

# Synthesis, stereochemistry and crystal structures of cobalt(III) complexes containing 5,8-diphenyl-2,11-dithia-5,8-diphosphadodecane or 5,9-diphenyl-2,12-dithia-5,9-diphosphatridecane

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Twelve new cobalt(III) complexes containing a tetradentate phosphine ligand of the type MeS(CH<sub>2</sub>)<sub>2</sub>PPh(CH<sub>2</sub>)<sub>n</sub>PPh(CH<sub>2</sub>)<sub>2</sub>SMe (*n* = 2 L<sup>1</sup> or 3 L<sup>2</sup>) were prepared. Their structures were assigned on the basis of electronic absorption and <sup>1</sup>H NMR spectra and the molecular structures of *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]BF<sub>4</sub> and *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]BF<sub>4</sub> were determined by single-crystal X-ray diffraction. The last two complexes comprise a slightly distorted octahedron with bond distances Co–P 2.210(1), Co–S 2.254(1) and Co–Cl 2.281(1) and Co–P 2.227(3), Co–S 2.327(3) and Co–Cl 2.241(3) Å (all averages) respectively. The differences in Co–S and Co–Cl bond distances are attributable to the strong *trans* influence of the phosphino group. Acetylacetonate complexes of *rac*(P)-SPPS in organic solvents form equilibrium mixtures of the *cis-α* and *cis-β* isomers, the molar ratio in MeNO<sub>2</sub> solution at 60 °C being 2 : 1 for the L<sup>1</sup> complex and 3 : 2 for the L<sup>2</sup> complex.

Linear tetradentate tetraphosphine ligands exist as *racemic* (*RR/SS*) and *meso* (*RS*) diastereomers by virtue of the absolute configurations of the two internal phosphorus atoms in the skeletons.<sup>1</sup> Each of the diastereomers generates stereospecific co-ordination modes upon complexation.<sup>2</sup> We have prepared a large number of linear tetradentate phosphine(soft base)–amine(hard base) hybrid compounds where the phosphorus donor atoms are chiral, examined the complexation to cobalt(III) of a typical Lewis hard acid, and found that these complexes have quite different properties from those of analogous tetradentate tetramines.<sup>3–6</sup> In a previous paper<sup>7</sup> we extended the study to a tetradentate phosphorus–sulfur hybrid bearing only soft donor groups, 5,8-diphenyl-2,11-dithia-5,8-diphosphadodecane (L<sup>1</sup>), and obtained [Co(acac)<sub>2</sub>L<sup>1</sup>]<sup>+</sup> (acac = pentane-2,4-dionate) in which L<sup>1</sup> acts only as a didentate ligand through two phosphorus atoms. The purpose of this paper is to examine more thoroughly the complexation ability of L<sup>1</sup> and the related L<sup>2</sup> (5,9-diphenyl-2,12-dithia-5,9-diphosphatridecane) to cobalt(III) and clarify the correlations between the co-ordination modes and the absolute configurations of the chiral phosphorus atoms and/or the conformations (or size) of the central P–Co–P chelate rings.

Bosnich *et al.*<sup>8,9</sup> reported the preparation of a series of cobalt(III) complexes with the linear tetradentate tetraarsine [Me<sub>2</sub>As(CH<sub>2</sub>)<sub>3</sub>As(Ph)CH<sub>2</sub>]<sub>2</sub>, and clarified the optical stability of the chiral arsine atoms and topological stabilities of various geometrical isomers of the complexes. However, this arsine differs in the kind of donor atoms and the skeletal structure from our present phosphines: the number of methylene groups of the arsine is 3,2,3, while our phosphines have 2,2,2 and 2,3,2. Such differences often result in different topological preferences and stabilities upon complexation.

To our knowledge, only two papers have appeared on metal complexes of SPPS-type tetradentate ligands. Issleib and Gans<sup>10</sup> prepared [MX(NH<sub>3</sub>)(SCH<sub>2</sub>CH<sub>2</sub>PHCH<sub>2</sub>CH<sub>2</sub>PHCH<sub>2</sub>CH<sub>2</sub>S)] (M = Co, X = Br; M = Rh, X = Cl) and [M{SCH(R)CH<sub>2</sub>PHCH<sub>2</sub>CH<sub>2</sub>PHCH<sub>2</sub>CH(R)S}] (M = Ni, Pd or Pt; R = H or Me). However, the stereochemistry of the complexes was not well defined. Schmelzer and Schwarzenbach<sup>11</sup> reported the

crystal structure of *racemic*(P) and *meso*(P) isomers of [Ni(SCH<sub>2</sub>CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>S)], but experimental details and chemical properties were not described.

## Experimental

The phosphines were handled under an atmosphere of nitrogen using Schlenk techniques until the cobalt(III) complexes were formed. All of the solvents used for the preparation of ligands and complexes were made oxygen-free by bubbling nitrogen for 20 min immediately before use. Absorption spectra were recorded on a Hitachi U3400 spectrophotometer and NMR spectra on Hitachi R-90H and Varian INOVA 500 spectrometers.

## Preparation of phosphines

**L<sup>1</sup>.** This compound was prepared from 1,2-bis(phenylphosphino)ethane and 2-chloroethyl methyl sulfide according to a previous method.<sup>7</sup>

**L<sup>2</sup>.** A 15% hexane solution of butyllithium (30 cm<sup>3</sup>, 48.6 mmol) was added dropwise with stirring to a tetrahydrofuran solution (400 cm<sup>3</sup>) of 1,3-bis(phenylphosphino)propane (Strem Chem. Inc.) (5 g, 19.2 mmol). After stirring for 30 min, 2-chloroethyl methyl sulfide (4.25 g, 38.4 mmol) was added portionwise to the resulting yellow solution. The solution was stirred for 1 h at 50 °C, and then overnight at room temperature. Water (50 cm<sup>3</sup>) was added dropwise with stirring. After a while the ethereal layer was separated, dried over MgSO<sub>4</sub> (5 g) overnight, filtered, and the filtrate evaporated to give a viscous syrup. The product could not be distilled because of the very high boiling point, and was used as such for the preparation of cobalt(III) complexes. Yield: 6.92 g (88%). It was found to be a mixture of *racemic* and *meso* isomers (*ca.* 1 : 1 according to the NMR spectra. (CDCl<sub>3</sub>): <sup>31</sup>P-{<sup>1</sup>H}, δ –25.64 and –25.69; <sup>13</sup>C-{<sup>1</sup>H}, δ 15.40 (s, SCH<sub>3</sub>), 15.41 (s, SCH<sub>3</sub>), 22.34 (t, *J* = 14.96, CH<sub>2</sub>), 22.44 (t, *J* = 14.96, CH<sub>2</sub>), 28.20 (d, *J* = 13.24, PCH<sub>2</sub>), 28.31 (d, *J* = 14.39, PCH<sub>2</sub>), 29.34 (t, *J* = 12.09, PCH<sub>2</sub>), 29.41 (t, *J* = 12.09, PCH<sub>2</sub>), 30.58 (d,

$J = 17.84$ , SCH<sub>2</sub>), 30.62 (d,  $J = 17.84$ , SCH<sub>2</sub>), 128.42 (d,  $J = 6.91$ , *m*-C), 128.44 (d,  $J = 7.48$ , *m*-C), 129.01 (s, *p*-C), 132.33 (d,  $J = 18.99$ , *o*-C), 132.34 (d,  $J = 18.99$ , *o*-C), 137.19 (d,  $J = 11.51$ , *ipso*-C) and 137.31 (d,  $J = 11.51$  Hz, *ipso*-C); <sup>1</sup>H, δ 1.45 (m, CH<sub>2</sub>), 1.80 (m, PCH<sub>2</sub>), 1.92 (m, PCH<sub>2</sub>), 2.01 (s, SCH<sub>3</sub>), 2.02 (s, SCH<sub>3</sub>), 2.42 (m, SCH<sub>2</sub>), 7.31 (m, C<sub>6</sub>H<sub>5</sub>) and 7.43 (m, C<sub>6</sub>H<sub>5</sub>).

### Preparation of complexes

**trans-[CoCl<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sub>2</sub>BF<sub>4</sub> 1 and cis-α-[CoCl<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]BF<sub>4</sub> 2.** A methanol solution (120 cm<sup>3</sup>) containing *trans*-[CoCl<sub>2</sub>(py)<sub>4</sub>]Cl·6H<sub>2</sub>O<sup>12</sup> (py = pyridine) (2.45 g, 4.13 mmol) and L<sup>1</sup> (1.63 g, 4.13 mmol) was stirred overnight at room temperature, and then concentrated to a small volume. The concentrate was chromatographed with a column (3 × 35 cm) of Toyopearl HW-40 and methanol as eluent. Two large green and red bands were obtained separately, the former being eluted faster. Each eluate was evaporated to dryness under reduced pressure, and the residue mixed with a small amount of methanol to extract the complex. On addition of an excess of LiBF<sub>4</sub> the methanol extract gave a green or a red precipitate, which was filtered off and recrystallized from acetonitrile and diethyl ether to afford green (**1**) and red (**2**) crystals, respectively. Yield: 0.48 (12) for **1** and 0.79 g (31%) for **2** (Found: C, 47.5; H, 5.5. Calc. for C<sub>40</sub>H<sub>56</sub>BCl<sub>2</sub>CoF<sub>4</sub>P<sub>4</sub>S<sub>4</sub> **1**: C, 47.75; H, 5.6. Found: C, 39.5; H, 4.8. Calc. for C<sub>20</sub>H<sub>28</sub>BCl<sub>2</sub>CoF<sub>4</sub>P<sub>2</sub>S<sub>2</sub> **2**: C, 39.3; H, 4.6%). Both complexes **1** and **2** are soluble in nitromethane, acetonitrile, acetone, chloroform, or dichloromethane, but insoluble in water or diethyl ether; **1** is slightly soluble in methanol or ethanol.

**cis-β-[Co(acac){*rac*(P)-L<sup>1</sup>}]SbF<sub>6</sub> 3 and cis-α-[Co(acac){*rac*(P)-L<sup>1</sup>}]SbF<sub>6</sub> 4.** A methanol solution (50 cm<sup>3</sup>) of Li(acac) (0.087 g, 0.82 mmol) was added to an acetonitrile solution (60 cm<sup>3</sup>) of *cis*-α-[CoCl<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]BF<sub>4</sub> (0.50 g, 0.82 mmol). The solution was stirred overnight at room temperature, then diluted ten times with water, and applied to a column (3 × 130 cm) of SP-Sephadex C-25. By elution with an aqueous 0.15 mol dm<sup>-3</sup> NaCl solution a small dark red band of [Co(acac)<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]<sup>+</sup> and then two large red-orange and red bands were eluted separately. Each eluate of the two large bands was evaporated to dryness under reduced pressure at 20 °C. The residue was mixed with a small amount of ethanol to extract the complex, and the extract evaporated again to dryness under reduced pressure at 20 °C. The residue was dissolved in a small amount of water. On addition of an excess of NaSbF<sub>6</sub> the solution yielded a red-orange (**3**) or red (**4**) precipitate, which was filtered off and recrystallized from methanol and diethyl ether to afford the crystals, respectively. Yields: 0.084 (10) for **3** and 0.352 g (42%) for **4** (Found: C, 29.55; H, 3.2 for **3**. C, 29.2; H, 3.45 for **4**. Calc. for C<sub>25</sub>H<sub>35</sub>CoF<sub>12</sub>O<sub>2</sub>-P<sub>2</sub>S<sub>2</sub>Sb<sub>2</sub>: C, 29.3; H, 3.45%). Both complexes **3** and **4** are soluble in nitromethane, acetonitrile, acetone, methanol or ethanol, slightly soluble in chloroform, dichloromethane or water, but insoluble in diethyl ether.

**[Co(acac){*meso*(P)-L<sup>1</sup>}]<sub>2</sub>[SbF<sub>6</sub>]<sub>2</sub>·3H<sub>2</sub>O 5.** A methanol solution (30 cm<sup>3</sup>) of Li(acac) (0.023 g, 0.22 mmol) was added to an acetonitrile solution (50 cm<sup>3</sup>) of *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sub>2</sub>BF<sub>4</sub> (0.217 g, 0.22 mmol). The solution was stirred for 5 h at room temperature, diluted ten times with water, and filtered. The filtrate was applied to a column (3 × 60 cm) of SP-Sephadex C-25, and the adsorbed products were eluted with an aqueous 0.15 mol dm<sup>-3</sup> NaCl solution to give two large dark red and red-orange bands. The eluate of the second red-orange band was evaporated to dryness under reduced pressure, and the complex extracted with ethanol from the residue. The extract was evaporated again to dryness under reduced pressure, and the residue was dissolved in a small amount of water. On addition of an excess of NaSbF<sub>6</sub> a red-orange precipitate

was obtained, filtered off and recrystallized from nitromethane and diethyl ether to afford the crystals. Yield: 0.042 g (14%) (Found: C, 36.5; H, 4.2. Calc. for C<sub>45</sub>H<sub>69</sub>CoF<sub>12</sub>O<sub>5</sub>P<sub>4</sub>S<sub>4</sub>Sb<sub>2</sub>: C, 36.7; H, 4.7%). The complex is soluble in nitromethane, acetonitrile, acetone, chloroform, dichloromethane, methanol or ethanol, slightly soluble in water, but insoluble in diethyl ether.

From the eluate of the first dark red band, [Co(acac)<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]SbF<sub>6</sub><sup>7</sup> was obtained in 15% yield by the same method as that for complex **5**.

**trans-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]BF<sub>4</sub> 6 and cis-α-[CoCl<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]BF<sub>4</sub> 7.** Complexes **6** (green) and **7** (red) were obtained by methods similar to those for the corresponding L<sup>1</sup> complexes **1** and **2**, respectively, using L<sup>2</sup>. Yields: 36% for **6** and 40% for **7** (Found: C, 40.3; H, 4.9 for **6**. C, 40.4; H, 4.9 for **7**. Calc. for C<sub>21</sub>H<sub>30</sub>BCl<sub>2</sub>CoF<sub>4</sub>P<sub>2</sub>S<sub>2</sub>: C, 40.35; H, 4.85%). Both complexes are soluble in nitromethane, acetonitrile, acetone, chloroform or dichloromethane, less soluble in methanol or ethanol, but insoluble in diethyl ether.

**cis-β-[Co(acac){*rac*(P)-L<sup>2</sup>}]SbF<sub>6</sub> 8 and cis-α-[Co(acac){*rac*(P)-L<sup>2</sup>}]SbF<sub>6</sub> 9.** Complexes **8** (red-orange) and **9** (red) were prepared from *cis*-α-[CoCl<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]BF<sub>4</sub> and Li(acac) by methods similar to those for the corresponding L<sup>1</sup> complexes **3** and **4**, respectively. In contrast to the case of L<sup>1</sup>, [Co(acac)<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]<sup>+</sup> was not formed. Yields: 24% for **8** and 48% for **9** (Found: C, 29.8; H, 3.6 for **8**. C, 29.3; H, 3.45 for **9**. Calc. for C<sub>26</sub>H<sub>37</sub>CoF<sub>12</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>Sb<sub>2</sub>: C, 30.1; H, 3.6%). The solubilities of **8** and **9** are similar to those of **3** and **4**.

**cis-β-[Co(acac){*meso*(P)-L<sup>2</sup>}]SbF<sub>6</sub> 10.** To an acetonitrile solution (20 cm<sup>3</sup>) of *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]BF<sub>4</sub> (0.20 g, 0.32 mmol) were added a methanol solution (40 cm<sup>3</sup>) of Li(acac) (0.034 g, 0.32 mmol) and active charcoal (0.05 g). The mixture was stirred for 24 h at room temperature, and then filtered to remove charcoal. The filtrate was diluted ten times with water, and applied to a column (3 × 60 cm) of SP-Sephadex C-25. By elution with an aqueous 0.15 mol dm<sup>-3</sup> NaCl solution, a red-orange band was developed. The eluate of the band was evaporated to dryness under reduced pressure, and the residue dissolved in a small amount of water. On addition of an excess of NaSbF<sub>6</sub> the solution gave a red precipitate, which was filtered off and recrystallized from methanol and diisopropyl ether to afford the crystals. Yield: 0.05 g (15%) (Found: C, 30.1; H, 3.55. Calc. for C<sub>26</sub>H<sub>37</sub>CoF<sub>12</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>Sb<sub>2</sub>: C, 30.1; H, 3.6%). The solubility of the complex is similar to those of **8** and **9**.

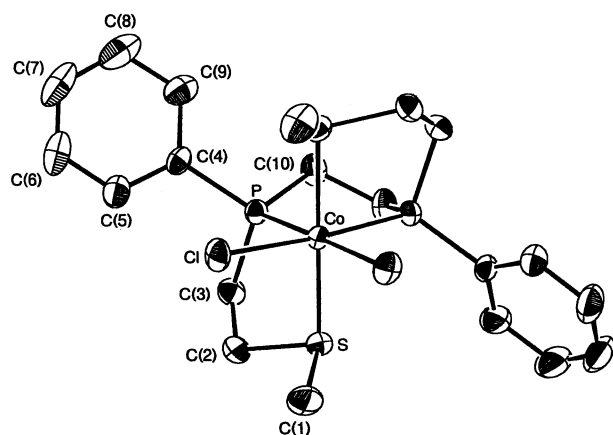
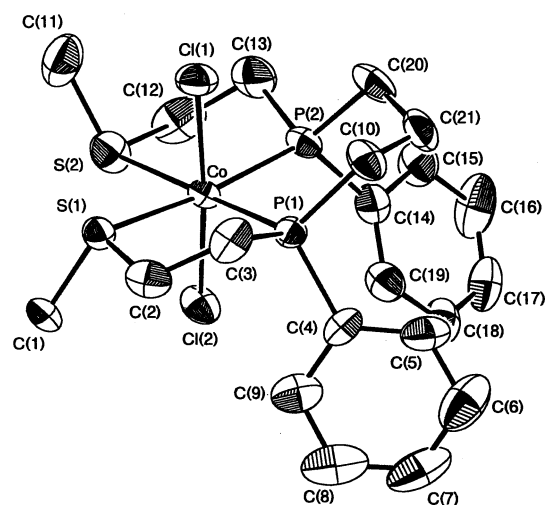
**[Co(acac)<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]SbF<sub>6</sub> 11 and Δ(*RR*)/Λ(*SS*)-[Co(acac)<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]SbF<sub>6</sub> 12.** A mixture of [Co(acac)<sub>3</sub>]<sup>13</sup> (0.44 g, 1.22 mmol), L<sup>2</sup> (0.50 g, 1.22 mmol), and active charcoal (0.05 g) in methanol (50 cm<sup>3</sup>) was stirred for 15 h at room temperature, and then filtered to remove charcoal. The filtrate was diluted ten times with water, and applied to a column (3 × 20 cm) of SP-Sephadex C-25. By elution with an aqueous 0.05 mol dm<sup>-3</sup> NaCl solution, two large dark red bands of complexes **11** and **12** appeared, the former being eluted faster. Each eluate of these bands was evaporated to dryness under reduced pressure, and the complex extracted from the residue with dichloromethane. The extract was evaporated again to dryness under reduced pressure, and the residue dissolved in a small amount of water. On addition of an excess of NaSbF<sub>6</sub> the solution yielded orange-brown crystals, which were filtered off and recrystallized from hot methanol. Yields: 0.22 (20) for **11** and 0.18 g (16%) for **12** (Found: C, 41.3; H, 4.9 for **11**. C, 41.2; H, 4.9 for **12**. Calc. for C<sub>31</sub>H<sub>44</sub>CoF<sub>6</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub>Sb: C, 41.3; H, 4.9%). The complexes are soluble in methanol, ethanol, chloroform or acetone, and slightly soluble in water or diethyl ether.



**Table 1** Crystallographic data for *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]BF<sub>4</sub> **2** and *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]BF<sub>4</sub> **6**\*

	<b>2</b>	<b>6</b>
Formula	C <sub>20</sub> H <sub>28</sub> BCl <sub>2</sub> CoF <sub>4</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>21</sub> H <sub>30</sub> BCl <sub>2</sub> CoF <sub>4</sub> P <sub>2</sub> S <sub>2</sub>
<i>M</i>	611.16	625.19
Space group	<i>Pnma</i> (no. 52)	<i>Pbc2</i> <sub>1</sub> (no. 29)
<i>a</i> /Å	12.392(1)	9.914(2)
<i>b</i> /Å	18.808(4)	29.945(4)
<i>c</i> /Å	10.900(1)	8.946(1)
<i>U</i> /Å <sup>3</sup>	2540.4(7)	2655.8(9)
μ(Mo-Kα)/cm <sup>-1</sup>	12.06	11.55
Crystal colour	Red	Green
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.60	1.56
<i>D</i> <sub>m</sub> /g cm <sup>-3</sup>	1.59	—
Scan range/°	1.15 + 0.50 tan θ	0.735 + 0.50 tan θ
Reflections measured	0 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 26, 0 ≤ <i>l</i> ≤ 15	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 42, 0 ≤ <i>l</i> ≤ 12
No. reflections measured	3812	4203
No. reflections observed [ <i>I</i> <sub>o</sub> > 3σ( <i>I</i> <sub>o</sub> )]	2297	2161
<i>R</i>	0.047	0.058
<i>R</i> '	0.055	0.059
<i>S</i>	1.72	1.61
Largest difference peak, hole/e Å <sup>-3</sup>	0.93, -0.82	0.85, -0.78

\* Details in common: orthorhombic; *Z* = 4; prismatic; scan speed 8° min<sup>-1</sup>; 2θ<sub>max</sub> 60°; *R* = Σ ||*F*<sub>o</sub> - |*F*<sub>c</sub>||/Σ |*F*<sub>o</sub>|, *R*' = (Σ *w*|*F*<sub>o</sub> - |*F*<sub>c</sub>||<sup>2</sup>/Σ *w*|*F*<sub>o</sub>|<sup>2</sup>)<sup>1/2</sup>, *w* = [σ<sup>2</sup>(*F*<sub>o</sub>) + (0.015*F*<sub>o</sub>)<sup>2</sup>]<sup>-1</sup>.

**Fig. 1** Perspective view of *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]<sup>+</sup>, which crystallizes with molecular C<sub>2</sub> symmetry**Fig. 2** Perspective view of *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]<sup>+</sup>

atom in the *R* configuration points to the phenyl group to form a crowded structure, suggesting the preferential co-ordination of the *S* (or *R*)-sulfur atom in the  $\Lambda$  (or  $\Delta$ ) isomer.

For complex **6** the five- and six-membered chelate rings of the *meso*(P)-L<sup>2</sup> ligand take a *gauche* and a chair conformation, respectively. The chelate angles of L<sup>2</sup> are almost 90° and no

**Table 2** Selected bond distances (Å) and angles (°) for complex **2**

Co-Cl	2.281(1)	Co-P	2.210(1)
Co-S	2.254(1)		
Cl-Co-S	91.88(4)	Co-S-C(1)	109.6(2)
Cl-Co-P	89.72(3)	Co-S-C(2)	102.3(1)
Cl-Co-Cl'	93.93(4)	C(1)-S-C(2)	100.7(2)
Cl-Co-S'	89.82(4)	Co-P-C(3)	107.0(1)
Cl-Co-P'	175.35(4)	Co-P-C(4)	119.4(1)
S-Co-S'	177.51(5)	Co-P-C(10)	108.3(1)
S-Co-P	87.18(4)	C(3)-P-C(4)	107.7(2)
S-Co-P'	91.01(4)	C(3)-P-C(10)	105.5(2)
P-Co-P'	86.79(4)	C(4)-P-C(10)	108.1(2)

**Table 3** Selected bond distances (Å) and angles (°) for complex **6**

Co-Cl(1)	2.243(3)	Co-S(2)	2.329(3)
Co-Cl(2)	2.239(3)	Co-P(1)	2.223(3)
Co-S(1)	2.325(3)	Co-P(2)	2.230(3)
Cl(1)-Co-Cl(2)	174.5(1)	C(1)-S(1)-C(2)	101.7(6)
Cl(1)-Co-S(1)	84.6(1)	Co-S(2)-C(11)	115.0(5)
Cl(1)-Co-S(2)	92.1(1)	Co-S(2)-C(12)	100.6(5)
Cl(1)-Co-P(1)	86.3(1)	C(11)-S(2)-C(12)	99.9(6)
Cl(1)-Co-P(2)	87.9(1)	Co-P(1)-C(3)	105.2(4)
Cl(2)-Co-S(1)	93.7(1)	Co-P(1)-C(4)	120.8(4)
Cl(2)-Co-S(2)	82.7(1)	Co-P(1)-C(10)	114.3(4)
Cl(2)-Co-P(1)	98.8(1)	C(3)-P(1)-C(4)	104.5(5)
Cl(2)-Co-P(2)	93.9(1)	C(3)-P(1)-C(10)	104.2(5)
S(1)-Co-S(2)	90.7(1)	C(4)-P(1)-C(10)	106.3(5)
S(1)-Co-P(1)	88.3(1)	Co-P(2)-C(13)	104.2(4)
S(1)-Co-P(2)	172.5(1)	Co-P(2)-C(14)	121.7(4)
S(2)-Co-P(1)	178.2(1)	Co-P(2)-C(20)	114.1(4)
S(2)-Co-P(2)	90.0(1)	C(13)-P(2)-C(14)	105.9(5)
P(1)-Co-P(2)	90.8(1)	C(13)-P(2)-C(20)	108.4(6)
Co-S(1)-C(1)	111.1(4)	C(14)-P(2)-C(20)	101.8(5)
Co-S(1)-C(2)	104.9(4)		

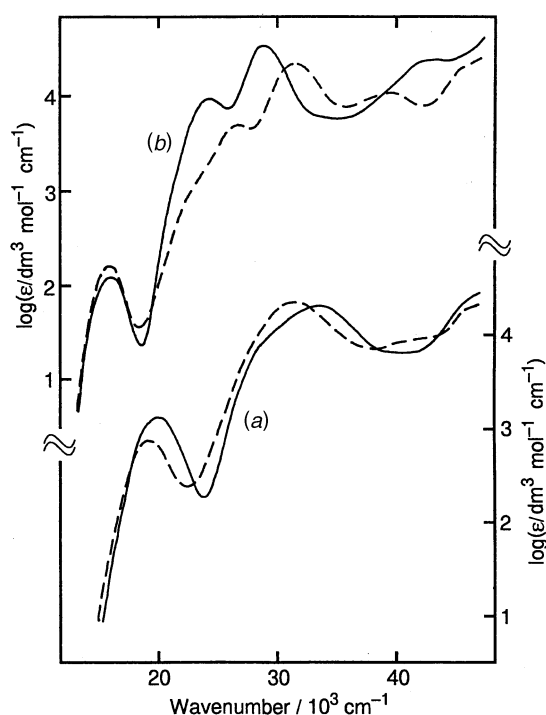
large deviation from an octahedron was observed at the Co atom.

Complex **7** exhibits a singlet SMe signal in the <sup>1</sup>H and <sup>13</sup>C NMR spectra at δ 2.28 and 18.6, respectively, indicating a *trans* or a *cis-α* configuration. The complex shows an absorption spectral pattern very similar to that of **2** [Fig. 3(a)], and is assigned to *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]<sup>+</sup>. The *meso*(P)-SPPS ligand cannot form a *cis-α* isomer since the two terminal P-S chelate arms point to the same apical site with respect to the P-Co-P plane.

**Table 4** Absorption and <sup>1</sup>H NMR spectral data

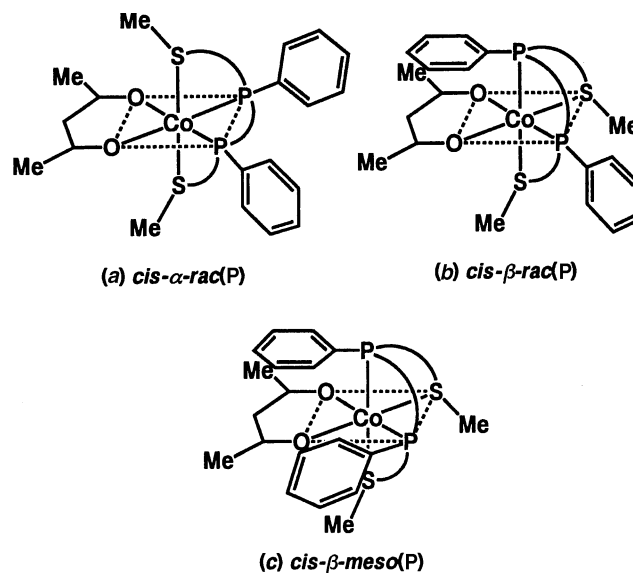
Complex	Absorption <sup>a</sup>	<sup>1</sup> H NMR (δ) <sup>b</sup>	
		CH <sub>3</sub>	=CH-
<b>1</b> <i>trans</i> -[CoCl <sub>2</sub> { <i>meso</i> (P)-L <sup>1</sup> }] <sub>2</sub> <sup>+</sup>	16.4 (2.15)	1.92	
<b>6</b> <i>trans</i> -[CoCl <sub>2</sub> { <i>meso</i> (P)-L <sup>2</sup> }] <sup>+</sup>	16.1 (2.25)	2.37	
<b>2</b> <i>cis-α</i> -[CoCl <sub>2</sub> { <i>rac</i> (P)-L <sup>1</sup> }] <sup>+</sup>	20.0 (3.19)	2.35	
<b>7</b> <i>cis-α</i> -[CoCl <sub>2</sub> { <i>rac</i> (P)-L <sup>2</sup> }] <sup>+</sup>	19.4 (2.91)	2.28	
<b>3</b> <i>cis-β</i> -[Co(acac){ <i>rac</i> (P)-L <sup>1</sup> }] <sub>2</sub> <sup>2+</sup>	20.5 (3.12)	1.76, 1.89 2.00, 2.07	4.97
<b>4</b> <i>cis-α</i> -[Co(acac){ <i>rac</i> (P)-L <sup>1</sup> }] <sub>2</sub> <sup>2+</sup>	19.5 (3.04)	1.95, 2.29	5.84
<b>5</b> [Co(acac){ <i>meso</i> (P)-L <sup>1</sup> }] <sub>2</sub> <sup>2+</sup>	20.2 (3.28)	0.96, 1.72, 1.80 1.89, 2.06, 2.21	4.68
<b>8</b> <i>cis-β</i> -[Co(acac){ <i>rac</i> (P)-L <sup>2</sup> }] <sub>2</sub> <sup>2+</sup>	19 (sh) (3.0) 20.7 (3.14)	1.79, 2.11 2.56, 2.60	5.24
<b>9</b> <i>cis-α</i> -[Co(acac){ <i>rac</i> (P)-L <sup>2</sup> }] <sub>2</sub> <sup>2+</sup>	18.9 (2.86)	1.73, 2.20	5.69
<b>10</b> <i>cis-β</i> -[Co(acac){ <i>meso</i> (P)-L <sup>2</sup> }] <sub>2</sub> <sup>2+</sup>	19 (sh) (2.8) 21.3 (2.98)	1.07, 1.75 2.08, 2.41	4.96
<b>11</b> [Co(acac) <sub>2</sub> { <i>meso</i> (P)-L <sup>2</sup> }] <sup>+</sup>	19 (sh) (2.7) 21.6 (2.87)	1.52, 1.64, 1.67 1.90, 2.07, 2.11	4.72
<b>12</b> [Co(acac) <sub>2</sub> { <i>rac</i> (P)-L <sup>2</sup> }] <sup>+</sup>	19 (sh) (2.6) 21.6 (2.82)	1.64, 1.78 1.97	5.34
<b>13</b> [Co(acac) <sub>2</sub> { <i>meso</i> (P)-L <sup>1</sup> }] <sup>+</sup>	21.3 (2.98)	0.96, 1.58, 1.94 2.03, 2.06, 2.16	4.74
<b>14</b> [Co(acac) <sub>2</sub> { <i>rac</i> (P)-L <sup>1</sup> }] <sup>+</sup>	21.2 (3.07)	1.34, 1.98, 2.04	5.51 4.86

<sup>a</sup> First absorption bands: ν/10<sup>3</sup> cm<sup>-1</sup> (log ε), solvent MeCN, sh = shoulder. <sup>b</sup> Solvents: CD<sub>3</sub>NO<sub>2</sub> for complexes **1–10** and CDCl<sub>3</sub> for **11–14**.



**Fig. 3** Absorption spectra of (a) *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L<sup>1</sup>}]<sub>2</sub><sup>+</sup> (—) and *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]<sub>2</sub><sup>+</sup> (----), (b) *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sub>2</sub><sup>+</sup> (—) and *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]<sub>2</sub><sup>+</sup> (----) in MeCN

Complex **1** which has the composition [CoCl<sub>2</sub>L<sub>2</sub>]<sup>+</sup> was obtained by the reaction of [CoCl<sub>2</sub>(py)<sub>4</sub>]<sup>+</sup> and L<sup>1</sup> in a molar ratio of 1 : 1. It shows a singlet signal for the SMe group in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, and the absorption spectral pattern is similar to those of **6** [Fig. 3(b)] and *trans*-[CoCl<sub>2</sub>(Bu<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PBu<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (first absorption peak: 16 610 cm<sup>-1</sup> with log ε = 2.05).<sup>22</sup> Thus complex **1** is a *trans*-dichloro isomer with two didentate L<sup>1</sup> ligands chelated through two phosphorus atoms. The reaction of **1** with Li(acac) yielded only [Co(acac)<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sup>+</sup> **13** and no *rac*(P)-L<sup>1</sup> complex was observed. Thus **1** is *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sub>2</sub><sup>+</sup>, although no assignment can be made for two diastereomers, *trans*[P(*R*)P(*R*)] or P(*S*)P(*S*) and *trans*[P(*R*)P(*S*)]. When *meso*(P)-L<sup>1</sup> acts as a

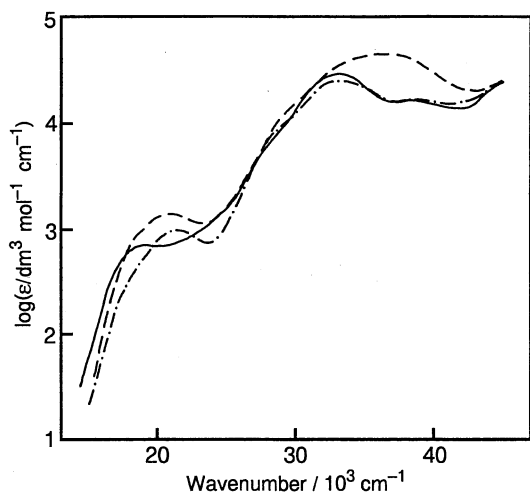


**Fig. 4** Three possible isomers of *cis*-[Co(acac)L]<sub>2</sub><sup>2+</sup>

tetradentate ligand to form a *trans* isomer the central five-membered P-Co-P chelate ring is forced to take an envelope conformation, and the complex will be unstable.

#### Acetylacetonato complexes

By the reaction with an equimolar amount of Li(acac), *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L}]<sup>+</sup> (L = L<sup>1</sup> or L<sup>2</sup>) yielded both *cis-α* and *cis-β*-[Co(acac){*rac*(P)-L}]<sub>2</sub><sup>2+</sup>. Since the *cis-α* and *cis-β* complexes have C<sub>2</sub> and C<sub>1</sub> symmetry, respectively (Fig. 4), the structures can be assigned easily from the <sup>1</sup>H NMR spectra (Table 4). The *cis-β*-[Co(acac){*meso*(P)-L<sup>2</sup>}]<sub>2</sub><sup>2+</sup> complex was prepared from *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]<sup>+</sup> by a similar method. However, neither *cis-β*-[Co(acac){*meso*(P)-L<sup>1</sup>}]<sub>2</sub><sup>2+</sup> nor related complexes in which *meso*(P)-L<sup>1</sup> acts as a tetradentate ligand were obtained. The reaction of *trans*-[CoCl<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sub>2</sub><sup>+</sup> with an equimolar amount of Li(acac) afforded [Co(acac){*meso*(P)-L<sup>1</sup>}]<sub>2</sub><sup>2+</sup> and [Co(acac)<sub>2</sub>{*meso*(P)-L<sup>1</sup>}]<sup>+</sup> in similar yields. When the tetradentate *meso*(P)-L<sup>1</sup> forms a *cis-β* structure the remaining two coordination sites are surrounded by the two bulky phenyl groups of L<sup>1</sup>, and seem to hinder the co-ordination of a six-membered



**Fig. 5** Absorption spectra of *cis-α*-[Co(acac){*rac*(P)-L<sup>2</sup>}]<sup>2+</sup> (—), *cis-β*-[Co(acac){*rac*(P)-L<sup>2</sup>}]<sup>2+</sup> (---), and *cis-β*-[Co(acac){*meso*(P)-L<sup>2</sup>}]<sup>2+</sup> (-·-·-) in MeCN

acac chelate ring. An analogous ligand *meso*(P)-NH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>(L<sup>3</sup>) yielded a *cis-β* isomer with acac in small yield, but the complex decomposed slowly in water.<sup>4</sup>

The <sup>1</sup>H NMR spectra of the acac ligand in *cis-α* and *cis-β*-[Co(acac){*rac*(P)- or *meso*(P)-L}<sup>2+</sup> (L = L<sup>1</sup> or L<sup>2</sup>) reflect the structures of three geometrical isomers shown in Fig. 4. The resonance peaks of the methine proton of *cis-β*-[Co(acac){*rac*(P)-L<sup>1</sup>}]<sup>2+</sup> and the methine and one methyl group protons of *cis-β*-[Co(acac){*meso*(P)-L<sup>2</sup>}]<sup>2+</sup> are observed at a fairly high field compared with those of the corresponding protons of other isomers (Table 4). The high-field shifts of these methine and methyl proton signals are attributed to the shielding effect of the phenyl group located near these protons. The complex [Co(acac){*meso*(P)-L<sup>1</sup>}]<sup>2+</sup> **5** shows six singlet methyl proton signals, one of which and the methine proton signal of acac are shifted to high field. This spectral pattern is consistent only with the molecular model of the *trans*[P(*R*)P(*S*)] isomer.

Fig. 5 shows the absorption spectra of *cis-α*- and *cis-β*-[Co(acac){*rac*(P)-L<sup>2</sup>}]<sup>2+</sup> and *cis-β*-[Co(acac){*meso*(P)-L<sup>2</sup>}]<sup>2+</sup>. These are similar to those of the corresponding isomers of [Co(acac)L<sup>4</sup>]<sup>2+</sup> (L<sup>4</sup> = NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPhCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>); the first d-d bands of the *cis-β* isomers are broader than that of the *cis-α* isomer and have a shoulder to lower energy.<sup>4</sup> The similarity in spectra between the L<sup>2</sup> and the L<sup>4</sup> complexes indicates that the ligand-field strength of SMe is similar to that of NH<sub>2</sub>.<sup>23</sup> The spectra of the L<sup>1</sup> complexes are quite similar to those of the corresponding L<sup>2</sup> complexes.

Both *cis-α* and *cis-β* isomers of [Co(acac){*rac*(P)-L}<sup>2+</sup> (L = L<sup>1</sup> or L<sup>2</sup>) change in absorption spectra in organic solvents at elevated temperatures with isosbestic points, the final spectra being the same for both isomers. These results indicate that these two isomers isomerize to each other in solution to give an equilibrium mixture. The isomerization reactions were also monitored by the <sup>1</sup>H NMR spectral changes with time, and the molar ratios of the isomers at equilibrium in MeNO<sub>2</sub> solutions were obtained; *cis-α* : *cis-β* = 2 : 1 for the L<sup>1</sup> complex and 3 : 2 for the L<sup>2</sup> one. Such an isomerization reaction was not observed for the corresponding NPPN complexes.<sup>4</sup>

The reaction of L<sup>2</sup> [a mixture of *meso*(P) and *rac*(P) isomers] with [Co(acac)<sub>3</sub>] in methanol in the presence of active charcoal afforded [Co(acac)<sub>2</sub>{*meso*(P)-L<sup>2</sup>}]<sup>+</sup> and Δ(*RR*)/Λ(*SS*)-[Co(acac)<sub>2</sub>{*rac*(P)-L<sup>2</sup>}]<sup>+</sup>, and no Δ(*SS*)/Λ(*RR*) isomer of the *rac*(P)-L<sup>2</sup> complex was formed. The same reaction with L<sup>1</sup> did not yield the Δ(*SS*)/Λ(*RR*) isomer.<sup>7</sup> However, reactions of *cis-α*-[CoCl<sub>2</sub>{*rac*(P)-L}<sup>+</sup> (L = L<sup>1</sup> or L<sup>2</sup>) with Li(acac) in a molar ratio of 1 : 3 in the absence of active charcoal yielded a mixture

of Δ(*RR*)/Λ(*SS*)- and Δ(*SS*)/Λ(*RR*)-[Co(acac)<sub>2</sub>{*rac*(P)-L}<sup>+</sup>. Although the two isomers were not separated by column chromatography, their molar ratio was estimated to be Δ(*RR*)/Λ(*SS*) : Δ(*SS*)/Λ(*RR*) = 2 : 1 for both the L<sup>1</sup> and L<sup>2</sup> complexes from the intensity ratio of the methine proton of acac in the <sup>1</sup>H NMR spectra. Thus, [Co(acac)<sub>2</sub>{*rac*(P)-L}<sup>+</sup> seems to be more stable in the Δ(*RR*)/Λ(*SS*) than the Δ(*SS*)/Λ(*RR*) isomer. In the Δ(*RR*)/Λ(*SS*) isomer the phenyl group of the SPPS ligand is located over the acac chelate ring as indicated by the high-field shift of the methine proton of acac. This structure may be more stable than that of the other Δ(*SS*)/Λ(*RR*) isomer where the CH<sub>2</sub>CH<sub>2</sub>SMe group is located over the acac chelate ring.

## Conclusion

This study has revealed that L<sup>1</sup> and L<sup>2</sup> bearing only soft donor groups can function as a tetradentate ligand to a hard cobalt(III) ion to afford complexes of various geometrical isomers (*trans*, *cis-α*, and *cis-β*). The co-ordination modes are governed specifically by the absolute configurations of the inner chiral phosphorus atoms and the conformations of the P-Co-P chelate rings. Several complexes in which the SPPS compounds co-ordinate as didentate ligands through two phosphorus atoms were obtained (complexes **1**, **5**, **11** and **12**), such co-ordination modes not being observed for the corresponding NPPN compounds. The isomerization equilibrium between the *cis-α* and *cis-β* isomers of acac complexes was observed also only for the SPPS-type ligands and not the NPPN-type ones. These differences in behaviour may be caused by the weaker co-ordination ability of thioether than amino groups to a cobalt(III) ion.

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