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Synthesis and structure of the first cobalt(I)–siloxide complex

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Abstract

Synthesis, spectroscopic (^{1}H NMR, IR) characterisation and X-ray structure of the first cobalt(I)–siloxide complex, $[Co(PPh_3)_3(OSiMe_3)]$ (**I**), have been presented. Complex **I** is synthesised by the reaction of $[CoCl(PPh_3)_3]$ with trimethylsilanolate. The complex occupies a special position of the space group $P\bar{3}$ on the three-fold axis passing through the Co, O and Si atoms. The coordination of cobalt is tetrahedral. © 2001 Published by Elsevier Science Ltd.

Keywords: Siloxides; Cobalt(I); Crystal structures

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1. Introduction

Molecular and macromolecular compounds, incorporating M–O–Si groups (where M = metal), have attracted great interest because of their wide application [1] in material sciences and catalysis. Transition metal siloxides can be regarded as very good molecular models of metal complexes supported on silica and silicate surfaces [2,3].

According to a general idea presented by Wolczanski, alkoxide and siloxide ancillary ligands are alternatives to cyclopentadienyl complexes of transition metals. Thanks to a more positive character of the silicon atom when compared to carbon, siloxide ligands are generally less basic than alkoxides, and therefore can bind to a TM with slightly more ionic character [4]. Siloxy derivatives of the late transition metals, e.g. ruthenium [5–9], rhodium [10–14], nickel [15], platinum [16–18] and to a minor extent iron [19], osmium [20], iridium [18], palladium [16] and cobalt [21] have been synthesised and characterised, and the structures of a few of them have been resolved by X-ray examinations. A dimeric complex of cobalt(II), $[Co(OSiPh_3)_2\text{-}THF]_2$, was synthesised via a cobalt silylamide complex according to the following equation (yield 47%) [21]:

$$[\mu\text{-}N(SiMe_3)_2CoN(SiMe_3)_2]_2 + 4Ph_3SiOH$$
$$\rightarrow [\{Co(\mu\text{-}OSiPh_3)(OSiPh_3)\cdot THF\}_2] + 4NH(SiMe_3)_2$$

X-ray studies revealed the structure of this dimeric complex with two siloxy groups as bridging ligands. Each cobalt has a distorted tetrahedral geometry due to the coordination of one THF to each cobalt giving a central Co_2O_6 core.

In this paper, we present a synthetic procedure, spectroscopic characterisation and X-ray crystal structure of the first cobalt(I)–siloxide complex.

2. Experimental

2.1. General procedures

All manipulations were carried out using standard Schlenk techniques under carefully deoxygenated and dried argon. All solvents were freshly distilled in inert atmosphere prior to use. Triphenylphosphine (Fluka AG) and sodium trimethylsilanolate (Hulls-Petrarch) were used as purchased. $[CoCl(PPh_3)_3]$ was prepared according to the literature [22].

NMR spectra were recorded in a Varian 300 MHz instrument using 5 mm NMR tubes with silicon septa. IR spectra were recorded using a Brucker instrument.

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2.2. Synthesis of [Co(PPh_3)$_3$($OSiMe_3$)]

2.2.1. Synthetic procedure

Portions of 1 g (1.14 mmol) of [CoCl(PPh_3)$_3$] and 0.38 g (3.42 mmol) of $NaOSiMe_3$ were placed in a Schlenk vessel (cell, tube, flask in argon atmosphere). To the mixture 8 ml of benzene (dried and deoxygenated) was added. The reaction was conducted for 6 h at room temperature, while stirring the contents with a magnetic stirrer. After the reaction benzene was evaporated, 5 ml of pentane was added. The orange–brown precipitate was washed three times with pentane by decantation. The remaining precipitate was dissolved in toluene and filtered through a cannula system. The solution was concentrated and the desired complex was precipitated by addition of pentane. The yield of the complex was 75%.

FTIR (CsBr, cm^{-1}): 3052, 2944, 1645.8, 1481, 1434.8, 1249.5, 989.6, 820.2, 740.6, 694.8, 509.5, 485.2, 452.7, 405.1, 302.9. ^{1}H NMR (C_6D_6, δ, ppm): 0.45 (s, 9H) broad, 7.06 (m, 27H) broad, 7.41 (m, 18H) broad. *Anal.* Calc. for $C_{57}H_{54}CoOP_3Si$: C, 73.22; H, 5.82. Found: C, 72.39; H, 5.86%.

2.3. Crystal structure determination

Diffraction data from a colourless, plate-shaped crystal of size 0.1 × 0.25 × 0.3 mm, sealed in a glass capillary, were collected on a KUMA KM4CCD diffractometer [23] at 130(1) K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The temperature was controlled by an Oxford Cryosystem cooling device. The data collection was done in four separate runs in order to cover the symmetry-independent part of the reciprocal space. The ω-scan was used with the step of 0.75°, two reference frames were measured after every 50 frames and they did not show any systematic changes neither in the peak position nor in their intensities. A total of 532 frames was collected giving 13 670 reflections up to $2\theta = 60°$. The unit-cell parameters were determined by least-squares treatment of the setting angles of 1414 highest-intensity reflections, chosen from the whole experiment. Lorentz and polarisation corrections were applied [24], and then the reflections were merged and corrected for absorption ($A_{\min} = 0.876$, $A_{\max} = 0.905$) with SORTAV [25]. The merging procedure gave 4172 unique data with R_{int} of 0.053. The analysis of the reflection file suggested that the diffraction was negligible for the 2θ angles greater than 50°, and consequently, only the relevant subset was used in further calculations. The structure was solved by direct methods with the SHELXS-97 program [26], and refined with full-matrix least-squares by SHELXL-97 [27]. Non-hydrogen atoms were refined with anisotropically positions, hydrogen atoms were generated geometrically and were refined as a 'riding model' with their U_{iso} parameters set at $1.2 \times U_{\text{eq}}$ of the appropriate carrier atom. Large residual electron density in special position (0, 0, z) may be a diffraction ripple and has not been accounted for. Selected geometric parameters are listed in Table 1.

Table 1
Selected bond lengths (Å) and bond angles (°) for [Co(PPh_3)$_3$($OSiMe_3$)] with e.s.d.s in parentheses

Bond lengths	
Co(1)–O(1)	1.862(4)
Co(1)–P(1)	2.2864(9)
O(1)–Si(1)	1.605(4)
Si(1)–C(1)	1.881(4)
P(1)–C(11)	1.836(3)
P(1)–C(21)	1.851(3)
P(1)–C(31)	1.841(3)
Bond angles	
O(1)–Co(1)–P(1)	115.33(3)
P(1)–Co(1)–P(1)^{i}	103.03(3)
Si(1)–O(1)–Co(1)	180.0
O(1)–Si(1)–C(1)	110.94(13)
C(1)–Si(1)–C(1)^{i}	107.97(12)
C(11)–P(1)–C(21)	102.87(14)
C(11)–P(1)–C(31)	105.28(14)
C(11)–P(1)–C(21)	102.87(14)
C(31)–P(1)–C(21)	96.88(13)
C(11)–P(1)–Co(1)	121.36(10)
C(31)–P(1)–Co(1)	111.92(10)
C(21)–P(1)–Co(1)	115.31(10)

(i): $-x+y+1$, $-x+1$, z.

Crystallographic data for [Co(PPh_3)$_3$($OSiMe_3$)]: empirical formula: $CoP_3OSiC_{57}H_{54}$, trigonal, space group $P\bar{3}$, $a = 12.970(2)$ Å, $c = 17.406(3)$ Å, $V = 2535.8(7)$ Å^3, $Z = 2$, $d_x = 1.224$ g cm^{-3}, μ(Mo Kα) = 0.49 mm^{-1}, $F(000) = 980$, $R(F)$ $[F_o > 4(F_o)] = 0.048$, $R(F)$ [all data] = 0.069, $wR(F^2) = 0.118$, where $w^{-1} = [\sigma^2(F_o)^2 + (0.05P)^2 + 1.8P]^{-1}$, $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2/3)$, $S = 1.15$, $(\Delta/\sigma)_{\max} = 0.001$ in the last cycle of refinement, $\Delta\sigma_{\max} = 1.80$ e Å^{-3}, $\Delta\sigma_{\min} = -0.60$ e Å^{-3}.

3. Results and discussion

The reaction of [CoCl(PPh_3)$_3$] with sodium trimethylsilanolate was used effectively for the preparation of the corresponding phosphine cobalt–siloxide complex according to the following equation:

$$[CoCl(PPh_3)_3] + NaOSiMe_3 \rightarrow [Co(PPh_3)_3(OSiMe_3)] + NaCl$$

The X-ray structure of the molecule is shown in Fig. 1. Bond lengths, bond angles and torsion angles are listed in Table 1. The complex occupies a special position of the space group $P\bar{3}$, on the three-fold axis passing through the Co, O and Si atoms. The coordination of cobalt is tetrahedral; the Cambridge Crystallo-

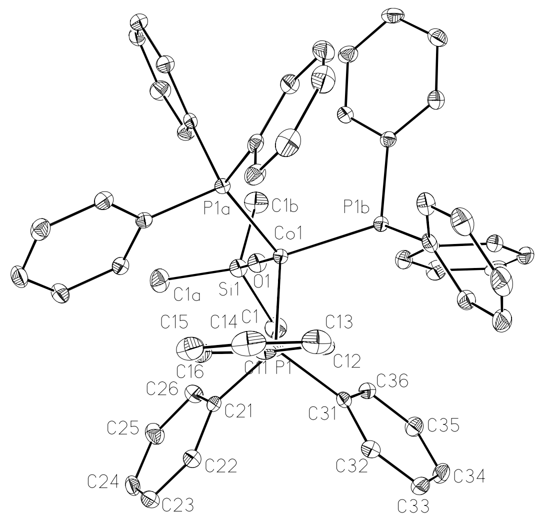

Fig. 1. The thermal ellipsoid view of the complex (at 50% probability level) with the numbering scheme [31]. The hydrogen atoms are omitted for clarity.

graphic Database [28] search shows that this coordination dominates for four-coordinated neutral monomeric cobalt complexes. For 602 fragments found in the March 2001 edition of CDB there is approximately 4:1 preference of tetrahedral over square-planar coordination, with a number of intermediate or strange conformations. In the present case, due to the internal symmetry of the complex, the tetrahedron is only slightly distorted. The Co–P and Co–O distances of 2.2867(8) and 1.863(3) Å, respectively, agree well with the values found in similar compounds [29,30]. The difference in the bond lengths leads to different bond angles within the coordination polyhedron (cf. Table 1). The special position of the complex accounts for the extremely large value of the Co–O–Si angle, 180°. The terminal OSiPh groups in the Co(II) siloxy dimer $[\{Co(\mu\text{-}OSiPh_3)(OSiPh_3)\cdot THF\}_2]$ have also an almost linear Co–O–Si angle, 170.7 and 161.3° [21].

The phenyl rings are planar within the experimental error, the mean value of the C_{ar}–C_{ar} bond length is 1.387(7) Å, and agrees well with the typical value. The mutual disposition of these rings can be described by the dihedral angles between their least-squares planes (A/B 56.48(9)°, B/C 89.90(10)°, A/C 52.83(13)°, where A, B, and C denote the rings with C11, C21, and C31 atoms, respectively), and by the angles between normal to the planes and the Co–O–Si direction (87.5(5), 98.6(5), and 124.2(6)°, for A, B, and C, respectively). Weak intramolecular C–H···O hydrogen bonds (H26···O1 2.50 Å, C26···O1 3.384(3) Å, C26–H26···O1 160°) enhance the stability of the molecule conformation. The crystal packing is determined mainly by van der Waals interactions.

The product was characterised by ^1H NMR and IR spectroscopy as well as by elemental analysis. It is well known that tetrahedral Co(I) compounds are high-spin, paramagnetic. Therefore, NMR study is not quite helpful. The width of a resonance line observed in the ^1H NMR spectrum was greater than 30 Hz and ^{31}P, ^{29}Si NMR spectra could not be taken. Besides, complex **I** is extremely sensitive in solution towards traces of air (oxygen) and gets easily oxidised to Co(II)—blue complexes. The IR spectrum shows a band at 982.6 consistent with the (Co)–O–$SiMe_3$ bond.

4. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 163776. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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