# Formation and Crystal Structure of Stable Five-coordinate Diorgano Cobalt(III) Complexes

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Abstract. The *mer*-octahedral complexes(2-carbonyl)(4-Me)(6-tBu)-phenolato[*C*,*O*]hydridotris(trimethylphosphine)cobalt(III) (1) or (1-carbonyl)(2-oxo)(1,2-diphenylethene)[*C*,*O*]hydridotris(trimethylphosphine)cobalt(III) (2) via formal insertion of propynoic acid ethyl ester into Co-H functions afford pentacoordinate vinylcobal-

### Introduction

Cobalt(III) with its low-spin d<sup>6</sup> configuration tends to form six-coordinate complexes in octahedral coordination geometry attaining 18 valence electrons. Cobalt(III) complexes with five-coordinate CoIII as stable species under ambient conditions are known in rare examples [1].Usually they are considered as reactive intermediates in ligand-exchange reactions [2]. The understanding that the active site of vitamin B12 contains a readily homolyzable Co<sup>III</sup>-carbon bond and a five-coordinate square pyramidal geometry has fuelled research into preparation and reactivity of cobalt complexes, in particular those compounds that serve as models for bioinorganic systems [3]. Examples of five-coordinate alkyl cobalt(III) complexes usually are macrocycle compounds because most of them were synthesized as model compounds for vitamin B12 as well as for cobalamins [4, 5]. Quite generally, complexes with five-coordinate cobalt(III) as coordinatively unsaturated compounds may have a potential in homogeneous catalysis.

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/zaac or from the author t(III) **3** and **4**, respectively, that are diamagnetic and attain a square pyramidal structure as exemplified by an X-ray diffraction analysis of **3**.

Keywords: Cobalt; Acyl(vinyl)cobalt; Penta-coordination; Phosphorus ligands; Crystal structure

The majority of these complexes that have been structurally characterized are of the square pyramidal type  $[CoL_4L'][4, 6]$ , where  $L_4$  is a square-planar system such as porphyrin, salen or other chelating ligands, and L' is an organo or a halide group [4, 6, 7]. Most of them are lowspin and diamagnetic. There have been few examples with structures of trigonal-bipyramidal coordination geometry. These high-spin cobalt(III) complexes can be spectroscopically studied with EXAFS to yield structural information [8]. Their paramagnetic properties can be easily investigated through solid or solution magnetic moments.

We have recently reported some insertion reactions of trimethylphosphine-supported hydrido(acyl)enolatocobalt(III) complexes with phenylethine, trimethylsilylethine and bis(trimethylsilyl)butadiyne [9]. Products of these reactions are complexes with five-coordinate cobalt(III), which were characterized by routine spectroscopy (NMR, IR) and elemental analysis, whereas the configuration of these lowspin diamagnetic complexes has not been structurally confirmed. Here we present some new insertion reactions of the Co-H bond with propynoic acid ethyl ester.

#### **Results and Discussion**

Complexes with two five-coordinate cobalt(III) atoms (3, 4) were obtained through the insertion reaction of acyl(hydrido)cobalt(III) complexes (1, 2) and propynoic ethyl ester [Equations (1), (2)].

Complexes 3 and 4 were obtained as red solids that are soluble in pentane or diethylether. The solids can be handled in air for several days without any sign of decomposition, while thermal degradation under argon begins above 145  $^{\circ}$ C and 140  $^{\circ}$ C, respectively.

In the infrared spectra typical bands for v(Co-H) or  $v(C\equiv C)$  vibrations are absent. The v(C=O) vibrations of the chelating ligand in complexes 3 and 4 experience a bathochromic shift of about  $30-50 \text{ cm}^{-1}$  with respect to 1 and 2.



From <sup>1</sup>H NMR data we assign a pseudo-triplett (0.9 – 1.1 ppm) with strong coupling ( $|^{2}J_{P,H} + {}^{4}J_{P,H}| = 8.1$  Hz) to the trans-PMe<sub>3</sub> ligands. Signals of two geminal protons in the alkenyl group are found in the range expected of alkenvl-CH groups with coupling constants  ${}^{2}J = 3$  Hz, which are typical for geminal alkenyl protons in a compound with five-coordinate cobalt(III). In the <sup>31</sup>P NMR spectra at -30 °C both compounds show singlets for the *trans*-PMe<sub>3</sub> groups. The diamagnetic properties of these compounds are compatible with a square pyramidal configuration. The acyl group occupies the axial position where its trans-effect and spacial distribution are accommodated more easily than in the presence of trimethylphosphine as sixth ligand. This assignment is verified through a single crystal X-ray diffraction study. From pentane crystals of 3 suitable for X-ray diffraction were obtained.

The molecular structure of compound **3** is shown in Figure 1. The cobalt atom is located above the basis of a square pyramid and attains penta-coordination with two equatorial phosphorus atoms of *trans*-trimethylphosphine ligands, a carbon atom of the vinyl group, and an oxygen atom of the phenoxy group. The carbon atom of the acyl group is located in the apex above the square pyramid.

The distance Co-C1 (1.865(2) Å) is shorter than that of the six-coordinate halogeno acyl phenolato cobalt(III) complexes where Co-C separations ranges from 1.910 to 1.942 Å [10], which is in turn shorter than those of hydrido(acyl)phenolato cobalt(III) complexes with Co-C distances ranging from 1.925 to 1.952 Å [11]. These findings can be rationalized by a stronger Co-C bonding interaction of the acyl group with an empty trans-position, where an additional donor would compete for the metal  $d_z^2$  orbital.

Presently the stabilization of complexes with five-coordinate cobalt(III) is not fully understood. It has been suggested that this coordination number is favoured by electron-rich ligand systems. This hypothesis was supported by a study in which axial base exchange rates for [CoR(saloph)] compounds were compared to exchange rates for



Figure 1 Molecular structure of 3; selected bond distances/Å and angles/deg:

glyoxime model systems and cobalamines [12]. In case of complex **3** and **4**, the coordination system with two phosphine ligands, one acyl group, one vinyl group and one phenoxy group certainly rates among the more electron-rich compounds. However, five-coordinate cobalt(III) species can be more stable thermally than their six-coordinate counterparts, which can be inferred from the equilibrium of compounds with five and six-coordinate cobalt(III) as observed in our earlier work [10].

To our knowledge, this presentation is the first example of a structurally characterized five-coordinate diorganocobalt(III) complex.

#### **Experimental Part**

General procedures and materials: Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Solvents were dried by known procedures and used freshly distilled. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. Literature methods were applied in the preparation of complexes 1 and 2 [12]. Propynoic acid ethyl ester was used as purchased. IR: Nujol mulls between KBr discs, Bruker spectrophotometer type FRA 106. <sup>1</sup>H and <sup>13</sup>C NMR spectra (300 MHz, 500 MHz, 75 MHz and 125 MHz) were recorded with Bruker ARX-300, ARX-500 spectrometer respectively, <sup>31</sup>P NMR spectra (81 MHz, 202 MHz) were recorded with Bruker AM-200 and ARX-500 spectrometer respectively, <sup>13</sup>C and <sup>31</sup>P NMR resonances were obtained with broad-band proton decoupling. C, H analyses were carried out in a german ELEMENTAR Vario ELIII analyser.

**Preparation of (3-***tert***-butyl-5-methyl-2-oxobenzoyl)(1-ethoxocarbonyl-1-vinyl)***trans***- bis(trimethylphosphine)cobalt(III) (3):** A sample of (3-*tert*-butyl-5-methyl-2-oxo-benzoyl)-hydridotris(trimethylphosphine)cobalt(III) (1) (0.64 g, 1.34 mmol) was dissolved in 50 mL of THF and propynoic ethyl ester (0.28 g, 2.86 mmol) was added dropwise with stirring at -80 °C. The reaction mixture was warmed to 20 °C and stirred for 18 h. During this period the reaction solution turned brown. After removal of the solvent at reduced pressure the solid residue was extracted with pentane (80 mL). The product precipitated as yellow crystalline material at at -27 °C. Yield: 0.67 g (26.6 %), m. p. 140–141 °C (dec.). C<sub>23</sub>H<sub>39</sub>CoO<sub>4</sub>P<sub>2</sub> (500.4): C 55.20 (calc. 55.59), H 7.86 (calc. 7.82) %.

**IR** (Nujol): v(C=O) 1659 s, 1641 s; (C=C) 1613 m, 1593 m, 1581 m, 1544 m cm<sup>-1</sup>. <sup>1</sup>**H NMR** (500 MHz, [D<sub>8</sub>]THF, 297 K):  $\delta = 0.92$  (t', 18 H,  $|^2J_{P,H} + ^4J_{P,H}| = 8.1$  Hz, PCH<sub>3</sub>), 1.22(t, 3H,  $^3J = 7.1$  Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.33 (s, C(CH<sub>3</sub>)<sub>3</sub>), 2.00 (s, CH<sub>3</sub>), 3.99 (q, 2H,  $^3J = 7.1$  Hz OCH<sub>2</sub>CH<sub>3</sub>), 5.90 (dt, 1 H,  $^4J_{P,H} = 4.8$  Hz,  $^2J = 3.0$  Hz, = CH<sub>2</sub>), 6.27 (dt, 1H,  $^4J_{P,H} = 6.4$  Hz,  $^2J = 3.0$  Hz, =CH<sub>2</sub>), 6.27 (dt, 1H,  $^4J_{P,H} = 6.4$  Hz,  $^2J = 3.0$  Hz, =CH<sub>2</sub>), 6.74 (d, 1H,  $^4J = 2.0$  Hz, CH) ppm.  $^{13}$ C NMR (75.4 MHz, [D<sub>8</sub>]THF, 297 K):  $\delta = 9.7$  (t',  $|^1J_{P,C} + ^3J_{P,C}| = 26.5$  Hz, PCH<sub>3</sub>), 12.7 (s, CH<sub>2</sub>CH<sub>3</sub>), 18.7 (s, CH<sub>3</sub>), 28.1 (s, C(CH<sub>3</sub>)<sub>3</sub>), 33.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 58.7 (s, OCH<sub>2</sub>), 129.7 (= CH<sub>2</sub>), 116.8, 129.0 (CH), 118.5, 136.5, 170.5, 173.7 (C). <sup>31</sup>P NMR (81.0 MHz, [D<sub>8</sub>]THF, 213 K):  $\delta = 13.3$  (s, PCH<sub>3</sub>).

**Preparation of (1-Carbonyl-2-oxo-1,2-diphenyl-diyl)(1-ethoxocarbonyl-1-vinyl)***trans***-bis (trimethylphosphine)cobalt(III), (4):** A sample of (1-carbonyl-2-oxo-1,2-diphenyldiyl) hydridotris(trimethylphosphine)cobalt(III) (2) (1.07 g, 2.10 mmol) was dissolved in 50 mL of THF and propynoic ethyl ester (0.42 g, 4.29 mmol) was added dropwise with stirring at -80 °C. The reaction mixture was warmed to 20 °C and stirred for 18 h. During this period the reaction solution turned red. After removal of the solvent at reduced pressure the solid residue was extracted with pentane (80 mL), and subsequently with diethyl ether (40 mL). The product precipitated as orange crystalline material at -27 °C. Yield: 0.37 g (33.0 %). m. p. 145-146 °C (dec.). C<sub>26</sub>H<sub>35</sub>CoO<sub>4</sub>P<sub>2</sub> (532.4): C 58.66 (calc. 58.83), H 6.63 (calc. 6.62) %.

IR (Nujol): v(C=O) 1621 s, 1615 s; v(C=C) 1578 s, 1561 s cm<sup>-1</sup>. <sup>1</sup>H NMR (500.1 MHz, [D<sub>8</sub>]THF, 300 K):  $\delta$  = 1.11 (t', 18H,  $|^2J_{P,H}|$ + <sup>4</sup>J<sub>P,H</sub>| = 8.1 Hz, PCH<sub>3</sub>), 1.18 (t, 3H, <sup>3</sup>J = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 3.98 (q, 3H, <sup>3</sup>J = 7.1 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 5.86 (dt, 1H, <sup>4</sup>J<sub>P,H</sub> = 4.7 Hz, <sup>2</sup>J = 3.0 Hz, =CH<sub>2</sub>), 6.23 (dt, 1H, <sup>4</sup>J<sub>P,H</sub> = 6.5 Hz, <sup>2</sup>J = 3.0 Hz, =CH<sub>2</sub>), 6.80–7.20 (m, 10H, CH), 8.79 (s, 1H). <sup>13</sup>C NMR (125.8 MHz, [D<sub>8</sub>]THF, 300 K):  $\delta$  = 10.7 (t',  $|^{1}J_{P,C} + {}^{3}J_{P,C}|$  = 26.4 Hz, PCH<sub>3</sub>), 14.0 (s, CH<sub>3</sub>), 59.8 (s, OCH<sub>2</sub>), 110.7 (s, CCO), 131.1(= CH<sub>2</sub>), 124.0, 127.4, 128.2, 128.9, 130.5 (CH), 137.1, 139.3 (C), 171.8 (s, CCO), 183.9 (s, C-O). <sup>31</sup>P NMR (202.4 MHz, [D<sub>8</sub>]THF, 300 K):  $\delta$  = 3.7 (s, PCH<sub>3</sub>).

## Crystallographic data for 3

 $(C_{23}H_{39}CoO_4P_2, M_r = 500.41)$ : crystal size  $0.40 \times 0.35 \times 0.12$  mm, triclinic, space group P-1, a = 9.2791(5), b = 11.5217(6), c =

13.8122(7) Å,  $\varphi = 111.661(1)$ ,  $\beta = 97.003(1)$ ,  $\gamma = 98.230(1)$ , ° V = 1333.52(12) Å<sup>3</sup>,  $D_c = 1.246$  g cm<sup>-3</sup> for Z = 2, F(000) = 532,  $\mu = 0.787$  mm<sup>-1</sup>, Bruker AXS SMART APEX diffractometer,  $\lambda = 0.71073$  Å, T = 293 K,  $\omega$ -scans, 18543 reflections,  $\Theta_{max} = 28.28^{\circ}$ , 6606 independent reflections [R (int) = 0.0347], semi-empirical absorption correction, hydrogens calculated, 282 refined parameters, R = 0.0365 (observed data),  $wR^2 = 0.0893$  (independent data). Crystallographic data (excluding structure factors) for the structure described in this publication have been deposited as supplementary material with the Cambridge Crystallographic Data Centre. Deposition number is CCDC-252876 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax:+44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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