Synthesis and Structure of Novel Dimethylcobalt(III) Complexes Containing Trimethylphosphine and Salicylaldiminato(*N:O*) Ligands

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Abstract. Dimethyl(salicylaldiminato[*N:O*])cobalt complexes $[CoMe_2(2\text{-}O\text{-}C_6H_1R^1R^2\ R^3\text{-}CH{=}NR^4)L_2]$ (L=PMe_3) (**1** - **6**) have been prepared through the reaction of $[CoMe_3(PMe_3)_3]$ with the corresponding substituted salicylaldimine. The complexes were characterized with IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and elemental analyses. The X-ray crystal structure of complex **1** shows an octahedral coordination of cobalt, with two equatorial *cis*-methyl groups opposite to the planar *N:O*-chelate ring.

Keywords: Cobalt; Methyl complexes; Salicylaldimine; Trimethylphosphine; Crystal structure

Introduction

Methyl cobalt(III) complexes are important intermediates for the cobalamin-dependent methionine synthase [1]. Some alkyl cobalt(III) complexes undergo insertion reactions with CO, an alkyne or an alkene to generate new C-C bonds [2]. If a complex bearing two alkyl groups reacts in this way, two new C-C bonds can be formed. Insertion followed by reduction elimination in the new acyl-alkyl, vinyl-alkyl, or dialkyl complexes can generate a ketone, olefin or alkane, respectively. Dimethyl cobalt(III) macrocycles can undergo photodealkylation [3]. In environmental chemistry dimethyl cobalt(III) complexes are used as methylation agents for germanium, tin and lead compounds [4, 5].

Schiff-base has many important applications in industrial chemical production and scientific research as chelating agent, stabilizer, bio-activator and analytical reagent. Complexes of transition metals with Schiff-bases can be widely used as catalysts for olefin polymerization [6], olefin epoxidation [7], olefin hydrogenation [8], C-H activation reaction [9], and copolymerization of CO_2/epoxides [10], as well as lactone polymerization [11].

The reaction of $[CoMe_3(PMe_3)_3]$ with salicylaldhyde and its derivatives affords us stable dimethyl phenolato cobalt(III) complexes [12]. We have introduced the isoelectronic Schiff base ligands under similar conditions and report here on the synthesis and structural properties of some novel mononuclear dimethyl cobalt(III) complexes.

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Experimental Details

General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive material. Microanalyses: Elemental analysis on C, H and N was carried out at Shandong University using a vario ELIII elemental analyzer, FRG. Melting points/decomposition temperatures: Sealed capillaries, uncorrected values. Literature methods were applied in the preparation of trimethyl-tris(trimethylphosphine)cobalt [14], Salicylaldimine Schiff base [15]. IR: Nujol mulls between KBr discs, Bruker Vector 22. ^{1}H and ^{31}P NMR spectra and ^{13}C NMR spectra (400 MHz, 162.0 MHz, and 100.6 MHz, respectively) were recorded with a Brucker AV 400MHz spectrometer, ^{13}C and ^{31}P NMR resonances were obtained with broadband proton decoupling.

Preparation of (N-methyl-salicylaldiminato-N:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt(III) (1)

0.36 g of *n*-methylsalicylaldimine (2.70 mmol) in 10 ml of pentane at −80 °C were combined with 0.90 g $[CoMe_3(PMe_3)_3]$ (2.71 mmol) in 50 ml of pentane. The mixture was warmed to 20 °C and stirred for 18 h. During this period the reaction solution turned nacarat, which was filtered and crystallization at −20 °C afforded red platelets of **1**. Yield 0.37 g (36 %); m. p. 139-141°C (dec.). Anal. Calc. for $C_{16}H_{32}NOP_2Co$ (375.3): C 51.20, H 8.53, N 3.73; found C 51.34, H 8.65, N 3.81 %.

IR (Nujol): 1613 s ν(C=N); 1144 m, 1133 m ν(Co-CH_3) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 300.2 K): δ = −1.08 (t, ^3J(PH) = 8.6 Hz, 3H, Co-CH_3), −0.15 (t, ^3J(PH) = 9.5 Hz, 3H, Co-CH_3), 1.11 (t′,$|^2J(PH) + {}^4J(PH)|$ = 6.1 Hz, 18H, PCH_3), 3.13 (s, 3H, NCH_3), 6.17 (t, ^3J(HH) = 7.2 Hz, 1H, C*H*), 6.44 (d, ^3J(HH) = 7.6 Hz, 1H,C*H*), 6.80 (dd, ^3J(HH) = 7.4 Hz, ^4J(HH) = 1.2 Hz, 1H, C*H*), 6.98 (dt, ^3J(HH) = 7.6 Hz, ^4J(HH) = 1.6 Hz, 1H, C*H*), 7.90(s, 1H, C*H*=N) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$, 300.2 K): 10.71 (t′,$|^1J(PC) + {}^3J(PC)|$ = 20.9 Hz, P*C*H$_3$), 52.07 (s, N*C*H$_3$), 109.9, 123.5, 132.2, 133.9 (*C*H), 119.4(*C*), 165.5 (s, *C*H=N), 168.9(s, *C*-O) ppm. **^{31}P NMR** (162.0 MHz, $CDCl_3$, 300.2 K): 8.0 (s br) ppm.

Preparation of (N-methyl-3,5-di-tert-butyl-salicylaldiminato-N:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt(III) (2)

In a similar procedure starting from 0.49 g of *n*-methyl-3,5-di-*tert*-butyl-salicylaldimine (1.98 mmol) and 0.66 g of $[CoMe_3(PMe_3)_3]$

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(1.99 mmol), 0.43 g dark red cubes of **2** (45 % yield) were obtained, m.p. 129-130 °C (dec.). Anal. Calc. for $C_{24}H_{48}NOP_2Co$ (487.5): calcd. C 59.13, H 9.85, N 2.87; found C 59.08, H 9.58, N 2.91 %.

IR (Nujol): 1610 s ν(C=N); 1163 m, 1125 m ν(Co-CH_3) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 296 K): δ = −1.02(t, ^{3}J(PH) = 7.8 Hz, 3H, CoCH_3), 0.04(t, ^{3}J(PH) = 7.8 Hz, 3H, CoCH_3), 1.22(s, 18H, PMe_3), 1.35 (s, 9 H, C(CH_3)$_3$, 1.37 (s, 9 H, C(CH_3)$_3$), 3.18 (s, 3H, NCH_3), 6.66 (s, 1H,C*H*), 7.19 (s, 1H, C*H*), 7.93(s, 1H, C*H*=N) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$, 300.2 K): δ = −19.8 (s br, CoCH_3), −8.4 (s br, CoCH_3), 11.92(t′, $|^1J(PC)+^3J(PC)|$ = 20.1 Hz, PCH_3), 29.8 (s, C(CH_3)$_3$), 30.9 (s, C(CH_3)$_3$), 33.0 (s, *C*(CH_3)$_3$),34.7 (s, *C*(CH_3)$_3$), 51.2 (s, NCH_3), 127.4, 127.7 (*C*H), 118.6, 130.6, 140.5(*C*), 167.1(s, CH=N), 167.2(s, *C*-O) ppm..

Preparation of (N-methyl-3-tert-butyl-5-methyl-salicylaldiminato-N:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt(III) (3)

In a similar synthesis 0.29 g *n*-methyl-3-*tert*-butyl-5-methyl-salicylaldimine (1.41 mmol) and 0.51 g CoL_3Me_3 (1.53 mmol) gave 0.31 g of red needles (49 % yield), m.p. 159-160 °C (dec.). Anal. Calc. for $C_{21}H_{42}NOP_2Co$ (445.4): C 56.63, H 9.50, N 3.14; found C 56.50, H 9.49, N 3.24 %.

IR (Nujol): 1610 s ν(C=N); 1163 m, 1133 m ν(Co-CH_3) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 300.2 K): δ = −1.17 (t, ^3J(PH) = 7.7 Hz, 3H, Co-C*H*$_3$), −0.09 (t, ^3J(PH) = 9.1 Hz, 3H, Co-C*H*$_3$), 1.06 (s, 18H, PC*H*$_3$), 1.21 (s, 9 H, C(CH_3)$_3$, 2.03 (s, 3 H, C*H*$_3$), 3.03 (s, 3H, NCH_3), 6.40 (s, 1H, C*H*), 6.80 (s, 1H, C*H*), 7.75 (s, 1H, C*H*=N) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$, 300.2 K): δ = −19.6 (s br, $CoCH_3$), −8.3 (s br, $CoCH_3$), 11.94 (t′, $|^1J(PC)+^3J(PC)|$ = 19.5 Hz, PCH_3), 19.9 (s, *C*H$_3$), 29.8 (s, C(*C*H$_3$)$_3$), 34.5 (s, *C*(CH_3)$_3$), 51.4 (s, NCH_3), 131.0, 131.9 (*C*H), 117.0, 119.3, 141.4 (*C*), 166.7(s, CH=N), 167.1(s, C-O) ppm.

Preparation of (N-methyl-3-methoxy-salicylaldiminato-N:O)-cis-dimethyl-trans-bis(trimethyl- phosphine)cobalt(III) (4)

In a similar procedure starting from 0.26 g *n*-methyl-3-methoxy-salicylaldimine (1.58 mmol) in 10 ml of ether and 0.53 g of [$CoMe_3$-(PMe_3)$_3$] (1.60 mmol) in 50 ml of ether, 0.39 g red-brown needles of **4** (61 % yield) were obtained, m. p. 140-141 °C (dec.). Anal. Calc. for $C_{17}H_{34}NO_2P_2Co$ (405.3): C50.37, H8.45, N3.45; found C50.44, H8.31, N3.55 %,

IR (Nujol): 1610 s ν(C=N); 1148 m, 1099 m ν(Co-CH_3) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, 300.2 K): δ = −1.08 (t, ^3J(PH) = 8.4 Hz, 3H, Co-C*H*$_3$), −0.08 (t, ^3J(PH) = 9.3 Hz, 3H, Co-C*H*$_3$), 1.12 (s, 18H, PC*H*$_3$), 3.13 (s, 3H, NC*H*$_3$), 3.75 (s, 3 H, OC*H*$_3$), 6.09 (t, ^3J(HH) = 7.3 Hz, 1H,C*H*), 6.52 (d, ^3J(HH) = 7.3 Hz, 1H,C*H*), 6.64 (d, ^3J(HH) = 7.0 Hz, 1H, C*H*) 7.91 (s, 1H, C*H*=N) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$, 300.2 K): δ = 10.73 (t′, $|^1J(PC)+^3J(PC)|$ = 20.9 Hz, PCH_3),52.1 (s, NCH_3), 57.4 (s, OCH_3),108.5, 116.2, 127.0 (*C*H), 119.7, 153.4 (*C*), 161.1(s, C-O), 165.3(s, CH=N) ppm.

Preparation of (N-methyl-naphtalaldiminato-N:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt(III) (5)

In a similar procedure starting from 0.31 g *n*-methyl-naphtalaldimine (1.69 mmol) in 10 ml of ether and 0.56 g of [$CoMe_3$(PMe_3)$_3$] (1.69 mmol) in 50 ml of ether, 0.29 g nacarat powder of **5** (41 % yield) were obtained, m. p. 159-160 °C (dec.). Anal. Calc. for $C_{24}H_{48}NOP_2Co$ (487.5): calcd. C59.13, H9.92, N2.87; found C59.08, H9.78, N2.91 %.

IR (Nujol): 1606 s ν(C=N); 1186 m, 1164 m ν(Co-CH_3) **^{1}H NMR** (400 MHz, $CDCl_3$, 300.2 K): δ = −1.03(t′, ^3J(PH) = 8.7 Hz, 3H, Co-C*H*$_3$), −0.18(t′, ^3J(PH) = 9.5 Hz, 3H, Co-C*H*$_3$), 1.12 (t′, $|^2J(PH)+^4J(PH)|$ = 6.6 Hz, 18H, PC*H*$_3$), 3.23 (s, 3H, NC*H*$_3$), 6.65 (d, ^3J(HH) = 9.2 Hz, 1H, C*H*), 7.01 (t, ^3J(HH) = 7.0 Hz, 1H, C*H*), 7.27 (t, ^3J(HH) = 6.0 Hz, 1H, C*H*), 7.37 (d, ^3J(HH) = 9.1 Hz, 1H, C*H*), 7.47 (d, ^3J(HH) = 8.5 Hz, 1H, C*H*), 7.74 (d, ^3J(HH) = 8.5 Hz, 1H, C*H*) 8.80 (s, 1H, C*H*=N) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$, 300.2 K): δ = 10.76(t, $|^1J(PC)+^3J(PC)|$ = 21.0 Hz, PCH_3), 52.9 (s, NCH_3), 116.6, 119.3, 126.0, 127.5, 128.2, 132.2 (*C*H), 108.0, 124.9, 135.1 (*C*), 159.6 (s, CH=N), 169.4 (s, C-O) ppm.

Preparation of (N-phenyl-salicylaldiminato-N:O)-cis-dimethyl-trans-bis(trimethylphosphine)cobalt(III) (6)

In a similar procedure starting from 0.43 g of *n*-phenyl-salicylaldimine (2.18 mmol) and 0.73 g of [$CoMe_3$(PMe_3)$_3$] (2.20 mmol), 0.34 g red crystals of **6** (36 % yield) were obtained, m.p. 115-116 °C (dec.). Anal. Calc. for $C_{21}H_{34}NOP_2Co$ (437.4): calcd. C57.66, H7.83, N3.20; found C57.62, H7.55, N3.27 %.

IR (Nujol): 1600 s ν(C=N); 1164 m, 1140 m ν(Co-CH_3) cm^{-1} **^{1}H NMR** (400 MHz, $CDCl_3$, 300.2 K): δ = −1.27(s br, 3H, Co-C*H*$_3$), 0.01(s, 3H, CoCH_3), 1.27(s br, 18H, PC*H*$_3$), 6.21 (s, 1H,C*H*), 6.53 (d, ^3J(HH) = 7.3 Hz, 1H, C*H*), 6.87 (d, ^3J(HH) = 6.1 Hz, 1H, C*H*), 6.95 (s, 2H, C*H*), 7.06 (s, 1H, C*H*), 7.18 (s, 1H, C*H*), 7.33 (s, 2H, C*H*), 8.0 (s, 1H, C*H*=N) ppm. **^{13}C NMR** (100.6 MHz, $CDCl_3$, 300.2 K): δ = 11.41(t′, $|^1J(PC)+^3J(PC)|$ = 20.4 Hz, PCH_3), 110.7, 123.6, 124.5, 127.8, 133.1, 135.2 (*C*H), 124.2, 155.2 (*C*), 167.3 (s, *C*H=N) ppm.

Crystallographic data for 1

($C_{16}H_{32}CoNOP_2$, M_r = 375.30): crystal size 0.37 × 0.22 × 0.17 mm^3, monoclinic, space group $P2_1/c$, a = 13.908(20), b = 11.060(16), c = 13.069(18) Å, β = 101.651(19)°, V = 1969(5) Å^3, D_c = 1.266 g cm^{-3} for Z = 4, F(000) = 800, μ = 1.033 mm^{-1}, Bruker AXS P4 diffractometer, λ = 0.71073 Å, T = 293 K, ω-scans, 9965 reflections, Θ_{max} = 25.03°, 3467 independent reflections [R (int) = 0.0754], semi-empirical absorption correction, hydrogens calculated, 190 refined parameters, R = 0.0629 (observed data), *wR2* = 0.1561 (independent data). Detailed data see "Supporting information".

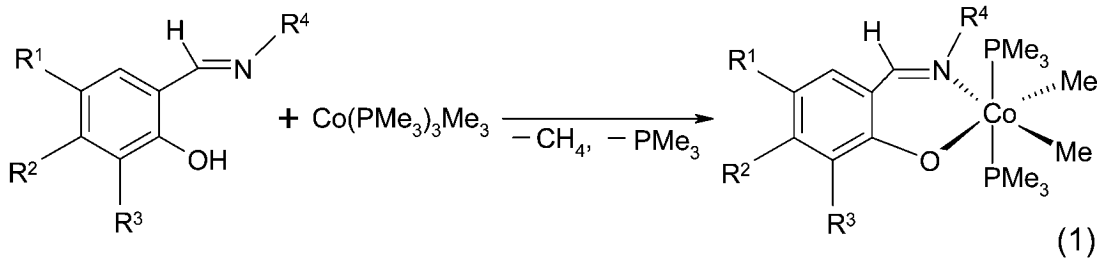
Crystallographic data (excluding structure factors) for the structure described in this publication have been deposited as supplementary material with the Cambridge Crystallographic Data Centre. Deposition number is CCDC-270616 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44-1223-336-033; E-mail: **deposit@ccdc.cam.ac.uk**].

Results and Discussion

Substituted salicylaldimines react with [$CoMe_3$(PMe_3)$_3$] (Eq. (1)) with the elimination of methane and subtraction of trimethylphosphine as well as utilizing both the phenolato-O and the imine-N atom to afford the six coordinate cobalt(III) complexes **1** to **6** as red solids that are soluble in pentane or diethyl ether.

In the infrared spectra, the characteristic bands for symmetric deformation vibration of (Co-Me)-bond can be found in the region of 1140−1190 cm^{-1}.

From ^{1}H-NMR spectroscopy we know that both of the *cis*-methyl groups have two triplet signals between −0.0 and −1.0 ppm with coupling constant ^3J(PH) = 8 − 10 Hz, which are created by coupling of two *trans*-phosphoratome at an angle of approximate 90°. A pseudo-triplet between 1,1 and 1,3 ppm with coupling constant $|^2J$(PH) +



(1)

Complex	1	2	3	4	5	6
R^1 =	H	^{t}Bu	Me	H	C_6H_4	H
R^2 =	H	H	H	H		H
R^3 =	H	^{t}Bu	^{t}Bu	OMe	H	H
R^4 =	Me	Me	Me	Me	Me	C_6H_5

$^4J(PH)| = 6-7$ Hz is recorded for two *trans*-PMe_3. The salicylaldimines protons are found in the range of 7.7 − 8.8 ppm as singlet signals. In the ^{13}C NMR Spektra a resonance at 160 − 170 ppm is generated by the salicylaldimine carbon atom. This value lies in the region of resonance for phenolato carbon nucleus. This result tells us that the salicylaldimine carbon atom and the phenolato carbon atom have the similar electronic properties, which is caused through the conjugation of the chelate ring. The resonances of the two cobalt-methyl carbon atoms in compound **2** and compound **3** are recorded at −19.8, −19.6 and −8.4, −8.3 ppm, respectively. In the ^{31}P NMR Spectra we got a singlet for complex **1** at ca. 8 ppm for two *trans*-PMe_3 at room temperature.

All of the spectroscopic data suggest an octahedral coordination with two *trans*-trimethylphosphine ligands, two *cis*-methyl groups and the conjugated chelating imine phenolato ligand at the cobalt atom. This conjecture is verified through X-ray single crystal diffraction.

By re-crystallization from pentane at 4 °C suitable crystals of **1** as red prism for X-ray diffraction analysis were obtained. The molecular geometry is shown in Figure **1** with selected bond distances and angles. The cobalt atom attains an octahedral coordination with two equatorial *cis*-methyl groups (C9-Co-C10=91.3(2)°) opposite to the planar *N:O*-chelate ring of a salicylaldiminato anion with the usual bite-angle (O1-Co-N1=90.6 (2)°) and by two axial trimethylphosphine which are slightly bent (P1-Co-P2= 174.0(5)°) towards the Co-Me groups. This structure is related to that of (2-acetyl-4-methyl-6-*tert*-butyl-phenolato-O:O)-*cis*-dimethyl-*trans*-bis(trimethyl-phosphane)cobalt(III)] [13]. Conjugational effects upon coordination shorten the original bond C1-C2 to 1.436(6) Å, there is no great difference between C1-C2 1.436(6) Å and C2-C3 1.409 (6) Å. The sum of internal angles of this chelating ring with 719.7° indicates the chelating with weak ring strain.

The complexes (**1-6**) are stable and can be handled in air for several months without any sign of decomposition.

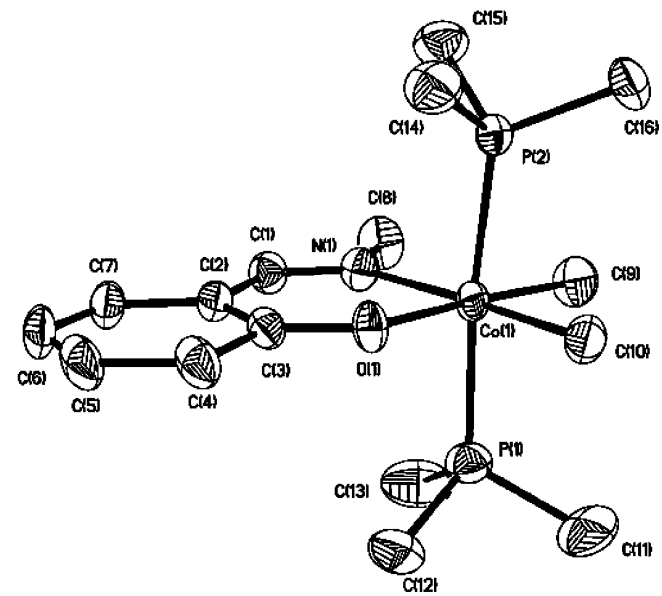


Fig. 1. Molecular structure of **1**; selected bond distances /Å and angles /deg:

Co1-O1 1.984(4), Co1-C10 1.998(5), Co1-C9 2.001(5), Co1-N1 2.026(4), Co1-P2 2.208(3), Co1-P1 2.215(3), C1-N1 1.276(6), N1-C8 1.468(6), O1-C3 1.288(5), C1-C2 1.436(6); C2-C3 1.409(6); O1-Co1-C10 83.4(2), O1-Co1-C9 174.6(2), C10-Co1-C9 91.3(2), O1-Co1-N1 90.6(2), C10-Co1-N1 173.9(2), C9-Co1-N1 94.8(2), O1-Co1-P2 91.27(9), C10-Co1-P2 87.1(2), C9-Co1-P2 88.8(2), N1-Co1-P2 93.1(1), O1-Co1-P1 91.2(1), C10-Co1-P1 87.8(2), C9-Co1-P1 88.3(2), N1-Co1-P1 92.3(1), P2-Co-P1 174.02(5), C1-N1-Co1 124.4(3), C3-O1-Co1 128.8(3), N1-C1-C2 128.6 (4), C1-C1-C3 122.5(4), C2-C3-O1 124.8(4).

They are very reactive to CO. We will report the results in the near future.

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