give the neutral [Rh(dppp){(*S*)-O$_2$C-CHR-NH$_2$}] (R = Me, **III**; Ph, **IV**) or [Rh(η^2 triphos){(*S*)-O$_2$C-CHR-NH$_2$}] (R = Me, **V**; Ph, **VI**). ^{1}H NMR spectra of the complexes show proton signals associated to dppp or triphos as well as (*S*)-O$_2$C-CHR-NH$_2$ (see experimental section), while no proton signals associated to the [Rh(η^4-cod)]$^+$ moiety are observed [12, 13, 15, 18]. ^{31}P{^{1}H} NMR spectra of **III** and **IV** are similar and show two sets of doublet of doublets (four lines in each) of equal intensities for two non-equivalent phosphorus atoms (see table 2 and figure 1), resulting from coordination and coupling of dppp to Rh(I) asymmetrically. The relatively high field shift of ^{31}P signals (at 31–44 ppm), in comparison to those in **I**–**II** (at 57.7 ppm), is typical of dppp chelation in neutral [Rh(dppp)(X)] complexes [10, 12, 17, 18]. The chemical shift difference between these two signals ($\Delta\delta = 12.3$–12.8) is due to the *trans effect* of the co-ordinated *N*,*O*-chelate on the P resonances [14]. The signals at relatively high magnetic field (at 31 ppm) are assigned to the P atom co-ordinated to the Rh(I) '*trans* to nitrogen' and at low field (at 44 ppm) to the P atom '*trans* to oxygen'. Similarly, the signals at high field correspond to the P atom '*trans* to the olefinic bond' and at low field to the P atom '*trans* to amido oxygen' in [Rh(dppp)(L)](BF$_4$) (L = R-(Z)-α-acetamidocinnamic acid and its esters or dehydrodipeptide and its derivatives) [10] and in [Rh(dppe)(L)](BF$_4$) (L = R-(Z)-α-acetamidocinnamic acid and its esters) [8a,c–d]. Complex **III**, in addition, shows a minor singlet at 33.3 ppm (for O=P(Ph$_2$)–) and two sets of doublets of doublets at 44.9 ppm ($J_{\text{P-RhN}} = 256$ Hz, $J_{\text{P–P}} = 52$ Hz);47.2 ppm ($J_{\text{P–RhO}} = 264$ Hz, $J_{\text{P–P}} = 52$ Hz) (see figure 1), due to formation of [{O=P(Ph$_2$)(CH$_2$)$_3$P(Ph$_2$)}$_2$Rh{(*S*)-O$_2$C-CHMe-NH$_2$}] (where dppp is monodentate). The formation of this species is confirmed by the mass spectral peck at 1046, assigned for [Rh(dppp + O)$_2$(AA) − H]$^+$ (AA = (*S*)-O$_2$C-CHMe-NH$_2$) (see experimental section). Similar results were found from reaction of dppp with [Rh(Q)(1,5-cod)] (Q = 1-phenyl-3-methyl-4-(2-furanoyl)-pyrazolonato-5-one) at a ratio of 1 : 1 in benzene, which affords the neutral [Rh(dppp)(Q)] complex [18]. ^{31}P signals show two sets of doublets of doublets (four lines in each) (see table 2), resulting from coordination and coupling of dppp to the Rh(I) asymmetrically. The X-ray structure of [Rh(dppp)(Q)] shows that the Rh(I) atom is in slightly distorted square-planar coordination due to the oxygen of acylpyrazolonate and to the phosphorus of dppp.

^{31}P{^{1}H} NMR spectra of [Rh(η^2-triphos){(*S*)-O$_2$C-CHR-NH$_2$}] (R = Me, **V**; Ph, **VI**) are quite different from those of **I**–**IV** and show three signals for three non-equivalent P atoms (see table 2). A singlet at −28.4, is assigned for one uncoordinated P atom, while the other two P atoms, coordinate and couple to the Rh(I) asymmetrically with two sets of eight lines (two doublets of doublets in each) of equal intensities (see table 2). In fact, such pattern of P signals (eight lines instead of four lines in **III**–**IV**) indicates the presence of two diastereomeric Rh(I)-complexes (at 1 : 1 ratio) in solution for **V** and **VI**. The prochiral triphos ligand acquires a *chiral* centre on the tertiary carbon atom upon coordination to the [Rh{(*S*)-O$_2$C-CHR-NH$_2$}], affording two diastereomeric Rh(I)-complexes. Similarly, [Rh(dppp)(L)](BF$_4$) and [Rh(dppp-*AE*)(L)](BF$_4$)

(L = *R*-(*Z*)-α-acetamidocinnamic acid) show the ^{31}P signals of two sets of eight lines (see table 2), indicating the presence of diastereomeric Rh(I)-complexes at 1 : 1 ratio in solution [10]. Here, the six-membered chelate ring exists in an equilibrium between λ- and δ-skew conformations [21]. So, the combination of prochiral faces of dehydroamino acid and skew conformations affords two diastereomeric Rh(I)-complexes, showing two sets of eight lines. However, the presence of one uncoordinated P atom at −28.4 ppm indicates that the triphos is bidentate chelate (as η^2-triphos) and hence, does not change the coordination sphere around the Rh(I) centre using triphos instead of dppe or dppp. Complexes **V** and **VI** thus take the distorted square planar symmetry like **I**–**IV**. Further, very minor ^{31}P resonances of complex pattern are observed in the range 13.25–13.35 ppm and 15.01–15.15 ppm, due to formation of oxidative adducts for **V** and **VI**. Formations of these species are confirmed by the presence of several corresponding peaks in the mass spectra.

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