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Reaction of acyl(hydrido)cobalt(III) complexes with (2-diphenylphosphanyl)thiophenol and the influence of chelating ligands containing hard/soft donor atoms on the stability of cobalt complexes

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Abstract

The reaction of acyl(hydrido)cobalt(III) complexes $Co^{III}(O^{\cap}C{=}O)(H)(PMe_3)_3$ (**1**–**5**) with (2-diphenylphosphanyl)thiophenol afforded four types of complexes $Co^{III}(O^{\cap}C{=}O)(P^{\cap}S)(PMe_3)_2$ (**6**–**7**), $Co^{III}(O^{\cap}C{=}O)(O^{\cap}OHC)(PMe_3)_2$ (**11**–**15**), $Co^{I}(P^{\cap}S)(PMe_3)_3$ (**16**), and $Co^{II}(P^{\cap}S)_2(PMe_3)$ (**17**). A mechanism for the formation of these complexes is proposed. The influences of chelating ligands containing hard/soft donor atoms on the stability of the cobalt complexes in different oxidation states are discussed with respect to the HSAB concept.

Keywords: Hydridocobalt(III) complex; [P, S]-chelating ligand; Hard/soft donor; Structure

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1. Introduction

Acyl(hydrido)cobalt species stabilized by a (2-acyl)-phenolato chelating ligand and supported by trimethylphosphine ligands were intensively studied by Klein and co-workers [1–5]. The reactions of (acylphenolato)hydridocobalt(III) complexes with 2-nitrophenol and (2-diphenylphosphanyl)phenol were reported [3,4]. The stability of these diorgano bis-chelating complexes was discussed according to HSAB theory. In order to better understand the relationship between the properties of different ligands, molecular structures of cobalt complexes, and stabilities of compounds in different oxidation states, instead of 2-nitrophenol and (2-diphenylphosphanyl)phenol, the soft/soft chelating (2-diphenylphosphanyl)thiophenolato ligand was introduced.

2. Experimental

2.1. Materials and methods

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Acyl(hydrido) cobalt(III) complexes (**1**–**5**) [1], (2-diphenylphosphanyl)thiophenol were synthesized according to literature procedures [6]. C, H analyses were carried out in an Elementor Vario III analyzer. Infrared spectra (4000–400 cm^{-1}), as obtained from Nujol mulls between KBr discs, were recorded on NICOLET 5700. ^{1}H,^{13}C and ^{31}P NMR spectra were obtained from Bruker AVANCE 300 spectrometer (300, 75 and 121 MHz, respectively) or

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Bruker AVANCE 400 spectrometer (400, 100 and 162 MHz, respectively). ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling. Melting points were measured in capillaries sealed under argon and are uncorrected.

2.2. Synthesis of the complexes

2.2.1. *trans-[(1-Carbonyl-2-oxo-cyclohexenediyl)-(2-diphenylphosphanyl)thiophenyl(S,P)]bis-(trimethylphosphine)cobalt(III) (**6**)*

To a suspension of *mer*-hydrido(1-carbonyl-2-oxo-cyclohexenediyl)tris(trimethylphosphine)cobalt(III) (**1**) (1.27 g, 3.07 mmol) in 60 ml of diethyl ether (2-diphenylphosphanyl)thiophenol (0.92 g, 3.12 mmol) dissolved in 20 ml of diethyl ether was added slowly at −80 °C. When the mixture was stirred at ambient temperature for 18 h, the solution changed from yellow to dark-red. After evaporating the volatiles under vacuum, the residue was extracted with pentane and diethyl ether. Both filtrates were crystallized at −27 °C. From pentane solution complex **6** was obtained as dark-red cubic crystals which turned to effloresce under vacuum. Yield: 0.17 g of **6** (9% based on **1**). **17** was also obtained from pentane as brown-yellow cubic crystals suitable for X-ray diffraction analysis. Yield: 0.09 g of **17** (8% based on (2-diphenylphosphanyl)thiophenol). From THF **11** could be obtained as red microcrystals: 0.18 g (yield 25%, based on **1**). From diethyl ether **16** was isolated as brown crystals: 0.61 g (yield 33% based on (2-diphenylphosphanyl)thiophenol). **6**: m.p. (dec.) > 142 °C. *Anal.* Calc. for $C_{31}H_{40}CoO_2P_3S$ (628.57 g/mol): C, 59.23; H, 6.41. Found: C, 59.31; H, 6.38%. IR (Nujol mull, 2600–1550 cm^{-1}): 1608 s, ν(C=O); 1557 s, ν(C=C). ^{1}H NMR (300 MHz, C_6D_6, 296 K, ppm): δ(PCH_3) 0.825 (t', $|^2J(PH) + {}^4J(PH)| = 8.1$ Hz, 18H); δ(C–CH$_2$–CH_2) 1.63 (m, 4H); δ(CCH_2) 2.37 (s, 2H); δ(CCH_2) 2.78 (s, 2H); δ(C$H_{\rm arom}$) 6.93–8.36 (m, 14H). ^{13}C NMR (75 MHz, C_6D_6, 298 K, ppm): δ(PCH$_3$) 13.22 (t', $|^1J(PC) + {}^3J(PC)| = 27$ Hz); δ(CH$_2$) 23.9, 24.2, 24.4, 33.3; δ(C$_{\rm arom}$) 113.4, 120.2, 125.6, 129.3, 131.6, 132.2, 133.6, 138.6, 140.5; δ(CO), 165.9; δ(CCO), 189.5. ^{31}P NMR (121 MHz, C_6D_6, 296 K, ppm): δ(PCH$_3$) −1.44 (s, 2P); δ(PPh$_2$), 32.9 (s, 1P). **11**: m.p. (dec.) > 145 °C. *Anal.* Calc. for $C_{20}H_{35}CoO_4P_2$ (460.37 g/mol): C, 52.18; H, 7.66. Found: C, 52.01; H, 7.72%. IR (Nujol mull, 2600–1500 cm^{-1}): 1592 s, ν(C=O); 1550, 1530 s, ν(C=C). ^{1}H NMR (300 MHz, CDCl$_3$, 293 K, ppm): *cis*/*trans*-**11** = 2/1. *cis*-**11**: δ(PCH_3) 1.18 (d, $^2J(PH) = 9.1$ Hz, 18H); δ(CHO) 7.55 (d, $^4J(PH) = 9.6$ Hz, 1H). *trans*-**11**: δ(PCH_3) 1.15 (s, 18H); δ(CHO) 8.40 (s, 1H); without assignmet: δ(CH_2) 1.40–2.53 (m, 16H). ^{31}P NMR (121 MHz, CDCl$_3$, 294 K, ppm): *cis*-**11**: δ(PCH$_3$) 19.0 (s, br); *trans*-**11**: δ(PCH$_3$) 12.4 (s, br).

17: m.p. (dec.) > 230 °C. *Anal.* Calc. for $C_{39}H_{37}CoP_3S_2$ (721.7 g/mol): C, 64.91; H, 5.17. Found: C, 64.83; H, 5.24%. IR (Nujol mull, 2600–1500 cm^{-1}): 1575 s, ν(C=C).

2.2.2. *[(3,5-Di-tert-butyl-2-oxobenzoyl)(2-diphenylphosphanyl)thiophenyl(S,P)]bis(trimethylphosphine)cobalt(III) (7) and [(3,5-di-tert-butyl-2-oxobenzoyl)(2,4-di-tert-butyl-6-formyl)-phenolato(O,O)]bis(trimethylphosphine)cobalt(III) (**12**)*

A sample of *mer*-hydrido(3,5-di-*tert*-butyl-2-oxobenzoyl) tris(trimethylphosphine)cobalt(III) (**2**) (1.45 g, 2.78 mmol) in 80 ml of diethyl ether and (2-diphenylphosphanyl)thiophenol (0.82 g, 2.79 mmol) in 10 ml of THF after stirring for 18 h at room temperature gave a red-brown suspension. After evaporating the volatiles in vacuo a red-brown residue was obtained. Pentane, diethyl ether, and THF were used in turn to extract the residue, and the three filtrates were crystallized at −27 °C. **7** was collected from pentane as a red needles: 0.10 g, yield 5% (based on **2**) from which some crystals of **17** could be mechanically separated. **16** was obtained from diethyl ether: 0.62 g (yield 38%). From THF **12** was obtained as dark-red cubic crystals: 0.26 g (yield 28% based on **2**). **7**: m.p. (dec.) > 132 °C. *Anal.* Calc. for $C_{39}H_{52}CoO_2P_3S$ (736.75 g/mol): C, 63.58; H, 7.11. Found: C, 63.61; H, 7.08%. IR (Nujol mull, 2600–1500 cm^{-1}): 1620 m, 1593 s ν(C=O); 1526 m, ν(C=C). ^{1}H NMR (300 MHz, CDCl$_3$, 295 K, ppm): δ(CCH_3) 1.12 (s, 9H); δ(PCH_3) 1.24 (t', $|^2J(PH) + {}^4J(PH)| = 8.1$ Hz, 18H); δ(CCH_3) 1.67 (s, 9H); δ(C$H_{\rm arom}$) 6.69–8.49 (m, 16H). ^{31}P NMR (121 MHz, CD$_3$Cl, 295 K, ppm): δ(PCH$_3$) 12.1 (s, 2P); δ(PPh$_2$) 20.1 (s, 1P). **12**: m.p. (dec.) > 187 °C. *Anal.* Calc. for $C_{36}H_{59}CoO_4P_2$ (676.73 g/mol): C, 63.89; H, 8.79. Found: C, 63.79; H, 8.83%. IR (Nujol mull, 2600–1500 cm^{-1}): 1656 s, 1608 s ν(C=O); 1513 m, ν(C=C). ^{1}H NMR (300 MHz, C_6D_6, 296 K, ppm): δ(PCH_3) 0.79 (d, $^2J(PH) = 8.1$ Hz, 18H); δ(CCH_3) 1.21 (s, 9H); δ(CCH_3) 1.32 (s, 9H); δ(CCH_3) 1.55 (s, 9H); δ(CCH_3) 1.61 (s, 9H); δ(C$H_{\rm arom}$) 6.96–7.99 (m, 4H); δ(CHO) 9.55 (s, 1H). ^{31}P NMR (121 MHz, C_6D_6, 296 K, ppm): δ(PCH$_3$) 14.2 (s).

2.2.3. *(2-Oxo-naphthalene-formyl)[(1-formyl)naphtholato-(O,O)]bis(trimethylphosphine)cobalt(III) (**13**)*

A sample of *mer*-hydrido(2-oxo-naphthalene-formyl) tris(trimethylphosphine)cobalt(III) (**3**) (1.49 g, 3.25 mmol) in 60 ml of diethyl ether and (2-diphenylphosphanyl)thiophenol (0.95 g, 3.25 mmol) in 20 ml of diethyl ether after stirring for 18 h at room temperature gave a red-brown suspension. After evaporating the volatiles in vacuo a red-brown residue was obtained. Pentane, diethyl ether and THF were used in turn to extract the residue, and the three filtrates were crystallized at −27 °C. 0.66 g **16** were obtained from diethyl ether (yield 35%). From THF **13** could be obtained as red microcrystals: 0.30 g (yield 33%, based on **3**). **13**: m.p. (dec.) > 257 °C. *Anal.* Calc. for $C_{28}H_{31}CoO_4P_2$ (552.42 g/mol): C, 60.88; H, 5.66. Found: C, 60.92; H, 5.50%. IR (Nujol mull, 2600–1500 cm^{-1}): 1613 s, 1584 s ν(C=O); 1552 m, 1536 m, ν(C=C). ^{1}H NMR (300 MHz, CDCl$_3$, 295 K, ppm): δ(PCH_3) 1.25 (t', $|^2J(PH) + {}^4J(PH)| = 9.4$ Hz, 18H); δ(CH) 6.68–9.51

(m, 12H); δ(CHO) 10.37 (s, 1 H). ^{31}P NMR (121 MHz, $CDCl_3$, 295 K, ppm): δ(PCH_3) 18.1 (s).

2.2.4. (1-Carbonyl-2-oxo-1,2-diphenylethenyl)[(1-formyl-2-oxo-1,2-diphenylethenyl)(O,O)]bis(trimethylphosphine)-cobalt(III) (**14**)

A sample of *mer*-hydrido(1-carbonyl-2-oxo-1,2-diphenylethenediyl)tris(trimethylphosphine)cobalt(III) (**4**) (0.64 g, 1.25 mmol) in 40 ml of diethyl ether and (2-diphenylphosphanyl)thiophenol (0.37 g, 1.23 mmol) in 10 ml of diethyl ether after stirring for 18 h at 20 °C gave a red-brown suspension. After evaporating the volatiles in vacuo a red-brown residue was obtained. Pentane, diethyl ether and THF were used in turn to extract the residue, and the three filtrates were crystallized at −27 °C. From diethyl ether 0.22 g of 16 were obtained (30% yield). From THF **14** was obtained as yellow powder: 0.10 g (yield 25% based on **4**). **14**: m.p. (dec.) > 168 °C. *Anal.* Calc. for $C_{36}H_{39}CoO_4P_2$ (656.57 g/mol): C, 65.85; H, 5.99. Found: C, 65.53; H, 5.54%. IR (Nujol mull, 2600–1500 cm^{-1}): 1692 s, 1608 s ν(C=O); 1531 m, 1536 s, ν(C=C). ^{1}H NMR (300 MHz, acetone-d_6, 296 K, ppm): δ(PCH_3) 1.37 (dd, ^2J(PH) = 9.9 Hz, ^4J(PH) = 1.8 Hz, 18 H); δ (CH) 6.89–7.94 (m, 15H); δ(CHO) 9.19 (s, 1H). ^{31}P NMR (121 MHz, acetone-d_6, 296 K, ppm): δ(PCH_3) 22.8 (s).

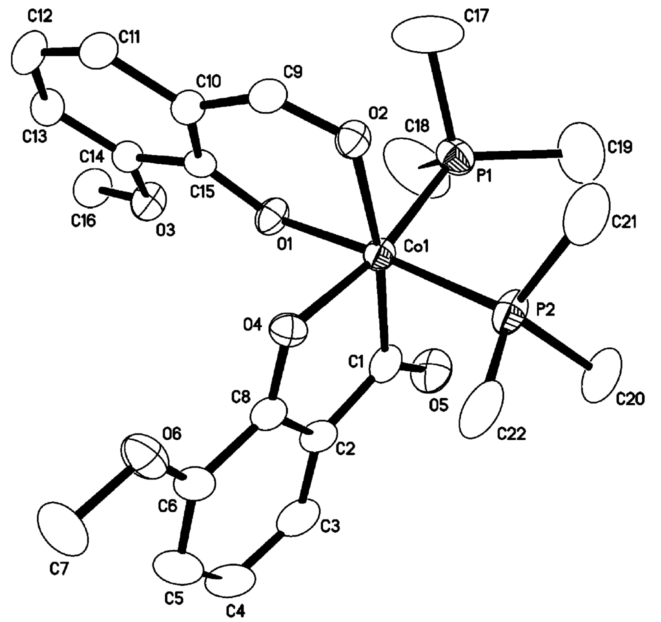


Fig. 1. Molecular structure of *cis*-**15**. Selected distances (Å) and angles (°): Co1–C1 1.914(6), Co1–O1 1.918(3), Co1–O4 1.926(3), Co1–O2 2.071(4), Co1–P2 2.1810(18), Co1–P1 2.2239(18), O2–C9 1.239(6), O5–C1 1.212(6); C1–Co1–O1 87.12(18), C1–Co1–O4 87.1(2), O1–Co1–O4 88.52(15), C1–Co1–O2 169.8(2), O1–Co1–O2 91.77(15), O4–Co1–O2 82.66(14), C1–Co1–P2 88.49(16), O1–Co1–P2 175.54(12), O4–Co1–P2 90.45(11), O2–Co1–P2 92.40(11), C1–Co1–P1 97.69(18), O1–Co1–P1 83.06(12), O4–Co1–P1 170.04(12), O2–Co1–P1 92.26(11), P2–Co1–P1 98.35(7).

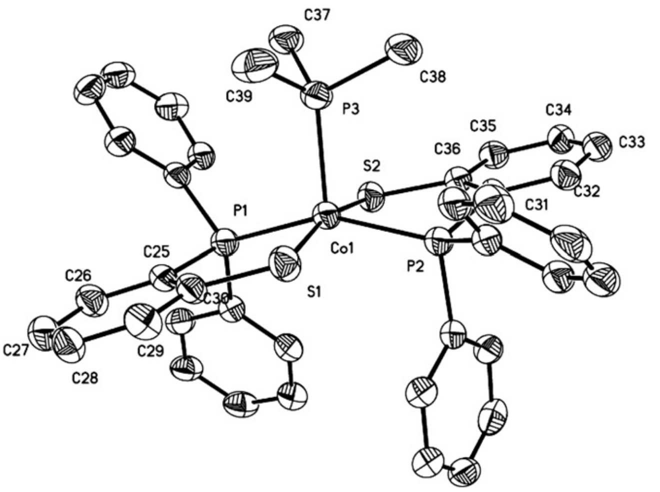


Fig. 2. Molecular structure of **17**. Selected distances (Å) and angles (°): Co1–P2 2.1949(18), Co1–P1 2.2055(18), Co1–S1 2.220(2), Co1–S2 2.70(2), Co1–P3 2.279(2); P2–Co1–P1 152.53(8), P2–Co1–S1 90.49(8), P1–Co1–S1 87.69(7), P2–Co1–S2 84.24(7), P1–Co1–S2 91.34(7), S1–Co1–S2 166.63(8), P2–Co1–P3 103.41(7), P1–Co1–P3 103.94(7), S1–Co1–P3 99.29(9), S2–Co1–P3 93.89(8).

2.2.5. (3-Methoxy-2-oxobenzoyl)[(2-methoxy-6-formyl)phenolato(O,O)]bis(trimethylphosphine) cobalt(III) (**15**)

A sample of *mer*-hydrido(3-methoxy-2-oxobenzoyl)-tris(trimethylphosphine)cobalt(III) (**5**) (1.40 g, 3.20 mmol) in 60 ml of diethyl ether and (2-diphenylphosphanyl)

Table 1
Crystallographic data of complexes **15** and **17**

	15	**17**
Formula	$C_{22}H_{31}CoO_6P_2$	$C_{43}H_{47}CoOP_3S_2$
M_r (g/mol)	512.34	795.77
Color	orange	brown-yellow
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	*P2(1)/n*
a (Å)	10.068(4)	15.051(3)
b (Å)	10.785(4)	12.076(2)
c (Å)	11.580(5)	21.916(4)
α (°)	90.701(7)	90
β (°)	107.007(7)	102.16(3)
γ (°)	96.529(7)	90
V (Å^3)	1193.3(8)	3894.0(13)
Z	2	4
$\rho_{calc.}$ (g/cm^3)	1.426	1.357
μ (mm^{-1})	0.888	0.705
Scan range (°)	$1.84 \leqslant \theta \leqslant 25.50$ $-10 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-11 \leqslant l \leqslant 14$	$1.84 \leqslant \theta \leqslant 25.05$ $-15 \leqslant h \leqslant 17$, $-12 \leqslant k \leqslant 14$, $-25 \leqslant l \leqslant 25$
Reflections collected	6380	12676
R_{int}	0.0504	0.0857
Independent reflections	4343	6678
Data/restraints/ parameters	4343/0/288	6678/0/54
Goodness-of-fit on F_2	0.951	0.811
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0739$, $wR_2 = 0.1464$	$R_1 = 0.0584$, $wR_2 = 0.1212$
R indices (all data)	$R_1 = 0.1129$, $wR_2 = 0.1643$	$R_1 = 0.1475$, $wR_2 = 0.1473$

thiophenol (0.94 g, 3.20 mmol) in 20 ml of diethyl ether after stirring for 18 h at 20 °C gave a red-brown suspension. After evaporating the volatiles in vacuo a red-brown residue was obtained. Pentane, diethyl ether and THF were used in turn to extract the residue, and the three filtrates were crystallized at −27 °C. From diethyl ether **16** was obtained (0.72 g, yield 40%). From THF **15** was obtained as orange crystals of (0.35 g yield 43% based on **5**). **15**: m.p. (dec.) > 202 °C. *Anal.* Calc. for $C_{22}H_{31}CoO_6P_2$ (512.36 g/mol): C, 51.57; H, 6.10. Found: C, 51.69; H, 6.28%. IR (Nujol mull, 2600–1500 cm^{-1}): 1646 s, 1616 s, ν(C=O); 1579 s, 1537 s, ν(C=C). ^1H NMR (400 MHz, $CDCl_3$, 293 K, ppm): *cis*/*trans*-**15** = 1/3. *cis*-**15**: $\delta(PCH_3)$ 1.01 (t', $|^2J(PH) + {}^4J(PH)| = 13.4$ Hz, 9H); $\delta(PCH_3)$ 1.22 (t', $|^2J(PH) + {}^4J(PH)| = 10.9$ Hz, 9H); $\delta(OCH_3)$ 3.72 (s, 3H); $\delta(OCH_3)$ 3.77 (s, 3H); $\delta(CHO)$ 9.7 (s, 1H). *trans*-**15**: $\delta(PCH_3)$ 1.24 (t', $|^2J(PH) + {}^4J(PH)| = 13.7$ Hz, 18H); $\delta(OCH_3)$ 3.32 (s, 3H); $\delta(OCH_3)$ 3.57 (s, 3H); $\delta(CHO)$ 9.46 (s, 1H), without assignmet: $\delta(CH)$ 6.89–7.94 (m, 15H). ^{31}P NMR (121 MHz, $CDCl_3$, 296 K, ppm): *cis*-**15**: $\delta(PCH_3)$ 4.1(s, 1P), 8.1(s, 1P); *trans*-**15**: $\delta(PCH_3)$ 2.3 (s, 1P).

2.3. X-ray diffraction

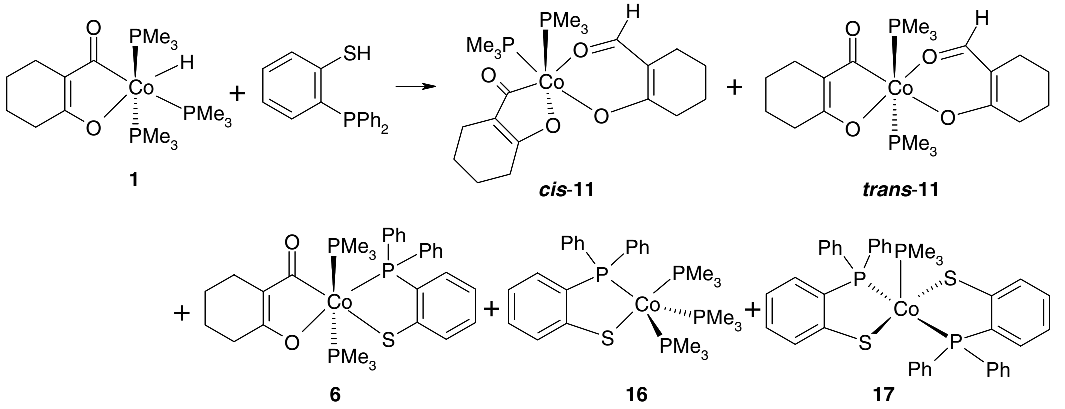
Crystals of complexes **15** and **17** suitable for X-ray diffraction analysis were grown from THF and pentane at 6 °C. The molecular structures are shown in Fig. 1 and Fig. 2, respectively, and related crystallographic data are included in Table 1. The structures were solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropically.

3. Results and discussion

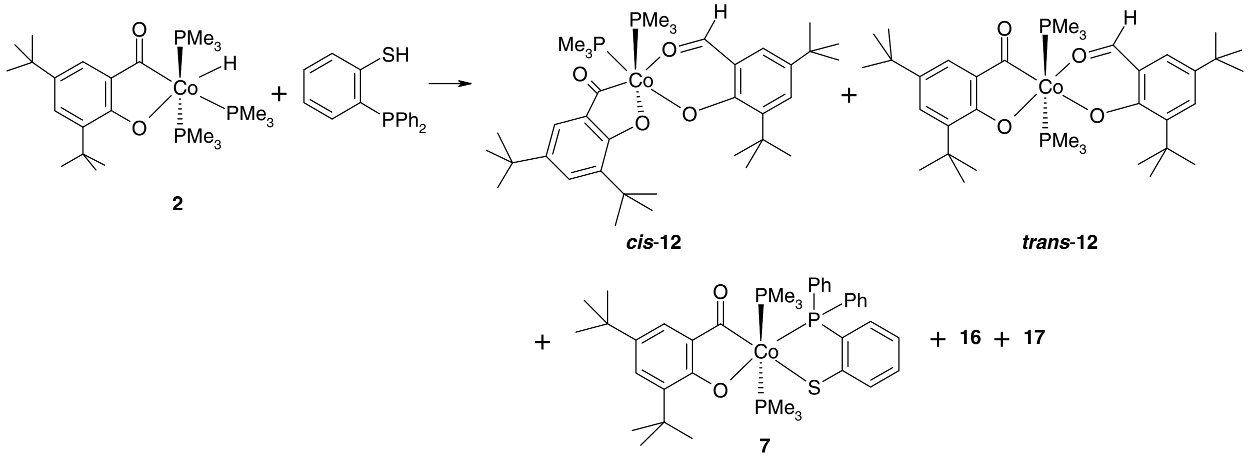
The acyl(hydrido)cobalt complexes **1** and **2** were reacted with (2-diphenylphosphanyl)thiophenol in diethyl ether. After careful work-up, apart from the expected novel cobalt complexes **6** and **7** containing one 2-acylphenolato ligand and one (2-diphenylphosphanyl)thiophenolato ligand, three additional types of cobalt complexes, **11**, **12**, **16**, and **17** were successfully isolated and shown to exist in different formal oxidation states (Eqs. (1) and (2)).

Complexes **6** and **7** are stable below 142 °C and 132 °C under inert atmosphere. In the IR spectra the conspicuous ν(Co–H) absorption of the acyl(hydrido)cobalt complexes (complex **1** and **2**) are absent.

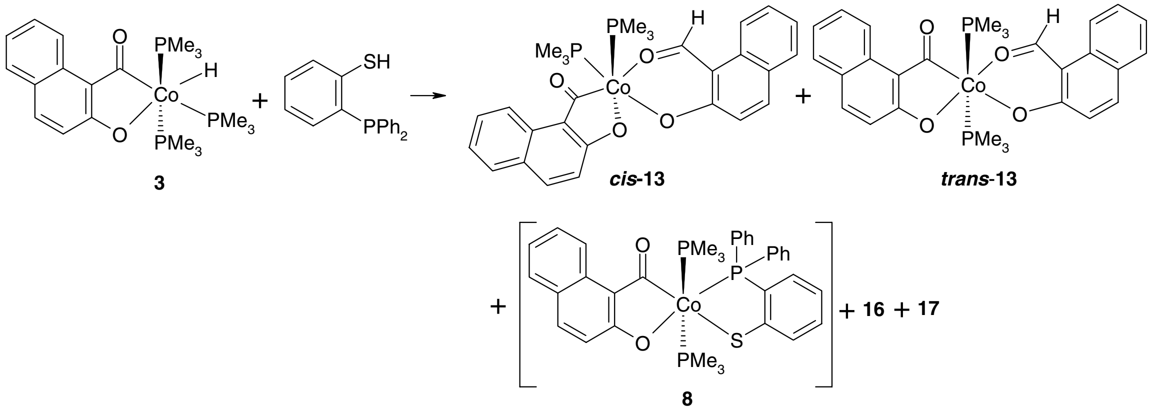
The ^1H and ^{31}P NMR spectra of complexes **6** and **7** are well resolved. The pattern of PCH_3 signals as pseudotriplets are is consistent with an octahedral coordination geometry and two *trans*-trimethylphosphine ligands. Two ^{31}P NMR singlets represent one diphenylphosphanyl group and two isochronic trimethylphosphine ligands. Due to



(1)



(2)



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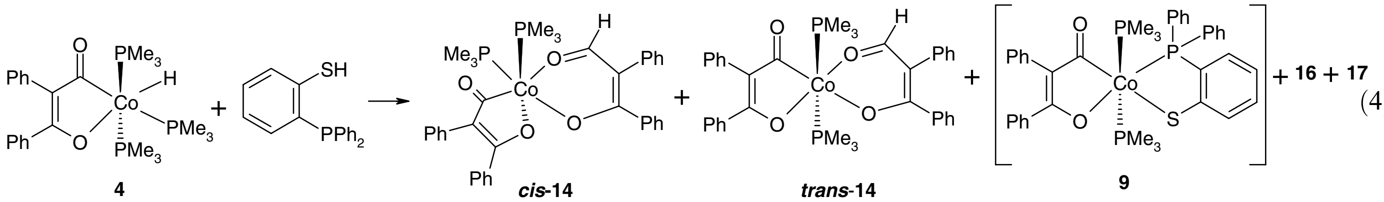

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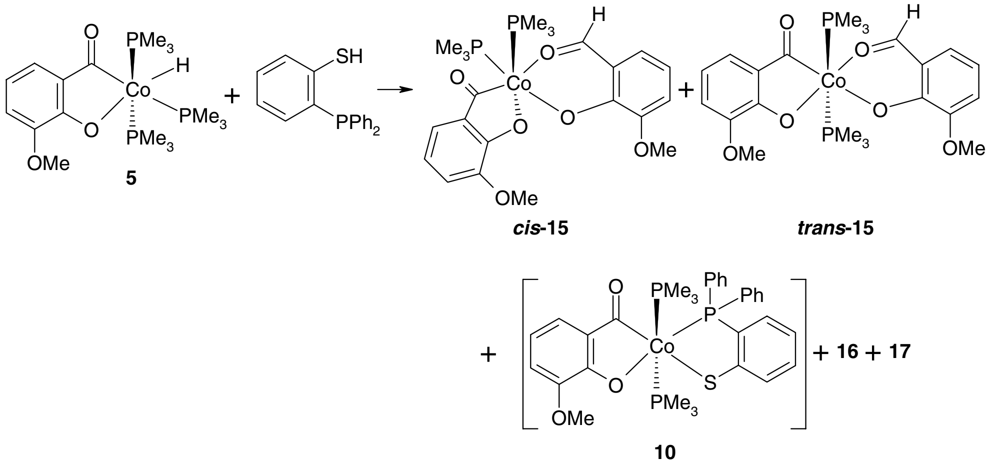


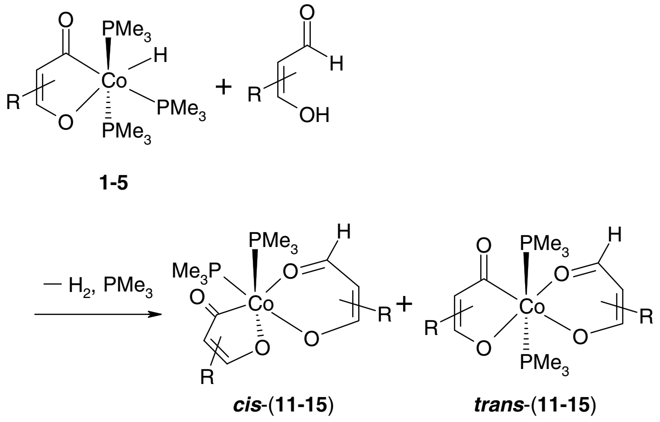
(5)

efflorescence of crystals the crystal structure of complex **6** could not be determined by X-ray diffraction.

In the case of complexes **3**–**5**, the analogous reactions according to Eqs. (3)–(5) have been carried out without successfully isolating the expected complexes **8**, **9**, and **10** due to very low yields of these compounds.

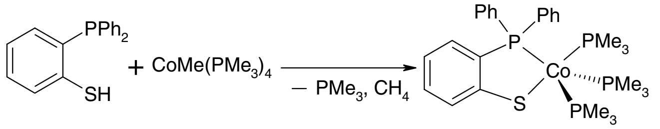
As by-products, the bis-chelate complexes **11**–**15** were obtained from the reactions (Eqs. (1)–(5)) as yellow to orange crystals. In the ^{1}H NMR spectra the aldehyde protons appear between 9 and 10 ppm. X-ray diffraction indicates that complex **15** attains an octahedral configuration with two trimethylphosphine groups in *cis*-positions, while the two 2-acylphenolato ligands are arranged perpendicular to each other (Fig. 1). Complexes **11**–**15** could be isolated as *cis* and *trans* isomers. The ratio of the isomers was determined from ^{1}H NMR and ^{13}P NMR data. Crystalline materials of all these complexes are stable in the air at room temperature.

Complexes **11**–**15** can be directly prepared by the reaction of acyl(hydrido)cobalt **1**–**5** with the corresponding β-hydroxy aldehyde (Eq. (6)) [5].



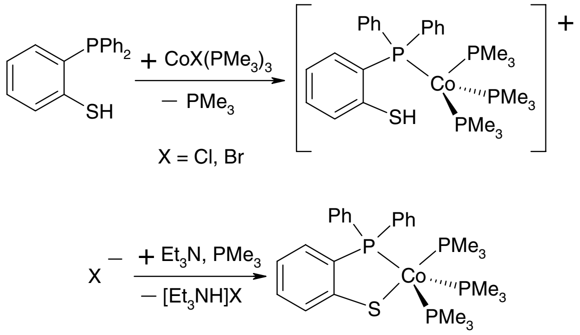
(6)

From each reaction in Eqs. (1)–(5) cobalt(I) complex **16** with one [P,S]-chelating ligand was obtained in good yield (>30%). The direct synthesis of complex **16** can be achieved by reaction of (2-diphenylphosphanyl)thiophenol with methyl tetrakis(trimethylphosphine)cobalt(I), $CoMe(PMe_3)_4$, or by reaction of (2-diphenylphosphanyl)thiophenol with tris(trimethylphosphine)cobalt(I), $CoX(PMe_3)_3$, (Eqs. (7) and (8)) [7].



16

(7)

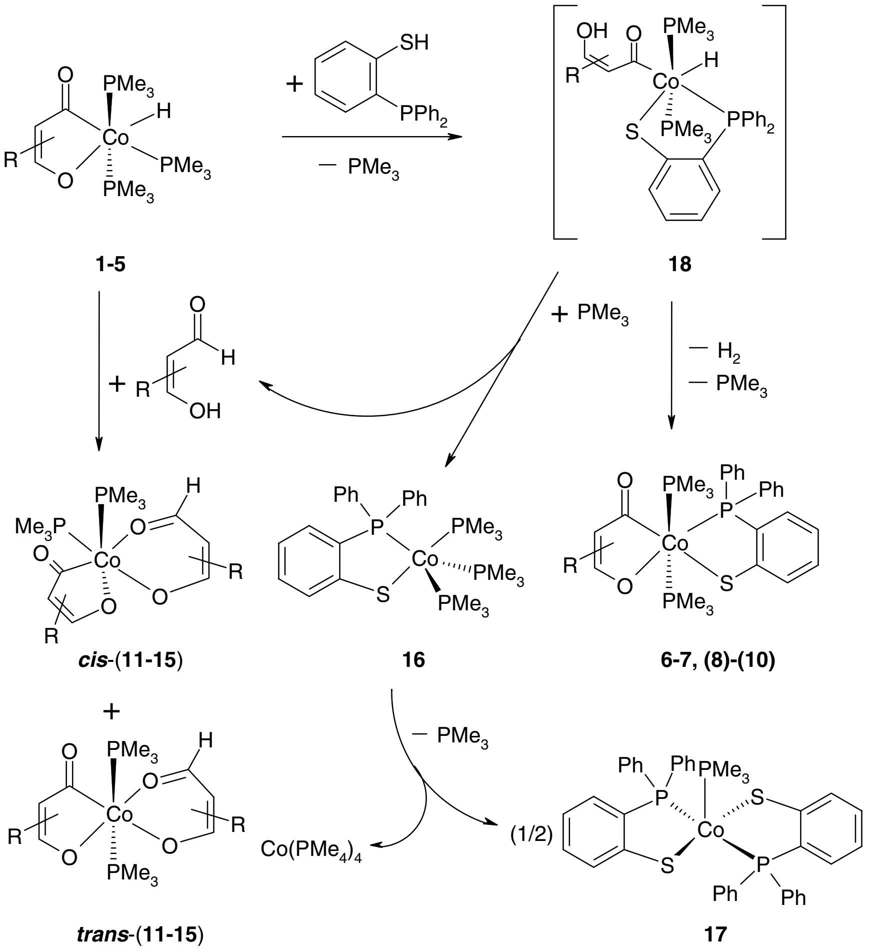


(8)

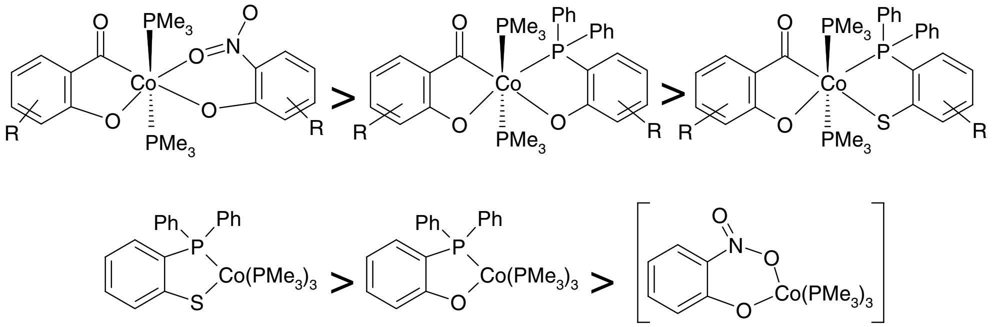
16

At the same time a penta-coordinate cobalt(II) complex with two [P,S]-chelating ligands (**17**) was also isolated from the mother liquor in small amount as tiny brown-yellow cubic crystals. The molecular structure (Fig. 2) shows the expected square-pyramidal geometry of complex **17**. The cobalt atom is located above the center of a plane containing two P-donor and two S-donor atoms of the diphenylphosphanylthiophenolato ligands arranged in mutual *trans*-positions. The P-donor atom of trimethylphosphine is located at the apical point of the pyramid.

Regarding all information obtained from this complicated reaction system (Eqs. (1) and (2)) a mechanism is proposed as given in Scheme 1. In the first step the phenoxy O-donor of the 2-acylphenolato chelating ligand in complexes **1**–**5** is substituted by a (2-diphenylphosphanyl)thiophenolato chelating ligand leading to an intermediate hydridocobalt complex **18**. In the presence of trimethylphosphine, **18** undergoes a reductive elimination to generate the [P,S]-chelate cobalt(I) complex **16** with liberation of a β-hydroxy aldehyde. Subsequently, hydrogen is evolved from the acyl(hydrido)cobalt(III) complexes **1**–**5** and the β-hydroxy aldehyde to afford the bis-chelate cobalt(III) complexes **11**–**15**. Disproportionation of complex **16** gives rise to the bis-chelate complex **17** and tetrakis(trimethylphosphine)cobalt(0). In a parallel reaction of complexes **1**–**5** with 2-diphenylphosphanylthiophenol the bis-chelate complexes **6**–**7** are formed with evolution of hydrogen.



Scheme 1. A proposed mechanism of reaction of acyl(hydrido)cobalt(III) complexes with (2-diphenylphosphanyl)thiophenol.



Scheme 2. Influence of chelating ligands containing hard/soft donor atoms on the stability of cobalt complexes.

According to the earlier work of Klein [1–5] and Sun [8], when reacting an acyl(hydrido)cobalt(III) complex with 2-nitrophenol and (2-diphenylphosphanyl)phenol, respectively, to form cobalt(III) complexes with chelating 2-nitrophenolato ligands, in the light of the HSAB rule, the hard/hard product is expected to be more stable than the hard/soft product with (2-diphenylphosphanyl)phenolato ligands. In combination with our present work, the influence of chelating ligands containing hard/soft donor atoms on the relative stabilities of cobalt complexes can be described as in Scheme 2. In the reaction system with 2-nitrophenol the stable 2-acylphenolato cobalt(III) complex was obtained, while a corresponding cobalt(I) complex could not be experimentally verified [8]. In the present work, the cobalt(I) complex **16** was isolated in high yield, while relatively low yields were attained for complexes **6**–**7** and **8**–**10**. Derivatives of salicylaldehyde released in situ react with starting materials to generate bis-chelate cobalt(III) complexes **11**–**15**, and no formation of salicylalcohol was observed, while salicylalcohol was identified in the reaction system with (2-diphenyl)phosphanylphenol [8]. This result confirms the key role of (2-diphenylphosphanyl)phenol in the formation of salicylalcohol.

4. Conclusions

The reaction of acyl(hydrido)cobalt(III) complexes **1**–**5** with (2-diphenylphosphanyl)thiophenol generated two types of chelate cobalt(III) complexes (**6**–**7**, **8**–**10** and **11**–**15**), one chelate cobalt(I) complex (**16**) and one chelate cobalt(II) complex (**17**). Complex **16** bearing a soft/soft [P,S]-chelate ligand and a soft low-valent cobalt(I) central atom was obtained in the highest yield of about 30–40%, while the expected products with a soft/soft [P,S]-chelate ligand and a hard high-valent cobalt(III) central atom (**6**, **7** and **8**–**10**) show low yields (less than 10%). The by-products **11**–**15** with a hard/hard [O,O]-chelating ligand and a hard cobalt(III) center are very stable. Cobalt(II) complex **17** could be separated as a result of a disproportionation reaction of complex **16**. A possible mechanism is proposed. Coordination of chelating ligands at Co(III) decreases as [N,O] > [P,O] > [P,S], while at Co(I) this order is reversed, which is in accord with the HSAB rule.

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Appendix A. Supplementary material

CCDC 641640 contains the supplementary crystallographic data for **17**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.11.010.

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