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Reactivity of *mer*-hydrido(2-mercaptobenzoyl)tris(trimethylphosphine)cobalt(III) complex<sup>†</sup>

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The reactivity of *mer*-hydrido(2-mercaptobenzoyl)tris(trimethylphosphine)cobalt(III) complex **1** was intensively studied. A series of sulfur-coordinated organocobalt complexes (**2–8**) were obtained through the reactions of **1** with RX (RX = HCl,  $C_2H_5Br$  and  $CH_3I$ ), 2-(diphenylphosphanyl)phenol, 2-(diphenylphosphino)benzenethiol, and CO. The reaction of complex **1** with ethynyltrimethylsilane under 1 bar of CO afforded a penta-coordinate cobalt(II) complex **11** *via* insertion reaction of C $\equiv$ C bond of ethynyl-trimethylsilane into Co–H bond and subsequent C,C-coupling reaction (reductive elimination). The formation mechanism of **11** was proposed and partly-experimentally verified. As an intermediate, the tetra-coordinate cobalt(I) complex **13** was isolated through the reaction of complex **1** with ethynyl-trimethylsilane in the absence of CO. The crystal structures of complexes **2–4**, **8** and **11** were determined by X-ray diffraction.

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## Introduction

The chemistry of thiosalicylaldehydes through the replacement of an oxygen atom (hard base) in salicylaldehydes by a sulfur atom (soft base) attracts considerable attention from an increasing number of researchers. The sulfur atom of thiosalicylaldehydes can easily coordinate soft acid, such as a lowvalent metal center Co(i), to form stable complexes.<sup>1–10</sup> Thiosalicylaldehydes with two functional groups as pre-chelate ligands are especially interesting because they are able to form [C,S]- or [O,S]-chelate complexes or to bridge transition metals affording multinuclear complexes or clusters. Until now the research on the chemistry of thiosalicylaldehydes is limited because it is not easy to prepare the derivatives of thiosalicylaldehydes. Finally, the unpleasant odor of sulfurcontaining compounds is another reason for this slow development.

Recently we reported the synthesis of sulfur-coordinated acyl(hydrido)cobalt(III) complex **1** by reaction of thiosalicylaldehyde with  $CoMe(PMe_3)_4$  (eqn (1)). Complex **1** was found to be an excellent catalyst for hydrosilylation of aldehydes and ketones under mild condition.<sup>11</sup>

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As a continuation to study the properties of *mer*-hydrido-(2-mercaptobenzoyl)tris(trimethylphosphine)cobalt(III) complex **1**, the reactivity of complex **1** was intensively studied and a series of novel sulfur-containing organocobalt complexes supported by trimethylphosphine ligands were successfully synthesized.

### Experimental

#### General procedures and materials

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. This standard vacuum technique was used in manipulations of volatile and air-sensitive materials. All the solvents were distilled from Na/benzophenone under nitrogen. Co(PMe<sub>3</sub>)<sub>4</sub>Me was prepared from the literature method.<sup>12</sup> Thiosalicylaldehyde was synthesized by our modified procedure.<sup>13</sup> All other chemicals were purchased from Aldrich or Acros and used as received without further purification. Infrared spectra, as obtained from Nujol mulls between KBr disks, were performed within the 4000–400 cm<sup>-1</sup> region on a Bruker ALPHA FT-IR Spectrometer. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra (300, 75 and 121 MHz, respectively) were



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recorded on a Bruker Avance 300 spectrometer with  $C_6D_6$  as the solvent without internal reference at room temperature. <sup>13</sup>C and <sup>31</sup>P NMR resonances were obtained with broad band proton decoupling. Elemental analyses were carried out on Elementar Vario ELIII. Melting points were measured in capillaries sealed under argon and are uncorrected. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

Synthesis of 2. A sample of 1 (0.70 g, 1.65 mmol) in 30 mL of  $Et_2O$  was combined with HCl (2.8 mL, 0.6 mmol mL<sup>-1</sup> in  $Et_2O$  in 20 mL of  $Et_2O$  at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. During this period, the reaction mixture turned brown-red in color. After being filtered in vacuo, the resulting solid was extracted with pentane (40 mL). Crystallization from Et<sub>2</sub>O at -20 °C afforded red crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.55 g (73%). Dec. >175 °C. IR (Nujol mull, 4000–400 cm<sup>-1</sup>): 3028  $\nu$ (C<sub>Ar</sub>–H), 1599  $\nu$ (C=O), 1561  $\nu$ (C=C), 941  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  1.23 (t',  $|^{2}J(PH) + {}^{4}J(PH)| = 6.0$  Hz, 18H, PCH<sub>3</sub>), 1.31  $(d, {}^{2}J(PH) = 8.4 \text{ Hz}, 9H, PCH_{3}), 6.77 (t, {}^{3}J(HH) = 6.0 \text{ Hz}, 1H,$ Ar-H), 7.03 (t,  ${}^{3}J(HH) = 6.0$  Hz, 1H, Ar-H), 7.54 (d,  ${}^{3}J(HH) =$ 6.0 Hz, 1H, Ar-*H*), 7.78 (d,  ${}^{3}J(HH) = 6.0$  Hz, 1H, Ar-*H*);  ${}^{31}P$  NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm): δ 3.0 (br s, 1P, PCH<sub>3</sub>), -5.9 (br s, 2P, *P*CH<sub>3</sub>). Anal. Calc. for  $C_{16}H_{31}ClCoOP_{3}S$  (458.79 g mol<sup>-1</sup>): C, 41.89; H, 6.81. Found: C, 41.63; H, 6.72.

Synthesis of 3. A sample of 1 (0.65 g, 1.53 mmol) in 20 mL of Et<sub>2</sub>O was combined with bromoethane (0.17 g, 1.53 mmol) in 20 mL of Et<sub>2</sub>O at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. During this period, the reaction mixture turned brown-red in color. After being filtered in vacuo, the resulting solid was extracted with pentane (30 mL). Crystallization from  $Et_2O$  at -20 °C afforded red crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.53 g (69%). Dec. >159 °C. IR (Nujol mull, 4000-400 cm<sup>-1</sup>): 3044  $\nu$ (C<sub>Ar</sub>-H), 1601  $\nu$ (C=O), 1564  $\nu$ (C=C), 939  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  1.28  $(t', |^2 J(PH) + {}^4 J(PH)| = 6$  Hz, 18H, PCH<sub>3</sub>), 1.33 (d,  ${}^2 J(PH) = 8.7$ Hz, 9H, PCH<sub>3</sub>), 6.77 (t,  ${}^{3}J(HH) = 6.0$  Hz, 1H, Ar-H), 7.03  $(t, {}^{3}J(HH) = 6.0 \text{ Hz}, 1H, \text{Ar-}H), 7.37 (d, {}^{3}J(HH) = 6.0 \text{ Hz}, 1H,$ Ar-*H*), 7.77 (d,  ${}^{3}J(HH) = 6.0$  Hz, 1H, Ar-*H*);  ${}^{31}P$  NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm): δ 3.8 (br s, 1P, PCH<sub>3</sub>), -9.3 (br s, 2P, PCH<sub>3</sub>). Anal. Calc. for  $C_{16}H_{31}BrCoOP_{3}S$  (503.24 g mol<sup>-1</sup>): C, 38.19; H, 6.21. Found: C, 37.87; H, 6.18.

Synthesis of 4. A sample of 1 (0.60 g, 1.42 mmol) in 20 mL of Et<sub>2</sub>O was combined with iodomethane (0.20 g, 1.42 mmol) in 20 mL of Et<sub>2</sub>O at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 14 h. During this period, the reaction mixture turned brown-red in color. After filtering *in vacuo*, the resulting solid was extracted with pentane (30 mL). Crystallization from Et<sub>2</sub>O at -20 °C afforded red crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.52 g (67%). Dec. >148 °C. IR (Nujol mull, 4000–400 cm<sup>-1</sup>): 3050  $\nu$ (C<sub>Ar</sub>-H), 1605  $\nu$ (C=O), 1565  $\nu$ (C=C), 940  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  1.34 (m, 27 H, PCH<sub>3</sub>), 6.76 (t, <sup>3</sup>*J*(HH) = 6.0 Hz, 1H, Ar-H), 7.02

(t,  ${}^{3}J(\text{HH}) = 6.0 \text{ Hz}$ , 1H, Ar-*H*), 7.56 (d,  ${}^{3}J(\text{HH}) = 6.0 \text{ Hz}$ , 1H, Ar-*H*), 7.75 (d,  ${}^{3}J(\text{HH}) = 6.0 \text{ Hz}$ , 1H, Ar-*H*);  ${}^{31}\text{P}$  NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  1.8 (br s, 1P, *P*CH<sub>3</sub>), -14.7 (br s, 2P, *P*CH<sub>3</sub>). Anal. Calc. for C<sub>16</sub>H<sub>31</sub>CoIOP<sub>3</sub>S (550.24 g mol<sup>-1</sup>): C, 34.92; H, 5.68. Found: C, 35.11; H, 5.51.

Synthesis of 5. A sample of 1 (0.55 g, 1.30 mmol) in 30 mL of Et<sub>2</sub>O was combined with 2-(diphenylphosphino)phenol (0.35 g, 1.30 mmol) in 30 mL of  $Et_2O$  at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned dark brown-red in color. After filtering, crystallization from Et<sub>2</sub>O at -20 °C afforded 5 as yellow needle crystals in the yield of 65% (0.52 g). Dec. >173 °C. IR (Nujol mull, 4000-400 cm<sup>-1</sup>): 3058  $\nu$ (C<sub>Ar</sub>-H), 1618  $\nu$ (C=O), 1570  $\nu$ (C=C), 1535  $\nu$ (C=C), 948  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  0.79 (t',  $|^{2}J(PH) + {}^{4}J(PH)| = 9.0$  Hz, 18H, PCH<sub>3</sub>), 6.88-6.92 (m, 1H, Ar-H), 6.93-6.96 (m, 1H, Ar-H), 6.98-7.02 (m, 2H, Ar-H), 7.05-7.10 (m, 5H, Ar-H), 7.69-7.76 (m, 2H, Ar-H), 7.95-8.00 (m, 2H, Ar-H), 8.09-8.13 (m, 1H, Ar-H), 8.28-8.34 (m, 4H, Ar-H); <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  -6.8 (br s, 2P, PCH<sub>3</sub>), 40.7 (br s, 1P, PPh); Anal. Calc. for C<sub>31</sub>H<sub>36</sub>CoO<sub>2</sub>P<sub>3</sub>S (624.54 g mol<sup>-1</sup>): C, 59.62; H, 5.81. Found: C, 59.95; H, 5.68.

Synthesis of 6. A sample of 1 (0.60 g, 1.42 mmol) in 30 mL of Et<sub>2</sub>O was combined with 2-(diphenylphosphino)benzenethiol (0.41 g, 1.40 mmol) in 30 mL of  $Et_2O$  at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned dark brown-red in color. After being filtered in vacuo, crystallization from  $Et_2O$  at -20 °C afforded 6 as yellow needle crystals in a yield of 60% (0.54 g). Dec. >179 °C. IR (Nujol mull, 4000-400 cm<sup>-1</sup>): 3052  $\nu$ (C<sub>Ar</sub>-H), 1618  $\nu$ (C=O), 1569  $\nu$ (C=C), 1553  $\nu$ (C=C), 946  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  0.79 (t',  $|^{2}J(PH) + {}^{4}J(PH)| = 9.0$  Hz, 18H, PCH<sub>3</sub>), 6.88-6.91 (m, 1H, Ar-H), 6.93-6.96 (m, 1H, Ar-H), 6.97-7.01 (m, 2H, Ar-H), 7.04-7.11 (m, 5H, Ar-H), 7.69-7.76 (m, 2H, Ar-H), 7.96-8.00 (m, 2H, Ar-H), 8.09-8.13 (m, 1H, Ar-H), 8.28-8.34 (m, 4H, Ar-*H*); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  15.1 (t',  $|{}^{1}J(PC) + {}^{3}J(PC)| = 29.3$  Hz, PCH<sub>3</sub>), 119.9–136.7 (s, C<sub>arom</sub>), 201.6 (s, C=O); <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm): δ -6.5 (br s, 2P, PCH<sub>3</sub>), 40.4 (br s, 1P, PPh); Anal. Calc. for C<sub>31</sub>H<sub>36</sub>CoOP<sub>3</sub>S<sub>2</sub> (640.60 g mol<sup>-1</sup>): C, 58.12; H, 5.66. Found: C, 57.91; H, 5.49.

**Synthesis of** 7. A sample of 2 (0.50 g, 1.31 mmol) in 40 mL of Et<sub>2</sub>O was stirred under 1 bar of CO at room temperature for 18 h. During this period, the reaction mixture turned clear red in color. After being filtered *in vacuo*, the resulting solid was extracted with pentane (40 mL). Crystallization from Et<sub>2</sub>O at -20 °C afforded red crystals of 7. Yield: 0.32 g (58%). Dec. >197 °C. IR (Nujol mull, 4000–400 cm<sup>-1</sup>): 3056  $\nu$ (C<sub>Ar</sub>-H), 2048  $\nu$ (CO), 1613  $\nu$ (C=O), 1569  $\nu$ (C=C), 942  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  1.20 (t', |<sup>2</sup>*J*(PH) + <sup>4</sup>*J*(PH)| = 9.0 Hz, 18H, PCH<sub>3</sub>), 6.73 (t, <sup>3</sup>*J*(HH) = 7.5 Hz, 1H, Ar-*H*), 6.95 (t, <sup>3</sup>*J*(HH) = 7.5 Hz, 1H, Ar-*H*), 7.43 (d, <sup>3</sup>*J*(HH) = 8.1 Hz, 1H, Ar-*H*), 7.58 (d, <sup>3</sup>*J*(HH) = 7.8 Hz, 1H, Ar-*H*); <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  2.2 (br s, *P*CH<sub>3</sub>). Anal. Calc. for

 $\rm C_{14}H_{22}ClCoO_2P_2S$  (410.72 g mol^-1): C, 40.94; H, 5.40. Found: C, 41.17; H, 5.60.

Synthesis of 8. A sample of 4 (0.55 g, 1.00 mmol) in 40 mL of Et<sub>2</sub>O was stirred under 1 bar of CO at room temperature for 18 h. During this period, the reaction mixture turned clear red in color. After being filtered *in vacuo*, the resulting solid was extracted with pentane (40 mL). Crystallization from Et<sub>2</sub>O at -20 °C afforded 8 as red crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.31 g (65%). Dec. >163 °C. IR (Nujol mull, 4000-400 cm<sup>-1</sup>): 3064  $\nu$ (C<sub>Ar</sub>-H), 2039  $\nu$ (CO), 1615  $\nu$ (C=O), 1574  $\nu$ (C=C), 952  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  1.27 (t', |<sup>2</sup>J(PH) + <sup>4</sup>J(PH)| = 9.0 Hz, 18H, PCH<sub>3</sub>), 6.71 (t, <sup>3</sup>J(HH) = 4.5 Hz, 1H, Ar-H), 6.95 (t, <sup>3</sup>J(HH) = 4.5 Hz, 1H, Ar-H), 7.57 (d, <sup>3</sup>J(HH) = 4.5 Hz, 1H, Ar-H); <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  -2.6 (br s, *P*CH<sub>3</sub>). Anal. Calc. for C<sub>14</sub>H<sub>22</sub>CoIO<sub>2</sub>P<sub>2</sub>S (502.17 g mol<sup>-1</sup>): C, 33.48; H, 4.42. Found: C, 33.12; H, 4.28.

Synthesis of 9.<sup>14</sup> A sample of 1 (0.70 g, 1.65 mmol) in 30 mL of Et<sub>2</sub>O was combined with 2-hydroxy-5-phenylcyclohex-1enecarbaldehyde (0.33 g, 1.65 mmol) in 20 mL of Et<sub>2</sub>O at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 14 h. During this period, the reaction mixture turned brown-red in color. After being filtered *in vacuo*, the resulting solid was extracted with pentane (30 mL). Crystallization from Et<sub>2</sub>O at -20 °C afforded 9 as yellow powder. Yield: 0.56 g (69%). Dec. >136 °C. IR (Nujol mull, 4000–400 cm<sup>-1</sup>): 1883  $\nu$ (Co–H), 1583  $\nu$ (C=O), 1541  $\nu$ (C=C), 938  $\rho$ (PMe<sub>3</sub>).

Synthesis of 11. A solution of 1 (0.65 g, 1.53 mmol) in 40 mL of Et<sub>2</sub>O was combined with trimethylsilylacetylene (0.15 g, 1.53 mmol) in Et<sub>2</sub>O (20 mL) at -80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred under 1 bar of CO at room temperature for 18 h. During this period, the reaction mixture turned red in color. After being filtered in vacuo, the resulting solid was extracted with pentane (40 mL). Crystallization from Et<sub>2</sub>O at -20 °C afforded yellow needle crystals suitable for single-crystal X-ray diffraction analysis. Yield: 0.31 g (62%). Dec. >175 °C. IR (Nujol mull, 4000-400 cm<sup>-1</sup>): 3033  $\nu$ (C<sub>Ar</sub>-H), 1966, 1899  $\nu$ (CO), 1663  $\nu$ (C=O), 1576  $\nu$ (C=C), 943  $\rho$ (PMe<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  0.087 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.17 (t',  $|^{2}J(PH) +$  ${}^{4}J(PH)$  = 8.4 Hz, 18H, PCH<sub>3</sub>), 6.92 (dt,  ${}^{3}J(HH)$  = 7.0 Hz,  ${}^{4}J$ (HH) = 1.5 Hz, 1H, Ar-H), 7.20 (dt,  ${}^{3}J(HH) = 7.8$  Hz,  ${}^{4}J(HH) =$ 1.5 Hz, 1H, Ar-*H*), 7.39 (dd,  ${}^{3}J(HH) = 7.8$  Hz,  ${}^{4}J(HH) = 1.5$  Hz, 1H, Ar-*H*), 7.39 (d,  ${}^{3}J(HH) = 18.6$  Hz, 1H, C=C(*H*)-SiMe<sub>3</sub>), 7.57  $(d, {}^{3}J(HH) = 18.9 \text{ Hz}, 1H, (H)C = CSiMe_{3}), 7.62 (d, {}^{3}J(HH) = 9.0 \text{ Hz},$ 1H, Ar-H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm): δ 1.79 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 17.7 (t',  $|{}^{1}J(PC) + {}^{3}J(PC)| = 34.4$  Hz, PCH<sub>3</sub>), 120.9 (s, C<sub>arom</sub>), 127.2 (s, C<sub>arom</sub>), 128.8 (s, C<sub>arom</sub>), 131.2 (s, C<sub>arom</sub>), 142.8 (s, C<sub>arom</sub>), 144.4 (s, C<sub>arom</sub>), 145.5 (s, HC=CHSi), 147.1 (s, HC=CHSi), 196.9 (s, C=O). <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K, ppm):  $\delta$  25.5 (s, PCH<sub>3</sub>). Anal. Calc. for C<sub>20</sub>H<sub>33</sub>CoO<sub>3</sub>P<sub>2</sub>SSi (502.48 g mol<sup>-1</sup>): C, 47.80; H, 6.62. Found: C, 47.52; H, 6.48.

Synthesis of 13. A solution of 1 (0.50 g, 1.17 mmol) in 40 mL of  $Et_2O$  was combined with trimethylsilylacetylene (0.12 g, 1.17 mmol) in  $Et_2O$  (20 mL) at -80 °C. The reaction

mixture was allowed to warm to ambient temperature and stirred for 14 h. During this period, the reaction mixture turned dark purple-red in color. After being filtered *in vacuo*, the resulting solid was extracted with pentane (40 mL). Crystallization from pentane at -20 °C afforded a purple-red solid **13**. Yield: 0.35 g (58%). Dec. >159 °C. IR (Nujol mull, 4000–400 cm<sup>-1</sup>): 3033  $\nu$ (C<sub>Ar</sub>-H), 1667  $\nu$ (C=O), 948  $\rho$ (PMe<sub>3</sub>). Anal. Calc. for C<sub>21</sub>H<sub>42</sub>CoOP<sub>3</sub>SSi (522.56 g mol<sup>-1</sup>): C, 48.27; H, 8.10. Found: C, 48.57; H, 7.98.

#### X-ray structure determination

Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 293 K. The crystallographic data for complexes 2–4, 8 and 11 are summarized in Table 1. The structures were solved by direct methods and refined with the full-matrix least-squares method on all  $F^2$  (SHELXL-97) with non-hydrogen atoms anisotropic.

### Results and discussion

#### Substitutions of the hydrido ligand of 1 by halogen ligands

The reaction of complex 1 with RX (RX = HCl,  $C_2H_5Br$  and  $CH_3I$ ) afforded three cobalt(m) complexes 2–4 *via* elimination of hydrogen or alkane (eqn (2)).



The halogenocobalt(III) complexes 2–4 were obtained as red crystals in high yield by crystallization from Et<sub>2</sub>O at -20 °C. Crystals of 2–4 remain stable at room temperature for more than three days but they quickly decompose when dissolved and exposed to air. In the <sup>1</sup>H NMR spectra of complexes 2–4 two signals of PMe<sub>3</sub> ligands were recorded in the integral ratio of 2 : 1. Two <sup>31</sup>P NMR resonances (3.05 and -5.9 ppm (2); 3.8 and -9.3 ppm (3) and 1.8 and -14.7 ppm (4)) were registered in the integral ratio of 2 : 1. This indicates a *mer*-orientation of the three phosphine ligands.

The molecular structures of complexes 2–4 confirm a hexacoordinate octahedral geometry in the crystals (Fig. 1–3). Comparing the structures of complexes 2–4 with that of complex  $1,^{11}$  we know that a transformation of the configuration of these complexes occurs during the ligand substitution. Because both hydrido and acyl groups are strong ligands, they are in the *cis*-arrangement in complex 1. In complexes 2–4, the halogen ligands are the weakest and the acyl group is the strongest, therefore, the halogen ligands are always located in the *trans*-positions to the acyl group. This transformation is in line with the *trans*-influence and therefore this coordination for complexes 2–4 is a stable configuration. Due to the order of atom size (Cl < Br < I) the order of the bond angle is P1–Co1–

#### Table 1 Crystallographic data for complexes 2, 3, 4, 8 and 11

	2	3	4	8	11
Empirical formula	C16H31ClCoOP3S	C <sub>16</sub> H <sub>31</sub> BrCoOP <sub>3</sub> S	C16H31CoIOP3S	C14H22CoIO2P2S	C <sub>20</sub> H <sub>33</sub> CoO <sub>3</sub> P <sub>2</sub> Si
FW	458.76	503.22	550.21	502.15	502.48
Cryst syst.	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P2(1)/c	P2(1)/n	P2(1)/n	Pna2(1)	P2(1)/n
a (Å)	8.937(8)	8.859(4)	8.7982(18)	18.283(4)	12.503(6)
b (Å)	15.682(13)	15.756(7)	15.754(3)	8.5829(17)	17.273(8)
c (Å)	17.238(13)	16.177(7)	17.424(4)	12.412(3)	13.307(6)
$\alpha$ (°)	90.00	90.00	90.00	90.00	90.00
$\beta$ (°)	113.86(4)	97.460(7)	98.14	90.00	114.85
γ (°)	90.00	90.00	90.00	90.00	90.00
$V(Å^3)$	2209(3)	2239.0(17)	2390.7(8)	1947.7(7)	2608(2)
Z	4	4	4	4	4
$D_x (g \text{ cm}^{-3})$	1.379	1.493	1.529	1.712	1.280
No. of rflns collected	10725	12 493	14 113	9171	12 628
No. of unique data	3899	4900	4216	4338	4578
R <sub>int</sub>	0.0569	0.0315	0.0169	0.0247	0.0562
$\theta_{\max}$ (°)	25.00	27.41	25.00	27.55	25.00
$R_1 \left( I > 2\sigma(I) \right)$	0.0539	0.0358	0.0239	0.0353	0.0607
$wR_2$ (all data)	0.1718	0.0951	0.0653	0.1042	0.1783



Fig. 1 Molecular structure of 2, selected distances (Å) and angles (°): Cl1–Co1 2.436(2), Co1–C7 1.937(5), Co1–S1 2.283(2), Co1–P3 2.272(2), Co1–P2 2.286(2), Co1–P1 2.271(2), C7–O1 1.218(6), C2–C7 1.402(4); S1–Co1–P1 86.29(7), P2–Co1–P1 92.72(7), S1–Co1–Cl1 89.27(6), P3–Co1–P1 169.05(6), S1–Co1–P2 175.11(6), C7–Co1–Cl1 176.4(2), P1–Co1–Cl1 86.53(8), P2–Co1–Cl1 95.45(6), P3–Co1–Cl1 85.03(9), S1–Co1–P3 86.63(7), P3–Co1–P2 95.02(6).

P3 (169.05(6)° (2) < P1–Co1–P3 (169.70(3)° (3) < P1–Co1–P2 (170.48(3)° (4). The order of the bond lengths (Co1–C7 (1.937(5)) Å (2) < Co1–C7 (1.950(3)) Å (3) < Co1–C1 (1.996(2)) Å (4)) can be explained with the order of *trans*-influence (I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>). The extraordinary long Co–X bonds (Co1–Cl1 (2.436(2) Å (2)); Co1–Br1 (2.5518(9) Å (3); Co1–I1 (2.8089(8) Å (4))) are also caused by the strong *trans*-influence of the carbon atom of the acyl group.

# Reactions of complex 1 with 2-(diphenylphosphino)phenol and 2-(diphenylphosphino)benzenethiol

The reactions of complex **1** with 2-(diphenylphosphino)phenol and 2-(diphenylphosphino)benzenethiol afforded two hexa-



Fig. 2 Molecular structure of 3, selected distances (Å) and angles (°): Br1–Co1 2.5518(9), Co1–C7 1.950(3), Co1–S1 2.288(1), Co1–P3 2.272(1), Co1–P2 2.293(1), Co1–P1 2.277(1), C7–O1 1.185(4); S1–Co1–P1 86.81(4), P2–Co1–P1 94.80(4), S1–Co1–Br1 88.43(3), P3–Co1–P1 169.70(3), S1–Co1–P2 175.34(4), C7–Co1–Br1 176.07(9), C7–Co1–P2 87.6(1), C7–Co1–S1 88.0(1), C7–Co1–P3 94.4(1), C7–Co1–P1 92.7(1), P1–Co1–Br1 85.43(4), P2–Co1–Br1 96.05(3), P3–Co1–Br1 86.94(4), S1–Co1–P3 86.07(4), P3–Co1–P2 92.88(4).

coordinate bis-chelate cobalt(m) complexes 5 and 6 as yellow crystals (eqn (3)).



Complexes 5 and 6 are stable in the air for more than one week. This stability might be supported by the bis-chelate effect. In the IR spectra of 5 and 6 the conspicuous  $\nu$ (Co-H)



Fig. 3 Molecular structure of 4, selected distances (Å) and angles (°): I1-Co1 2.8089(8), Co1-C1 1.996(2), Co1-S1 2.2749(8), Co1-P3 2.2840(8), Co1-P2 2.328(1), Co1-P1 2.331(1), S1-C7 1.796(3), C1-O1 1.224(3), C2-C7 1.402(4); S1-Co1-P3 174.83(3), C1-Co1-I1 175.34(7), P2-Co1-P1 170.48(3), C1-Co1-P2 88.82(8), S1-Co1-P2 86.26(3), P3-Co1-P2 94.94(3), C1-Co1-P1 97.08(8), P3-Co1-I1 96.63(2), P2-Co1-I1 89.22(3), P1-Co1-I1 84.33(2), S1-Co1-P1 86.56(3), P3-Co1-P1 92.76(3).

absorption of the complex **1** is absent. The carbonyl vibrations are found at 1618 (5) and 1617 cm<sup>-1</sup> (6). In the <sup>1</sup>H NMR spectra, the 18 protons of two trimethylphosphine ligands appear at 0.79 ppm as a triplet with  $|^{2}J(PH) + {}^{4}J(PH)| = 9.0$  Hz, which suggests that the two trimethylphosphine ligands are in axial orientation. Complexes **5** and **6** have similar structures to the reported organocobalt(m) complexes, which were obtained from the reactions of acyl(hydrido)cobalt(m) complexes with 2-(diphenylphosphanyl)phenol.<sup>14</sup>

It must be noted that two signals for complexes 2–6 in the <sup>31</sup>P NMR spectra should be one doublet and one triplet in the ratio of 2:1 because of the *meriodal*-orientation of the three trimethylphosphine ligands.<sup>14</sup> Two singlets indicate some dynamic equilibrium in the solution.

#### Reactions of complexes 2 and 4 with carbon monoxide

Complex 2 or 4 in a diethyl ether solution under 1 bar of CO at room temperature slowly transformed to complex 7 or 8 through the replacement of a  $PMe_3$  ligand by a CO ligand (eqn (4)). Complexes 7 and 8 were obtained as red crystals. They begin to decompose above 197 °C (7) and 163 °C (8).



The red crystals of 7 and 8 are very stable in the air for several days. The IR bands of the terminal carbonyl group are recorded at 2048 (7) and 2039 (8) cm<sup>-1</sup> while the acyl C=O vibrations are registered at 1613 (7) and 1615 (8) cm<sup>-1</sup>. The difference between complex 7 and 8 is caused by the change of Cl atom in 7 to I atom in 8. In the <sup>1</sup>H NMR spectra of the two complexes, the resonance of PMe<sub>3</sub> ligands was recorded as a



Fig. 4 Molecular structure of 8, selected distances (Å) and angles (°): I1-Co1 2.6845(6), Co1-C1 1.921(4), Co1-C11 1.781(4), Co1-S1 2.2425(9), Co1-P2 2.249(1), Co1-P1 2.258(1), S1-C7 1.796(3), C1-O1 1.234(5), C11-O2 1.131(4); S1-Co1-I1 91.94(3), C11-Co1-S1 179.4(1), C1-Co1-P1 91.2(1), C1-Co1-P2 87.6(1), C11-Co1-P1 90.9(1), S1-Co1-P2 87.77(4), P3-Co1-P2 94.94(3), C11-Co1-P2 92.7(1), C1-Co1-I1 178.5(1), P2-Co1-I1 91.28(3), C11-Co1-S1 89.0(1), S1-Co1-P1 88.57(4), P2-Co1-P1 176.17(4), C11-Co1-I1 88.5(1), C11-Co1-C1 90.6(2), Co1-C11-O2 177.9(3).

triplet at 1.20 (7) and 1.27 (8) ppm. All of the spectroscopic information implies that complexes 7 and 8 have hexa-coordinate geometry.

The molecular structure (Fig. 4) of **8** shows a hexa-coordinate octahedral geometry with two *trans*-phosphine ligands and one equatorial [C,S]-chelate ring. This is consistent with the observation from the spectroscopic data. The Co1–I1 distance (2.6845(6) Å) is shorter than that (2.8089(8) Å) in complex **4**. It is suggested that the Co1–I1 bond in **8** is reinforced through the increase of the positive charge at the cobalt center. This increase is caused by the  $\pi$ -backbonding between cobalt and CO in complex **8**. The shorter distance of C11–O2 (1.131(4) Å) compared to that of C1–O1 (1.234(5) Å) suggests that the coordination of the terminal carbonyl group is enhanced by the  $\pi$ -backbonding. For the same reason Co1–C1 (1.921(4) Å) is longer than Co1–C11 (1.781(4) Å).

#### Reaction of complex 1 with 2-hydroxy-5-phenylcyclohex-1enecarbaldehyde

The reaction of complex **1** with 2-hydroxy-5-phenylcyclohex-1enecarbaldehyde afforded a hydrido(acyl)enolatocobalt(m) complex **9**<sup>15</sup> as yellow powder in the yield of 69% and thiosalicylaldehyde<sup>16</sup> confirmed by IR (Scheme 1). This chelate ligand exchange shows that hydrido(acyl)enolatocobalt(m) complex **9** is more stable than hydrido(2-mercaptobenzoyl)cobalt(m) complex **1**. Under reaction conditions the expected bis-chelate complex **[10]** was not formed *via* the escape of one molecule of dihydrogen. This indicates that the enol-OH hydrogen of 2-hydroxy-5-phenylcyclohex-1-enecarbaldehyde is not acidic enough to react with the hydridic hydrogen of complex **1**. This experimental result can also be understood according to the



Scheme 1 Reaction of 1 with 2-hydroxy-5-phenylcyclohex-1-enecarbaldehyde.



Scheme 2 proposed mechanism of formation of 9.

HSAB rule. Complex 9 formed through hard/(O)-hard/(Co(m)) combination is more stable than complex 1 and 10 with soft/ (S)-hard/(Co(m)) combination.

The proposed mechanism of the formation of complex 9 is suggested in Scheme 2. The first step is the substitution of a trimethylphosphine ligand by the oxygen atom of the aldehyde group of 2-hydroxy-5-phenylcyclohex-1-enecarbaldehyde to form intermediate a. With this coordinated aldehyde group as the anchoring group, the reductive elimination between Co-H and Co-acyl occurs to afford the penta-coordinated cobalt(1) intermediate **b** with the recovery of the aldehyde group of the thiosalicylaldehyde ligand. The other hexa-coordinate hydrido cobalt(m) species c is produced from b via oxidative addition of the O-H bond of coordinated 2-hydroxy-5-phenylcyclohex-1enecarbaldehyde at the cobalt center. The reductive elimination between Co-S and Co-H bonds in the presence of trimethylphosphine delivers intermediate d. The end product 9 can be obtained by oxidative addition of the C-H bond of the aldehyde group of 2-hydroxy-5-phenylcyclohex-1-enecarbaldehyde.

# Insertion reaction of complex 1 with ethynyltrimethylsilane in the presence of carbon monoxide

The reaction of complex 1 with ethynyltrimethylsilane under 1 bar of CO in diethyl ether gave rise to a penta-coordinate

cobalt(1) complex **11** as yellow needle crystals *via* C,C-coupling (eqn (5)). The yellow needle crystals of complex **11** are stable in air and decompose above 175 °C.



In the IR spectra of complex **11** two strong absorptions at 1966 and 1899 cm<sup>-1</sup> belong to the two terminal carbonyl ligands. The acyl  $\nu$ (C=O) and  $\nu$ (C=C) bands are found at 1663 and 1576 cm<sup>-1</sup> respectively. In the <sup>1</sup>H NMR spectra, the resonance of -SiMe<sub>3</sub> was recorded as a singlet at 0.087 ppm while one triplet for two PMe<sub>3</sub> ligands at 1.17 ppm was recorded with  $|^2J(PH) + {}^4J(PH)| = 8.4$  Hz. The resonances of two vinyl-protons of CH=CH-SiMe<sub>3</sub> were recorded as two doublets at 7.39 ppm ( ${}^3J(HH) = 18.6$  Hz, CH=CH-SiMe<sub>3</sub>) and 7.57 ppm ( ${}^3J(HH) = 18.9$  Hz, CH=CHSiMe<sub>3</sub>) respectively, which are comparable with the related compounds reported by Pawluc.<sup>17</sup>

Complex **11** was further studied by X-ray diffraction. Complex **11** (Fig. 5) shows a trigonal bipyramidal configuration with two *trans*-phosphine ligands and three atoms (S1, C7 and

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Fig. 5 Molecular structure of **11**, selected distances (Å) and angles (°): O1-C8 1.143(6), O2-C7 1.136(6), O3-C15 1.205(6), C13-C15 1.471(6), C16-C17 1.291(7), Co1-C8 1.723(6), Co1-C7 1.741(6), Co1-P2 2.176(2), Co1-P1 2.176(2), Co1-S1 2.296(2), Si1-C17 1.841(6), C15-C16 1.481(7); C8-Co1-C7 128.1(3), C8-Co1-S1 108.8(2), C7-Co1-S1 123.1(2), P2-Co1-P1 176.80(6), C14-S1-Co1 115.9(2), C13-C15-C16 117.2(4), C17-C16-C15 125.5(5), C16-C17-Si1 127.0(5), C18-Si1-C17 110.2(3), C20-Si1-C17 107.2(3), C17-Si1-C19 109.9(3).

C8) in the triangular plane. The acyl and -SiMe<sub>3</sub> groups are in *E*-configuration of the olefin C=C bond. Interestingly, the plane of the conjugated acyl and olefin group is not coplanar with the phenyl ring. This might be caused by the packing effect. C16-C17 distance (1.291(7) Å) is a little bit shorter than the normal olefin C=C bond. The sum  $(360.0^{\circ})$  of the three bond angles (C8-C01-C7 128.1(3), C8-C01-S1 108.8(2) and C7-Co1-S1 123.08(17)°) around the central cobalt atom proves that the four atoms (Co1, S1, C7 and C8) are in the same plane. The angle P2-Co1-P1 (176.80(6)°) close to 180° bends to the direction of the Co1-S1 bond. A similar reaction of hydrido(acylenolato)cobalt(m) complex with ethynyltrimethylsilane gave rise to a penta-coordinate  $\pi$ -olefin cobalt(1) complex in the absence of CO.<sup>16</sup> It is proposed that the bulky -SiMe<sub>3</sub> group makes the coordination of the olefin group to the cobalt center impossible. In addition, the  $\pi$ -backbonding between the two carbonyl ligands and cobalt(1) center also lead to difficulty of the coordination of the olefin group to the cobalt(1) center. In addition, hexa-coordinate cobalt(1) complex (20 VE) is rare.

The proposed mechanism of formation of complex **11** is suggested in Scheme 3. The first step is insertion of an ethynyl group into the Co–H bond to give rise to a vinyl cobalt(m) intermediate **12**. The analogous cobalt(m) complexes with acylenolato ligand to **12** was structurally characterized.<sup>18</sup> Reductive elimination of both coordinated Co–C bonds of **12** delivers a tetra-coordinate cobalt(i) intermediate **13** *via* C,C-coupling. Substitution of PMe<sub>3</sub> by CO and coordination of CO lead to the transformation of **13** to end product, complex **11**.

In order to verify the proposed mechanism of formation of complex **11** in Scheme 3 experiments to isolate intermediates **12** and **13** were carried out. The reaction of complex **1** with ethynyltrimethylsilane in the absence of CO gave rise to red solid of **13**, which was isolated from diethyl ether solution. The band of  $\nu$ (C=O) at 1667 cm<sup>-1</sup> in the IR spectra of **13** indicated that the C,C-coupling occurred while the  $\nu$ (C=O) of **1** is



Scheme 3 Proposed mechanism of formation of 11.

1589  $\text{cm}^{-1}$ . Because intermediate 13 is paramagnetic, there are no reasonable NMR spectra to be observed. It could be concluded that no  $\pi$ -coordination of the olefin group to the cobalt center occurred because penta-coordinate cobalt(I) complex is antimagnetic. The comparable cobalt(1) complexes with acylenolato ligand was structurally characterized.<sup>18</sup> Possibly, the electron-withdrawing property of the -SiMe<sub>3</sub> group and steric effect make the  $\pi$ -coordination of the olefin group to the cobalt(1) center in 13 difficult. Under reaction conditions intermediate 12 could not be isolated. According to the HSAB rule<sup>19</sup> intermediate 12 formed through soft/(S)-hard/(Co(III)) combination is more unstable than the corresponding acylenolatocobalt(III) with O-coordination.<sup>18</sup> The tetra-coordinate 13 under 1 bar of CO in diethyl ether solution transformed to penta-coordinate complex 11 through the replacement of PMe<sub>3</sub> by CO. The molecular structure of 11 confirmed by X-ray single crystal diffraction is a strong evidence for the formation of intermediate 13.

### Conclusions

In summary, the reactivity of sulfur-coordinated acyl(hydrido)cobalt(III) complex 1 was intensively studied. Complex 1 has similar reaction properties to those of its oxo analogues, the hydrido(acylphenolato)cobalt(m) complexes, but the former is more reactive than the latter. This can be easily understood from the viewpoint of HSAB theory. For the reactions (2)-(4), no significant difference of the chemical properties between these two kinds of complexes could be perceived. From Schemes 1 and 2 it can be seen that reactive complex 1 was more easily converted into a more stable oxo complex 9. Reaction (5) was so fast that intermediate 12 could not be isolated or detected, while the similar intermediate of the corresponding oxo complex could possibly be separated.<sup>18</sup> In addition, the experiments proved that complex 1 is an excellent catalyst for hydrosilylation of aldehydes and ketones under mild conditions,<sup>11</sup> while its oxo analogues do not have catalytic activity for this transformation. The reason is that complex 1 as a cobalt(III) compound with a softer S coordination atom is more unstable than the corresponding cobalt(III) complex with a harder O coordination atom. This instability is the driving force for a catalytic cycle. We think that this instability of complex **1** may cause the following results: (1) Complex **1** is more prone to ligand dissociation to generate an unsaturated coordinate intermediate which is necessary for starting a catalytic cycle. (2) The hydrido hydrogen in complex **1** is more nucleophilic than that of its oxo analogue. (3) The unstable alkoxy cobalt(m) intermediate of complex **1** means the reductive elimination reaction is more likely to occur. All these factors indicate that complex **1** is a potential catalyst.<sup>11</sup>

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