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Mohammed Enamullah<sup>a</sup>

<sup>a</sup> Department of Chemistry, Jahangirnagar University, Dhaka 1342, Bangladesh

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## Synthetic and spectroscopic characterization of [Co(*triphos*)(chiral amino alcoholato)](BPh<sub>4</sub>) complexes

MOHAMMED ENAMULLAH\*

Department of Chemistry, Jahangirnagar University,  
Dhaka 1342, Bangladesh

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2,2,2-Tris(diphenylphosphinomethyl)ethane (*triphos*) coordinates to Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O giving red-violet intermediate [Co(*triphos*)(S)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (S = solvent) in THF/EtOH. The addition of an equimolar amount of chiral amino alcohol (L-alaninol, S-2-phenylglycinol, R-1-amino-2-propanol and (±)-2-amino-1-phenyl-ethanol) and Na(OH) into this solution affords the green [Co(*triphos*)(chiral amino alcoholato)](BF<sub>4</sub>) complexes. The addition of equimolar Na(BPh<sub>4</sub>) precipitates the deep green [Co(*triphos*)(L-alaninolato)](BPh<sub>4</sub>) (1), [Co(*triphos*)(S-2-phenylglycinolato)](BPh<sub>4</sub>) (2), [Co(*triphos*)(R-1-amino-2-propanolato)](BPh<sub>4</sub>) (3), and [Co(*triphos*)(±)-2-amino-1-phenyl-ethanolato)](BPh<sub>4</sub>) (4) complexes, respectively. The complexes are isolated in good yields and characterized by elemental analysis, IR-, UV-Vis-, <sup>1</sup>H-/<sup>31</sup>P-NMR- and mass-spectroscopy. <sup>1</sup>H-/<sup>31</sup>P-NMR results show the paramagnetic nature of the complexes and magnetic moment values are μ<sub>exptl</sub>(μB) = 3.65 (1), 3.78 (2), 3.82 (3), and 3.71 μB (4) in methanol at 25 °C.

**Keywords:** 2,2,2-Tris(diphenylphosphinomethyl)ethane (*triphos*); Co(II)(*triphos*)-complexes; Chiral amino alcohols; Paramagnetism

### 1. Introduction

Tripod ligands of the type RC(CH<sub>2</sub>X)(CH<sub>2</sub>Y)(CH<sub>2</sub>Z) (with X, Y, Z = donor groups) having neopentane backbone show unusual coordination toward transition metal ions (M<sup>x+</sup>) and lead to tripod-metal templates, [M(*tripod*)]<sup>x+</sup> [1–3]. These ligands have been used to block one half of the coordination sphere in tripod-metal templates. The shape of the donor groups in the tripod might play an important role in determining available coordination sphere around the metal in a specific and predictable way [4]. Tripods forming such sterically protected reaction pockets stabilizes many unstable [M(*tripod*)(L)<sub>n</sub>]<sup>x+</sup> complexes [2–5]. The tripod strongly influences the stereochemistry as well as the stability and reactivity of tripod-metal complexes. 2,2,2-Tris(diphenylphosphinomethyl)ethane (*triphos*), the simplest tripod, has been used to synthesize the Co(II)(*triphos*)-complexes containing chiral amino acids, 2-phenyldiamines/-hydroxythiols/-dithiols, 2-pyridinols/-mercaptopyridines, 2-hydroxyphenols/-aminophenols, formate/acetate, etc. as co-ligands [6–10]. We have

\*Email: enamullahju@yahoo.com

reported syntheses, spectroscopic characterizations, and crystal structures of chiral-*triphos* ligands, {rac-(±)-*triphos*} and their complexes with Co(II) containing enantiopure (*R/S*)-amino acids as co-ligands, [Co{rac-(±)-*triphos*}(*S/R*-amino acidato)](BPh<sub>4</sub>) [11]. The enantiopure *S*- or *R*-*triphos* was separated from racemic mixture, {rac-(±)-*triphos*} through crystallization of the complexes. Accordingly, we have reported the syntheses and spectroscopic characterizations of Co(II)(*triphos*)-complexes containing enantiopure (*S/R*)-2-hydroxy-2-*R*<sub>1</sub>*R*<sub>2</sub>-carboxylic acids as co-ligands [12] which exhibited temperature induced spin-crossover behavior in solution.

Prior to this work, no efforts were made to synthesize Co(II)(*triphos*)-complexes containing chiral amino alcohols as co-ligands [13]. This article reports synthetic and spectroscopic studies of Co(II)(*triphos*)-chiral amino alcohol complexes, [Co(*triphos*)(L-alaninolato)](BPh<sub>4</sub>) (**1**), [Co(*triphos*)(*S*-2-phenylglycinolato)](BPh<sub>4</sub>) (**2**), [Co(*triphos*)(*R*-1-amino-2-propanolato)](BPh<sub>4</sub>) (**3**), and [Co(*triphos*)(±)-2-amino-1-phenylethanolato)](BPh<sub>4</sub>) (**4**).

## 2. Experimental

### 2.1. Materials and methods

All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. The solvents were highly purified, dried, and deoxygenated through distillation under nitrogen: tetrahydrofuran (THF), petroleum ether (PE 40/60), dichloromethane over Na metal and ethanol over CaO. The salt Co(BF<sub>4</sub>)·6H<sub>2</sub>O was prepared following the literature [14]. Commercially available chiral amino alcohols (HAA) such as L-alaninol, *S*-2-phenylglycinol, *R*-1-amino-2-propanol, (±)-2-amino-1-phenyl-ethanol, and Na(BPh<sub>4</sub>) were used as received from Lancaster. The 2,2,2-*tris*(diphenylphosphinomethyl)ethane (*triphos*) was synthesized as described [15]. The electronic spectra of the complexes were recorded on a Shimadzu UV 3150 spectrophotometer at room temperature. The IR spectra as KBr disks were recorded on a FT-IR spectrometer (Bruker IFS 66) at ambient temperature. NMR spectra were run on a Bruker AC DPX 200 operating at 200 MHz (<sup>1</sup>H) and 81 MHz (<sup>31</sup>P) using NMR grade deoxygenated CDCl<sub>3</sub> as internal standard; <sup>31</sup>P chemical shift ( $\delta$ ) in ppm is reported with respect to 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P;  $\delta=0$ ) as external standard. For magnetic moment measurements a high precision NMR sample tube of type 528-PP (Wilma Glass Co., NJ, USA) with sealed Wilmad coaxial insert (WGS-5BL) containing 5% TMS in acetone-*d*<sub>6</sub> was used as external standard and as instrument lock. Cyclohexane 0.5% (v/v) was used as an internal reference in methanol. The experimental magnetic moment ( $\mu_{\text{exptl}}[\mu\text{B}]$ ) values of the complexes ( $1.25 \times 10^{-4}$ – $2.12 \times 10^{-4}$  M) were determined by Evan's method [16–18] based on the <sup>1</sup>H-NMR shifts in methanol at 25 °C. Mass (FAB, positive mode) spectra were recorded on a Finnigan MAT 8400 with integrated Spectro-System (SS) 300, *m*-nitrobenzylalcohol matrix, 150 °C ionization temperature (*m/z*-values show the most frequent/common isotope peaks for all complexes).

### 2.2. General procedure to synthesize the complexes

An equimolar amount of *triphos* dissolved in 20 mL THF was added to 20 mL ethanolic solution of Co(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and stirred for 30 min at room temperature. The color

changed from rose to red-violet forming the intermediate cationic  $[\text{Co}(\text{triphos})(\text{S})_2](\text{BF}_4)_2$  ( $\text{S} = \text{solvent}$ ) (**A**) in solution. Then, an equimolar amount of L-alaninol ( $\text{L-HOCH}_2\text{CHCH}_3\text{NH}_2$ ) and NaOH in 20 mL ethanol (for activation of chiral amino alcohol) was stirred for 30 min at room temperature and poured into the red-violet  $[\text{Co}(\text{triphos})(\text{S})_2](\text{BF}_4)_2$  solution; stirring was continued for 4–5 h at room temperature. The color quickly changed to green and afforded the  $[\text{Co}(\text{triphos})(\text{L-alaninolato})](\text{BF}_4)$  in solution. Finally, for anion exchange an equimolar amount of  $\text{Na}(\text{BPh}_4)$  (dissolved in 10 mL ethanol) was added to the reaction mixture, precipitating green product. This solution was stirred for 30 min more and the solvent evaporated very slowly in a water bath *in vacuo* (oil-vacuum-pump) to 60% until the deep green products fully precipitated. The products were filtered off and washed twice with ethanol (5 mL), eluted with 10 mL  $\text{CH}_2\text{Cl}_2$ , collected and dried *in vacuo* (0.2–0.3 mbar) for 3–4 h at room temperature obtaining deep green microcrystalline products of  $[\text{Co}(\text{triphos})(\text{L-alaninolato})](\text{BPh}_4)$  (**1a**). Repetition of this procedure in the absence of Na(OH) (i.e., without activation of chiral amino alcohol) gave the same complex (**1b**), showing similar analytical results but with low yields.

The same procedure was followed for  $[\text{Co}(\text{triphos})(\text{S-2-phenylglycinolato})](\text{BPh}_4)$  (**2**),  $[\text{Co}(\text{triphos})(\text{R-1-amino-2-propanolato})](\text{BPh}_4)$  (**3**), and  $[\text{Co}(\text{triphos})(\pm\text{-2-amino-1-phenyl-ethanolato})](\text{BPh}_4)$  (**4**) using the *S*-2-phenylglycinol (*S*- $\text{HOCH}_2\text{CHPhNH}_2$ ), *R*-1-amino-2-propanol (*R*- $\text{HOCHCH}_3\text{CH}_2\text{NH}_2$ ), and  $(\pm)$ -2-amino-1-phenyl-ethanol ( $(\pm)$ - $\text{HOCHPhCH}_2\text{NH}_2$ ), respectively. All the complexes are strongly hygroscopic and air sensitive.

**2.2.1.  $[\text{Co}(\text{triphos})(\text{L-alaninolato})](\text{BPh}_4)$  (**1a**).** *Triphos* (1.089 g, 1.74 mM),  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.594 g, 1.74 mM), L-alaninol ( $\text{L-HOCH}_2\text{CHCH}_3\text{NH}_2$ ) (0.14 mL, 1.80 mM), NaOH (0.072 g, 1.80 mM), and  $\text{Na}(\text{BPh}_4)$  (0.596 g, 1.74 mM). Yield: 1.450 g (72% with respect to *triphos*). Anal. Calcd (%) for  $(\text{C}_{68}\text{H}_{67}\text{P}_3\text{NOCOB})(\text{CH}_2\text{Cl}_2)$  (1161.88): C, 71.33; H, 5.99; N, 1.21. Found (%): C, 71.46; H, 6.20; N, 1.39. MS (FAB, Pos) [ $m/z$  (%): 757 (90)  $[\text{M}]^+$ , 699 (5)  $[\text{Co}(\text{triphos})+\text{O}]^+$ , 683 (80)  $[\text{Co}(\text{triphos})=\text{M-AA}]^+$ , 682 (100)  $[\text{Co}(\text{triphos})-\text{H}]^+$ , 656 (20)  $[(\text{triphos})+\text{O}_2]^+$ , 640 (20)  $[(\text{triphos})+\text{O}]^+$ , 547 (5)  $[(\text{triphos})-\text{Ph}]^+$ , 443 (45)  $[(\text{triphos})-\text{PPh}_2+2\text{H}_2]^+$  and 321 (32)  $[\text{HBPh}_4+\text{H}]$  ( $[\text{M}]^+ = [\text{Co}(\text{triphos})(\text{AA})]^+$ , AA = L-alaninolato =  $\text{L-OCH}_2\text{CHCH}_3\text{NH}_2$ ; *triphos* = 2,2,2-tris(diphenylphosphinomethyl)ethane; Ph =  $\text{C}_6\text{H}_5$ ).

**2.2.2.  $[\text{Co}(\text{triphos})(\text{L-alaninolato})](\text{BPh}_4)$  (**1b**).** Yield: 0.906 g (46% from *triphos*). Anal. Calcd (%) for  $(\text{C}_{68}\text{H}_{67}\text{P}_3\text{NOCOB})(0.5\text{CH}_2\text{Cl}_2)$  (1119.42): C, 73.50; H, 6.12; N, 1.25. Found (%): C, 73.25; H, 6.30; N 1.15. MS (FAB, Pos) [ $m/z$  (%): 757 (65)  $[\text{M}]^+$ , 699 (15)  $[\text{Co}(\text{triphos})+\text{O}]^+$ , 683 (100)  $[\text{Co}(\text{triphos})=\text{M-AA}]^+$ , 682 (85)  $[\text{Co}(\text{triphos})-\text{H}]^+$ , 656 (18)  $[(\text{triphos})+\text{O}_2]^+$ , 641 (10)  $[(\text{triphos})+\text{O}+\text{H}]^+$ , 563 (25)  $[(\text{triphos})+\text{O}-\text{Ph}]^+$ , 547 (20)  $[(\text{triphos})-\text{Ph}]^+$ , 443 (75)  $[(\text{triphos})-\text{PPh}_2+2\text{H}_2]^+$ , and 321 (40)  $[\text{HBPh}_4+\text{H}]$ .

**2.2.3.  $[\text{Co}(\text{triphos})(\text{S-2-phenylglycinolato})](\text{BPh}_4)$  (**2**).** *Triphos* (0.722 g, 1.16 mM),  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.394 g, 1.16 mM), *S*-2-phenylglycinol (*S*- $\text{HOCH}_2\text{CHPhNH}_2$ ) (0.158 g, 1.15 mM), NaOH (0.047 g, 1.18 mM), and  $\text{Na}(\text{BPh}_4)$  (0.398 g, 1.16 mM). Yield: 0.982 g (69% based on *triphos*). Anal. Calcd (%) for  $(\text{C}_{73}\text{H}_{69}\text{P}_3\text{NOCOB})(\text{CH}_2\text{Cl}_2)$  (1223.95): C, 72.62; H, 5.85; N, 1.14. Found (%): C, 72.98; H, 6.05; N, 1.06.

MS (FAB, Pos) [ $m/z$  (%): 819 (85)  $[M]^+$ , 699 (15)  $[Co(triphos)+O]^+$ , 683 (100)  $[Co(triphos)=M-AA]^+$ , 682 (80)  $[Co(triphos)-H]^+$ , 656 (15)  $[(triphos)+O_2]^+$ , 641 (10)  $[(triphos)+O+H]^+$ , 563 (20)  $[(triphos)+O-Ph]^+$ , 547 (10)  $[(triphos)-Ph]^+$ , 443 (70)  $[(triphos)-PPh_2+2H_2]^+$ , and 321 (45)  $[HBPh_4+H]$  ( $[M]^+=[Co(triphos)(AA)]^+$ , AA = *S*-2-phenylglycinolato = *S*-OCH<sub>2</sub>CHPhNH<sub>2</sub>).

**2.2.4.  $[Co(triphos)(R-1-amino-2-propanolato)](BPh_4)$  (3).** *Triphos* (0.660 g, 1.06 mM),  $Co(BF_4)_2 \cdot 6H_2O$  (0.360 g, 1.06 mM), *R*-1-amino-2-propanol (*R*-HOCHCH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>) (0.08 mL, 1.05 mM), NaOH (0.042 g, 1.05 mM), and Na(BPh<sub>4</sub>) (0.361 g, 1.05 mM). Yield: 0.811 g (66% from *triphos*). Anal. Calcd (%) for (C<sub>68</sub>H<sub>67</sub>P<sub>3</sub>NOCob)(CH<sub>2</sub>Cl<sub>2</sub>) (1161.88): C, 71.33; H, 5.99; N, 1.21. Found (%): C, 70.45; H, 5.83; N, 1.34. MS (FAB, Pos) [ $m/z$  (%): 757 (30)  $[M]^+$ , 754 (20)  $[M-H_2-H]^+$ , 699 (10)  $[Co(triphos)+O]^+$ , 683 (70)  $[Co(triphos)=M-AA]^+$ , 682 (45)  $[Co(triphos)-H]^+$ , 656 (10)  $[(triphos)+O_2]^+$ , 641 (15)  $[(triphos)+O+H]^+$ , 563 (10)  $[(triphos)+O-Ph]^+$ , 443 (45)  $[(triphos)-PPh_2+2H_2]^+$ , and 321 (22)  $[HBPh_4+H]$  ( $[M]^+=[Co(triphos)(AA)]^+$ , AA = *R*-1-amino-2-propanolato = *R*-OCHCH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>).

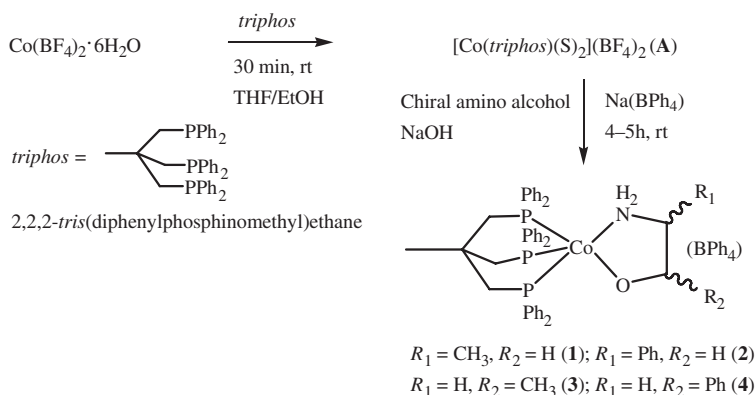
**2.2.5.  $[Co(triphos)((\pm)-2-amino-1-phenyl-ethanolato)](BPh_4)$  (4).** *Triphos* (0.624 g, 1.00 mM),  $Co(BF_4)_2 \cdot 6H_2O$  (0.340 g, 1.00 mM), ( $\pm$ )-2-amino-1-phenyl-ethanol ( $(\pm)$ -HOCHPhCH<sub>2</sub>NH<sub>2</sub>) (0.137 g, 1.00 mM), NaOH (0.038 g, 0.95 mM) and Na(BPh<sub>4</sub>) (0.342 g, 1.00 mM). Yield: 0.880 g (69% based on *triphos*). Anal. Calcd (%) for (C<sub>73</sub>H<sub>69</sub>P<sub>3</sub>NOCob)(1.5CH<sub>2</sub>Cl<sub>2</sub>) (1266.42): C, 70.66; H, 5.73; N, 1.11. Found (%): C, 70.34; H, 5.96; N, 1.19. MS (FAB, Pos) [ $m/z$  (%): 819 (65)  $[M]^+$ , 699 (10)  $[Co(triphos)+O]^+$ , 683 (100)  $[Co(triphos)=M-AA]^+$ , 682 (65)  $[Co(triphos)-H]^+$ , 656 (12)  $[(triphos)+O_2]^+$ , 641 (15)  $[(triphos)+O+H]^+$ , 563 (10)  $[(triphos)+O-Ph]^+$ , 547 (15)  $[(triphos)-Ph]^+$ , 443 (50)  $[(triphos)-PPh_2+2H_2]^+$  and 321 (35)  $[HBPh_4+H]$  ( $[M]^+=[Co(triphos)(AA)]^+$ , AA = ( $\pm$ )-2-amino-1-phenyl-ethanolato = ( $\pm$ )-OCHPhCH<sub>2</sub>NH<sub>2</sub>).

### 3. Results and discussion

The coordination of *triphos* to  $Co(BF_4)_2 \cdot 6H_2O$  gives an intermediate red-violet  $[Co(triphos)(S)_2](BF_4)_2$  (S = solvent) (A) which reacts with chiral amino alcohols (*L*-alaninol, *S*-2-phenylglycinol, *R*-1-amino-2-propanol and ( $\pm$ )-2-amino-1-phenyl-ethanol) in the presence of Na(OH), affording green  $[Co(triphos)(chiral\ amino\ alcoholato)](BF_4)$ . Deep green  $[Co(triphos)(L\text{-}alaninolato)](BPh_4)$  (1),  $[Co(triphos)(S\text{-}2\text{-phenylglycinolato)](BPh_4)$  (2),  $[Co(triphos)(R\text{-}1\text{-amino-}2\text{-propanolato)](BPh_4)$  (3), and  $[Co(triphos)((\pm)\text{-}2\text{-amino-}1\text{-phenyl-ethanolato)](BPh_4)$  (4) are precipitated by adding Na(BPh<sub>4</sub>) *via* anion exchange (scheme 1).

#### 3.1. Mass spectra

Mass spectra are dominated by the parent ion ( $[M]^+$ ) for the cationic complexes,  $[Co(triphos)(chiral\ amino\ alcoholato)]^+$  and  $[Co(triphos)]^{2+}$ . The spectra further show several ion peaks, including the oxidative adducts, correspond to  $[Co(triphos)+O]^{2+}$ ,  $[triphos+O_2]$ , and  $[triphos+O]$  species (see section 2), as the complexes are strongly air sensitive [10a, 12, 20].



Scheme 1. Synthetic route to the formation of the complexes (1–4).

### 3.2. NMR spectra

$^1\text{H}$ -NMR spectra show the paramagnetic nature of the complexes in solution.  $^{31}\text{P}$ -NMR spectra show a broad peak at  $\delta = 19.2\text{--}20.1$  ppm, indicating coordination of three P of *triphos* to Co(II) [12] (uncoordinated P of *triphos* show a singlet at  $\delta = -27.3$  ppm [15]). The magnetic moment values ( $\mu_{\text{exptl.}}[\mu\text{B}]$ ) of the complexes are determined by Evan's method [18] based on the  $^1\text{H}$ -NMR shifts [12, 16, 17]; the values are  $\mu_{\text{exptl.}}(\mu\text{B}) = 3.65$  (1), 3.78 (2), 3.82 (3), and 3.71 (4) in methanol at  $25^\circ\text{C}$ , which clearly fall into the range for related Co(II)(*triphos*)-complexes [10, 12].

### 3.3. Electronic spectra

The electronic spectra of 1–4 and  $[\text{Co}(\text{triphos})(\text{S})_2](\text{BF}_4)_2$  (A) (Supplementary Material) and spectral data are listed in table 1. The spectra of 1–4 are identical with each other and different from that of the intermediate A. The spectral analysis of A shows three common characteristic features: (1) a very strong band at  $<450$  nm, associated to the intra-ligand  $\Pi \rightarrow \Pi^*$  transitions of *triphos*-phenyl, (2) a strong band at 450–700 nm with absorption maximum at 510 nm ( $\lambda_{1\text{max}}$ ), assigned to *metal-to-ligand* charge transfer (*mlct*) transitions based on  $[\text{Co}(\text{triphos})(\text{S})_2]^{2+}$ , and (3) a moderate broad band at 750–1300 nm with absorption maximum at 994 nm ( $\lambda_{2\text{max}}$ ), assigned to three different d–d transitions [9a, 10a, 11–13, 19]. Similarly, *mlct* bands based on  $[\text{Co}(\text{triphos})(\text{amino alcoholato})]^+$  are found at 380–550 nm ( $\lambda_{1\text{max}}/\epsilon_{1\text{max}} = 407\text{ nm}/1510\text{ L M}^{-1}\text{ cm}^{-1}$  for 1; 406 nm/896  $\text{L M}^{-1}\text{ cm}^{-1}$  for 2; 409 nm/1897  $\text{L M}^{-1}\text{ cm}^{-1}$  for 3, and 408 nm/1580  $\text{L M}^{-1}\text{ cm}^{-1}$  for 4. A moderate broad band at 550–1300 nm consists of three different d–d transitions: (1) a weak shoulder at 550–700 nm, (2) a weak broad band at 700–1000 nm with identical absorption maxima at  $\lambda_{2\text{max}} = 826\text{ nm}$  ( $\epsilon_{2\text{max}}/230\text{ L M}^{-1}\text{ cm}^{-1}$ ) for 1; 825 nm ( $148\text{ L M}^{-1}\text{ cm}^{-1}$ ) for 2; 825 nm ( $289\text{ L M}^{-1}\text{ cm}^{-1}$ ) for 3 and 825 nm ( $220\text{ L M}^{-1}\text{ cm}^{-1}$ ) for 4, and finally, (3) a weak broad shoulder at longer wavelength, 1000–1300 nm [19]. The high intensity of the d–d bands with values from 148 to 294  $\text{L M}^{-1}\text{ cm}^{-1}$  is indicative of a non-centrosymmetric structure [19].

Table 1. Electronic spectral data of [Co(*triphos*)(S)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**A**) and [Co(*triphos*)(amino alcoholato)](BPh<sub>4</sub>) (**1–4**) in THF at 25 °C.

Complexes	<i>mlct</i> transitions <sup>a</sup>	d–d transitions <sup>a</sup>
[Co( <i>triphos</i> )(S) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ( <b>A</b> ) <sup>b</sup>	450–750 nm (λ <sub>1max</sub> /510 nm)	750–900 nm (sh) 900–1100 nm (λ <sub>2max</sub> /994 nm) 1100–1300 nm (sh)
[Co( <i>triphos</i> )(L-alaninato)](BPh <sub>4</sub> ) ( <b>1</b> ) (8.921 × 10 <sup>-4</sup> M)	380–550 nm (λ <sub>1max</sub> /407 nm ε <sub>1max</sub> /1510)	550–700 nm (sh) 700–1000 nm (λ <sub>2max</sub> /826 nm, ε <sub>2max</sub> /230) 1000–1300 nm (sh)
[Co( <i>triphos</i> )(S-2-phenylglycinolato)](BPh <sub>4</sub> ) ( <b>2</b> ) (9.804 × 10 <sup>-4</sup> M)	380–550 nm (λ <sub>1max</sub> /406 nm, ε <sub>1max</sub> /896)	550–700 nm (sh) 700–1000 nm (λ <sub>2max</sub> /825 nm, ε <sub>2max</sub> /148) 1000–1300 nm (sh)
[Co( <i>triphos</i> )(R-1-amino-2-propanolato)](BPh <sub>4</sub> ) ( <b>3</b> ) (9.037 × 10 <sup>-4</sup> M)	380–550 nm (λ <sub>1max</sub> /409 nm, ε <sub>1max</sub> /1897)	550–700 nm (sh) 700–1000 nm (λ <sub>2max</sub> /825 nm, ε <sub>2max</sub> /289) 1000–1300 nm (sh)
[Co( <i>triphos</i> )(±)-2-amino-1-phenyl-ethanolato)](BPh <sub>4</sub> ) ( <b>4</b> ) (9.011 × 10 <sup>-4</sup> M)	380–550 nm (λ <sub>1max</sub> /408 nm, ε <sub>1max</sub> /1580)	550–700 nm (sh) 700–1000 nm (λ <sub>2max</sub> /825 nm, ε <sub>2max</sub> /220) 1000–1300 nm (sh)

<sup>a</sup>ε<sub>max</sub> values are in LM<sup>-1</sup> cm<sup>-1</sup>; <sup>b</sup>In THF/EtOH (50% v/v); and sh = shoulder.

The spectra shift to higher energy (blue shift) in comparison to [Co(*triphos*)(S)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (**A**) by replacement of solvent molecules with chiral amino alcoholate in [Co(*triphos*)(amino alcoholato)](BPh<sub>4</sub>) (**1–4**). This blue shift results from strong interaction of the amino alcoholate to Co(II) (i.e., *via* ionic bond formation) in **1–4**, which is absent in **A**. This result is in good agreement with the formation of a five-membered chelate ring of amino alcoholate to the Co(II) in [Co(amino alcoholato)]<sup>+</sup> species in addition to two six-membered chelate rings in [Co(*triphos*)]<sup>2+</sup>, which further stabilizes **1–4**. The *mlct* band is much more intense for **1–4** and the intensity ratio of this band to the corresponding d–d band is higher (i.e., ε<sub>1max</sub>:ε<sub>2max</sub> = 5–6 for **1–4**) in comparison to that found for **A** (1.3), strongly suggesting that the *mlct* transitions are dominated by interaction of amino alcoholate with Co(II).

The complexes are very sensitive to air and readily decompose, resulting in a color change from deep green to red-brown and finally, to colorless in THF. This is clearly shown by a change in the electronic spectra of the complex with time (Supplementary material). Reaction of Co(*triphos*)-complexes with dioxygen from air gives the mixed phosphine/phosphine oxide ligands, *triphosO* and *triphosO*<sub>2</sub>, where the metal is catalyst [12, 20]. Mass spectra also show the formation of different oxidation adducts.

### 3.4. Vibrational spectra

The most common IR bands of the complexes are summarized in table 2. The absence of any ν(O–H) (observed as a strong band at 3630 cm<sup>-1</sup> for free O–H of alaninol [21])

Table 2. Vibrational spectral data ( $\text{cm}^{-1}$ , KBr) of **1–4** at ambient temperature.

Assignments	Complexes			
	<b>1a/1b</b>	<b>2</b>	<b>3</b>	<b>4</b>
$\nu(\text{N-H})_{\text{asym}}$	3312 m	3318 m	3322 m	3320 m
$\nu(\text{N-H})_{\text{sym}}$	3266 w	3259 w	3273 w	3267 w
$\nu(\text{H-Ar})$	3053 s	3054 s	3053 s	3053 s
$\delta\text{N-H}_{\text{def}}$	1579 s	1578 s	1578 s	1580 s
$\delta\text{CH}_2_{\text{def}}$	1482 s	1481 s	1480 s	1480 s
$\delta\text{CH}_3_{\text{asym, def}}$	1435 vs	1435 vs	1435 s	1435 s
$\nu(\text{P=O})$	1185 s	1190 s	1188 s	1195 s
$\nu(\text{BPh}_4)$	1010–1095 sb	1015–1095 sb	1012–1089 sb	1012–1089 sb

sb, strong broad; vs, very strong; s, strong; m, medium; w, weak; asym, asymmetric; sym, symmetric; Ar, aromatic; and def, deformation.

indicates deprotonation during formation of **1–4**. The free  $-\text{NH}_2$  of alaninol exhibits two stretching vibrations at  $3370 \text{ cm}^{-1}$   $\nu(\text{N-H}_{\text{asym}})$  and  $3300 \text{ cm}^{-1}$   $\nu(\text{N-H}_{\text{sym}})$  [21] which shift to  $3312, 3266 \text{ cm}^{-1}$  (**1**);  $3318, 3259 \text{ cm}^{-1}$  (**2**);  $3322, 3273 \text{ cm}^{-1}$  (**3**), and  $3320, 3267 \text{ cm}^{-1}$  (**4**) upon coordination to Co(II) [9a, 11, 13, 22–26]. A strong  $\nu\text{H-Ar}$  at  $3050\text{--}3055 \text{ cm}^{-1}$  confirms the presence of phenyl (from *triphos* and amino alcohol). N–H deformation vibrations are observed at  $1578\text{--}1580 \text{ cm}^{-1}$  ( $1590 \text{ cm}^{-1}$  for alaninol [21]). The bands at  $1480$  and  $1435 \text{ cm}^{-1}$  are assigned to  $\text{CH}_2$  deformation and  $\text{CH}_3$  asymmetric deformation, respectively [21]. The complexes show a strong band at  $1185\text{--}1195 \text{ cm}^{-1}$  assigned to the  $\nu(\text{P=O})$  from  $[\text{Co}(\text{triphos})+\text{O}]^{2+}$  and  $[\text{triphos}+\text{O}/\text{O}_2]$  [20a] and a strong broad band at  $1010\text{--}1095 \text{ cm}^{-1}$  assigned to  $\nu(\text{BPh}_4^-)$  in all complexes. The vibrational results strongly suggest that the amino alcoholate is bound to Co(II) by nitrogen and oxygen as five-membered *N,O*-chelates forming the complexes depicted in scheme 1.

In conclusion, reaction of 2,2,2-*tris*(diphenylphosphinomethyl)ethane (*triphos*) with Co(II) followed by reaction with activated chiral amino alcohol leads to **1–4**. Similar reactions using achiral/chiral-*triphos* and other co-ligands such as achiral/chiral-amino acids and chiral 2-hydroxy-2- $R_1R_2$ -carboxylic acids provide the analogues  $[\text{Co}(\text{achiral}/\text{chiral-}i\text{triphos})(\text{achiral}/\text{chiral-amino acidato})(\text{BPh}_4)]$  [9a, 11] and  $[\text{Co}(\text{triphos})(\text{chiral 2-hydroxy-2-}R_1R_2\text{-carboxylato})]$  [12]. The synthetic and spectroscopic results as well as the comparison with literature strongly suggest that the *triphos* and amino alcoholate are bound to the Co(II) in a trigonal bipyramidal symmetry [9a, 11, 12]. The co-ligand plays a key role in stabilizing the *triphos*-Co(II) template, and hence influences the stereochemistry and reactivity of the complexes. This study helps to understand the coordination behavior of *triphos* and amino alcohol to Co(II), and to extend the field of current investigations.

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