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Reactions of Trimethylphosphane-Supported Cobalt Complexes with Salicylaldimines – Formation and Structures of Cobalt Compounds Containing Salicylaldiminato [N:O] Ligands

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The reactions of low-valent cobalt complexes $CoMe(PMe_3)_4$, $CoCl(PMe_3)_3$ and $Co(PMe_3)_4$ with salicylaldimines are described to give tetrahedral complexes **7–12**, an octahedral complex **13** and a π -coordinated imine complex **15**. The crys-

tal structures of **13** and **15** are reported. The formation and likely mechanisms are discussed. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

Introduction

At present, there is increasing interest in N-containing chelate ligands forming metallacyclic compounds.^[1-6] Large numbers of complexes of transition metals with Schiff bases, which are used as agents in organic synthesis, catalysts and anticancer or antitoxin drugs, have been synthesized and studied in many laboratories.^[7-12] Recent progress has been made in the study of Schiff base–Co(II) complexes as dioxygen carriers. These reports have considerable significance in chemical and biochemical processes.^[13–15]

Chelate-assisted oxidative addition is a reaction of potential utility for the selective activation of organic functional groups.^[16–18] 2-Phosphanylacyl ligands or 2-phosphanylphenol groups containing weakly acidic protons react with metal halides to afford metal hydrides with the oxidative addition of an O–H or C–H bond at the metal centre.^[19] According to Equation (1), acylcobalt(III) hydrides are obtained by the reaction of halogenotris(trimethylphosphane)cobalt(I) complexes with 2-diphenylphosphanylbenzaldehyde.^[20] There is increasing interest in this process, since it is generally accepted that acyl hydride intermediates are involved in certain metal-catalyzed carbonylation^[21] and decarbonylation processes.^[22]

Recently, we have introduced the salicylaldimine ligands, which are isoelectronic to 2-diphenylphosphanylbenzaldehyde. We now report the reactions of electron-rich, lowvalent cobalt complexes $CoMe(PMe_3)_4$, $CoCl(PMe_3)_3$ and $Co(PMe_3)_4$ with salicylaldimines, which have afforded tetrahedral bis(chelate) cobalt(II) imine complexes (7–12), an oc-

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X = CI, Br, I

tahedral tris(chelate) cobalt(III) imine complex 13 as well as a π -coordinate imine complex 15, which includes trimethylphosphane as a supporting ligand. The neighbouring N-donor of the salicylaldimine ligand plays an active part in the formation of these complexes. The molecular structures of 13 and 15 were determined by X-ray diffraction. Possible formation routes are proposed.

Results and Discussion

1. Reactions of CoMe(PMe₃)₄ with Salicylaldimines

The reaction between $CoMe(PMe_3)_4$ and salicylaldimines 1–4 liberated methane and utilized both the phenolato and N-donor functions to form the paramagnetic cobalt(II) complexes 7–10, which include two salicylaldiminato[*N*:*O*] chelating ligands. The reaction occurs by a disproportionation route, with the concomitant production of tetrakis(trimethylphosphane)cobalt(0) (Scheme 1, route a). Analogous reactions, e.g., leading to a five-membered metallacycle (route b), did not occur, and the corresponding iminoacyl(hydrido)cobalt(III) species was not detected among the products.

In the infrared spectra of complexes 7–10, the characteristic v(C=N) bands are found between 1600 and 1634 cm⁻¹. Complex 10 has pseudo-tetrahedral geometry; the crystal structure of this complex was reported in our previous work.^[23]



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Scheme 1.

An oxidative addition of salicylaldimine iminoacyl C–H bonds did not occur upon reaction with methyltetrakis(trimethylphosphane)cobalt(I) (Scheme 1, route b). It appears that the preferred coordination of the N-donor prevents the attack of cobalt at the C–H bond. This assumption would also explain the scarcity of iminoacyl metal complexes arising from C–H activation.^[24,25]

2. Reactions of CoCl(PMe₃)₃ with Salicylaldimines

Chloridotris(trimethylphosphane)cobalt(I) reacts with salicylaldimines 3-5 to afford the cobalt(II) complexes 9-11, which include two salicylaldiminato[N:O] ligands, together with tetrakis(trimethylphosphane)cobalt(0) (Scheme 2). A cobalt hydride is suggested as a plausible intermediate. This unstable species undergoes a reductive elimination reaction liberating hydrogen chloride and giving rise to a reactive cobalt(I) complex, which disproportionates to afford complexes 9-11 and tetrakis(trimethylphosphane)cobalt(0).

3-methoxy-*N*-methylsalicylaldimine [ligand **6**, Equation (2)] reacts with chloridotris(trimethylphosphane)cobalt(I) to afford not only the cobalt(II) complex **12** containing salicylaldiminato[N:O] ligands but also the cobalt(III) com-

plex 13 containing three salicylaldiminato[N:O] ligands [Equation (2)]. To the best of our knowledge, complex 13 is the first cobalt(III) complex with three Schiff base anions.



The ¹H NMR spectrum of complex **13** shows a resonance at $\delta = 7.72$ ppm clearly representing the protons of the imino groups. Protons of the benzene rings lie in the range 6.39–6.80 ppm. The CH₃O protons are found at $\delta =$ 3.75 ppm, and the CH₃N protons of are located at $\delta =$ 3.55 ppm. In the ¹³C NMR spectrum, resonances at 164.9–166.5 ppm are assigned to the imino carbon atoms. The CH₃O and CH₃N carbon atoms are situated at $\delta =$ 48.0 and 56.0 ppm, respectively. As only the NMR resonances of a single aldimine ligand are observed, the spectra suggest that **13** undergoes a rapid ligand exchange process in CDCl₃ solution. It is insoluble in pentane and diethyl ether. Crys-



Scheme 2.

tals of **13** were obtained from THF and were analysed by X-ray diffraction. The structure of **13** is shown in Figure 1.



Figure 1. Molecular structure of **13**; selected distances [Å] and angles [°]: Co1–O4 1.883(3), Co1–O6 1.892(3), Co1–O2 1.900(3), Co1–N3 1.935(4), Co1–N2 1.947(3), Co1–N1 1.948(4), N1–C7 1.277(6), N1–C8 1.457(6), N2–C16 1.260(6), N2–C17 1.469(6), N3–C25 1.290(7); O4–Co1–O6 172.33(15), O6–Co1–N3 93.80(16), O4–Co1–N2 92.50(14), O2–Co1–N2 174.11(15), O2–Co1–N1 91.93(15), N3–Co1–N1 176.79(15).

The cobalt atom occupies the central position in an octahedral geometry. Three equivalent salicylaldimine ligands have Co–O and Co–N bond lengths of Co1–O2 1.900(3), Co1–O4 1.883(3), Co1–O6 1.892(3), Co1–N1 1.948(4), Co1–N2 1.947(3), Co1–N3 1.935(4) Å, respectively. Average Co–O and Co–N bond lengths are 1.892 and 1.943 Å, respectively. Complex **13** is a chiral molecule with a meridional configuration. There are two pairs of enantiomers in every crystal cell.

The formation of the cobalt(II) complex 12 is similar to that of complexes 9–11 in Scheme 2. A proposed mechanism for the generation of cobalt(III) complex 13 via a cobalt hydride intermediate is illustrated in Scheme 3. The hy-

dridocobalt(III) intermediate, initially formed by oxidative addition of an imino C–H group, reacts with two molecules of Schiff base to afford the cobalt(III) complex **13** with concomitant elimination of hydrogen and hydrogen chloride.



Scheme 3.

The formation of complexes 12 and 13 is a competitive process. The stability of the intermediate hydride complex is advantageous for the formation of complex 13. In Scheme 2, the steric hindrance of groups R^1 , R^2 and R^3 and the electronegativities of the substituents have an effect on the stability of the hydride intermediate and therefore on the relative proportions of complexes 12 and 13. The details of this dependence are not clear and should be further studied with a greater selection of ligands.

3. Reactions of Co(PMe₃)₄ with Salicylaldimines

Reaction of tetrakis(trimethylphosphane)cobalt(0) with 3-*tert*-butyl-*N*,5-dimethylsalicylaldimine (ligand 4) should afford a cobalt(II) hydride complex 14 if oxidative addition of the phenolic hydoxy group at the cobalt centre prevails (Scheme 4, route a). However, in the experiment two products were obtained, i.e., the cobalt(II) complex 10 and the π -imine cobalt(II) complex 15.



Scheme 4.

The proposed mechanism through an intermediate cobalt(II) hydride complex 14 is illustrated in Scheme 4. The Co–H bond of the reactive hydrido cobalt(II) complex 14 reacts with a phenolic OH group of a further salicylaldimine. Meanwhile, the C=N donor of salicylaldimine π -coordinates to the cobalt atom affording 15 with the elimination of H_2 (Scheme 4, route **b**). Dissociation of trimethylphosphane from **15** affords the cobalt(II) complex **10** (Scheme 4, route **c**). We propose that the presence of a trimethylphosphane ligand in complex **15** results from π -imine coordination at the cobalt centre, which competes with the usual N-coordination. In the presence of trimethylphosphane, the interconversion of complexes **15** and **10** is a reversible process.

Yellow crystals of **15** were obtained from pentane at 0 °C. A view of the molecular structure of crystal **15** is given in Figure 2. The cobalt atom occupies the central position of a square plane in a pseudo-square-pyramidal configuration with P1 in the apical position. Two salicylaldimine ligands lie in the square plane with out-of-plane distortion of the π -coordinated C=N bond. The distance between Co1 and C25 [1.929(5) Å] is shorter than that between Co1 and N2 [1.980(4) Å]. Few reports on π -imine compounds of cobalt(II) have appeared.^[26]



Figure 2. Molecular structure of **15**; selected distances [Å] and angles [°]: Co1–O1 1.918(3), Co1–O2 1.923(3), Co1–C25 1.929(5), Co1–N2 1.980(4), Co1–N1 1.992(4), Co1–P1 2.1954(13); O1–Co1–O2 174.93(13), O1–Co1–C25 89.84(16), O2–Co1–C25 85.28(16), O1–Co1–N2 84.78(15), O2–Co1–N2 90.70(14), C25–Co1–N2 43.15(17), O1–Co1–N1 91.73(14), C25–Co1–N1 156.72(18), N2–Co1–N1 113.91(16), O1–Co1–P1 94.88(10), O2–Co1–P1 87.76(10), C25–Co1–P1 105.46(15), N2–Co1–P1 148.55(13), N1–Co1–P1 97.54(12).

Conclusions

Methyltetrakis(trimethylphosphane)cobalt(I) and chloridotris(trimethylphosphane)cobalt(I) react with salicylaldimines to form cobalt(II) complexes 7–12 which bond to both the phenolato and N-donor functions of two salicylaldiminato[N:O] ligands. The reaction involves the liberation of methane or hydrochloric acid and subsequent disproportionation to give complexes 7–12 and tetrakis(trimethylphosphane)cobalt(0). Steric hindrance and the electronegativities of substituents in the ligands influence the ratio of products in the reaction between chloridotris(trimethylphosphane)cobalt(I) and salicylaldimines. 3-methoxy-N-methylsalicylaldimine reacts with chloridotris(trimethylphosphane)cobalt(I) to afford not only cobalt(II) complex 12, which includes two salicylaldiminato[N:O] li-

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gands, but also the cobalt(III) complex **13**, which includes three salicylaldiminato[N:O] ligands. Tetrakis(trimethylphosphane)cobalt(0) reacts with salicylaldimine to afford the π -imine cobalt(II) complex **15** and the cobalt(II) complex **10** through a possible cobalt hydride intermediate. However, a chelate-assisted oxidative addition of the OC–H bond, that has been shown to proceed with 2-donor substituted benzaldehydes in complexes of low-valent cobalt,^[27] could not be observed for the NC–H group of salicylaldimines under otherwise similar conditions. Such a reaction is probably suppressed by the greater stability of the N-coordination in comparison to an O-coordination in the sixmembered cobaltacycle.

Experimental Section

General Procedures and Materials: Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Microanalyses: Elemental analysis (C, H and N) was carried out at Shandong University by using a Vario ELIII elemental analyzer. Melting points/decomposition temperatures were determined by using sealed capillaries, uncorrected values are reported. Literature methods were used in the preparation of methyltetrakis(trimethylphosphane)cobalt(I), tetrakis(trimethylphosphane)cobalt(0)^[28] and chloridotris(trimethylphosphane)cobalt(I).^[29] Salicylaldimines were obtained by the condensation of salicylaldehyde or substituted salicylaldehydes with amines. Other chemicals were used as purchased. All solvents were dehydrated and degassed before use. IR samples were prepared as Nujol mulls and placed between KBr discs; samples were analyzed with a Bruker spectrophotometer of type VECTOR 22. ¹H NMR spectra were recorded with a Bruker AV 400 MHz spectrometer. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer.

Bis(*N***-methylsalicylaldiminato)cobalt(II)** (7): Methyltetrakis(trimethylphosphane)cobalt(I) (1.82 g, 4.81 mmol) was dissolved in pentane (50 mL). *N*-Methylsalicylaldimine (0.65 g, 4.81 mmol) in pentane (10 mL) was then added to this solution. The resulting solution was stirred at ambient temperature for 17 h. During this period the solution turned orange, indicating that a reaction had occurred. The mixture was then filtered. The filtrate afforded red crystals of complex 7 (0.57 g, 36.5%). M.p. 165.2–170.5 °C. $C_{16}H_{14}CoN_2O_2$ (325.23): calcd. C 5.91, H 4.34, N 8.61; found C 5.82, H 4.24, N 8.64. IR (Nujol): 1634 s v(C=N) cm⁻¹.

Bis(*N***-tert-butylsalicylaldiminato)cobalt(II) (8):** Methyltetrakis(trimethylphosphane)cobalt(I) (1.0 g, 2.65 mmol) was dissolved in pentane (50 mL). *N*-tert-Butylsalicylaldimine (0.47 g, 2.66 mmol) dissolved in pentane (10 mL) was then added to this solution. After being stirred for 18 h at 20 °C, the red-brown mixture was filtered. The filtrate that was stored at -20 °C afforded red microcrystals of complex 8 (0.17 g, 41%). M.p. 208.7–212.5 °C. C₂₂H₂₈CoN₂O₂ (411.40): calcd. C 64.23, H 6.86, N 6.81; found C 64.20, H 6.81, N 6.78. IR (Nujol): 1600 (s) v(C=N) cm⁻¹.

Bis(N-phenylsalicylaldiminato)cobalt(II) (9): Method a: Methyltetrakis(trimethylphosphane)cobalt(I) (0.68 g, 1.80 mmol) was dissolved in pentane (50 mL). *N*-Phenylsalicylaldimine (0.35 g, 1.80 mmol) dissolved in pentane (10 mL) was then added to this solution. The resulting solution was stirred at ambient temperature for 18 h. During this period the reaction solution turned coffee brown. After filtration, the precipitate was recrystallized from diethyl ether at 4 °C to afford red-brown crystals of complex **9** (0.25 g, 31%). **Method b:** *N*-Phenylsalicylaldimine (1.17 g, 5.94 mmol) in diethyl ether (10 mL) was combined with chloridotris(trimethylphosphane)cobalt(I) (1.92 g, 5.95 mmol) in diethyl ether (50 mL) at room temperature. The mixture was stirred for 18 h, during which time a brown-yellow solution formed. The solution was filtered. The filtrate at -27 °C gave red crystals of complex **9** (0.23 g, 17.2%). M.p. 152–155.4 °C. C₂₆H₂₀CoN₂O₂ (451.38): calcd. C 69.1, H 4.47, N 6.21; found C 69.08, H 4.52, N 6.31. IR (Nujol): 1604 v(C=N), 1582 v(C=C) cm⁻¹.

Bis(3-tert-butyl-N,5-dimethylsalicylaldiminato)cobalt(II) (10): Method a: See ref.^[23] Method b: A solution of 3-tert-butyl-N,5-dimethylsalicylaldimine (0.67 g, 3.27 mmol) in diethyl ether (10 mL) was added to a stirred solution of chloridotris(trimethylphosphane)cobalt(I) (1.05 g, 3.26 mmol) in diethyl ether (50 mL) at -80 °C. After being warmed up, the mixture was stirred for 18 h at 20 °C. The turbid yellow-brown solution was filtered. The solid residue was then extracted with diethyl ether. The filtrate and ether extracts were combined and kept at 0 °C to afford red crystals 10 (0.16 g, 21%). Method c: 3-tert-Butyl-N,5-dimethylsalicylaldimine (0.90 g, 4.39 mmol) in pentane (10 mL) was combined with tetrakis(trimethylphosphane)cobalt(0) (0.80 g, 2.20 mmol) in pentane (50 mL) at -80 °C. After being warmed up, the mixture was kept stirring for 18 h at 20 °C, during which time a brown-yellow solution formed. The solution was filtered, and the filtrate afforded red crystals of complex 10 (0.20 g, 39%) and yellow crystals of complex 15 (0.27 g, 45%) at 4 °C, respectively, which were separated manually. Crystals of 10: dec.>159 °C. C₂₆H₃₆CoN₂O₂ (467.5): calcd. C 56.6, H 9.44, N 3.15; found C 56.5, H 9.49, N 3.24. IR (Nujol): 1615 v(C=N), 1538 v(C=C) cm⁻¹.

Bis(3-methoxy-N-phenylsalicylaldiminato)cobalt(II) (11): 3-methoxy-*N*-phenylsalicylaldimine (1.30 g, 5.73 mmol) in diethyl ether (10 mL) was combined with chloridotris(trimethylphosphane)cobalt(I) (0.62 g, 1.92 mmol) in diethyl ether (50 mL) at room temperature. The mixture was stirred for 18 h, during which time a brown-yellow solution formed. The solution was filtered, and the solid residue was recrystallized from THF at -27 °C affording red crystals of complex **11** (0.13 g, 27%). M.p. ≈ 250 °C (dec.). C₂₈H₂₄CoN₂O₄ (511.43): calcd. C 65.76, H 4.73, N 5.48; found C 65.59, H 4.78, N 5.36. IR (Nujol): 1604 v(C=N), 1582 v(C=C) cm⁻¹.

Bis(3-methoxy-N-methylsalicylaldiminato)cobalt(II) (12) and Tris(3methoxy-N-methylsalicylaldiminato)cobalt(III) (13): A solution of 3-methoxy-N-methylsalicylaldimine (1.25 g, 7.58 mmol) in diethyl ether (10 mL) was added to a stirred solution of chloridotris(trimethylphosphane)cobalt(I) (0.80 g, 2.48 mmol) in diethyl ether (50 mL) at room temperature. After stirring for 18 h, a brown-yellow turbid solution was obtained. The suspension was filtered, and the filtrate was stored at -27 °C to give red crystals of complex 12 (0.06 g, 19%). The solid residue was recrystallized from THF at -27 °C to afford dark green crystals of 13 (0.10 g, 20%). Crystals of 12: m.p. >250 °C. C₁₈H₂₀CoN₂O₄ (387.29): calcd. C 55.82, H 5.20, N 7.23; found C 55.66, H 5.27, N 7.20. IR (Nujol): v = 1616 v(C=N); 1599, 1543 v(C=C) cm⁻¹. Crystals of 13: m.p. dec.>140 °C. C₂₉H₃₄CoN₃O_{6.5} (587.52): calcd. C 59.32, H 5.83, N 7.15; found C 59.34, H 5.79, N 7.22. IR (Nujol): v = 1633 v(C=N); 1597, 1546 v(C=C) cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 3.55 (s, 3 H, NCH₃), 3.75 (s, 3 H, OCH₃), 6.39, 6.64, 6.80 (3 H, CH), 7.72 (s, 1 H, N=CH) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K): $\delta = 47.715$, 48.381 (s, NCH₃), 56.354, 56.678 (s, OCH₃), 112.7, 115.4, 116.4, 116.9, 123.3, 124.9, 125.4, 125.5 (s, CH), 153.3, 153.8, 155.5 (s, C–O), 164.9, 166.5 (s, C=N) ppm.

[$\eta^2(N, C)$ -(3-tert-Butyl-N,5-dimethylsalicylaldiminato)](3-tert-butyl-N,5-dimethylsalicylaldiminato)(trimethylphosphane)cobalt(II) (15): 3-tert-Butyl-N,5-dimethylsalicylaldimine (0.90 g, 4.39 mmol) in pentane (10 mL) was combined with tetrakis(trimethylphosphane) cobalt(0) (0.80 g, 2.20 mmol) in pentane (50 mL) at -80 °C. After being warmed up, the mixture was stirred for 18 h, during which time a turbid brown-yellow solution formed. The suspension was filtered, and the filtrate was stored at 4 °C to give red crystals of complex **8** (0.20 g, 38.8%) and yellow crystals of complex **15** (0.27 g, 45.0%), respectively, which were separated manually. Crystals of **15**: m.p. 225.7–228.5 °C (dec.). C₂₉H₄₅CoN₂O₂P (543.57): calcd. C 64.08, H 8.34, N 5.15; found C 64.02, H 8.30, N 5.21. IR (Nujol): 1624 (C=N), 1540 (C=C) cm⁻¹.

X-ray Diffraction: Crystals of complexes **13** and **15** suitable for X-ray diffraction analysis were grown from THF and pentane at 6 °C. The molecular structures are shown in Figure 1 and Figure 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.

Table 1. Crystallographic data of complexes 13 and 15.

C ₂₉ H ₃₄ CoN ₃ O _{6.5}	C ₂₉ H ₄₅ CoN ₂ O ₂ P
587.52	543.57
dark green	yellow
orthorhombic	monoclinic
Pna2(1)	P2(1)/c
13.7090(16)	8.6517(10)
11.2224(13)	48.670(6)
19.773(2)	7.7008(9)
90	107.281(2)
3042.0(6)	3096.3(6)
4	4
1.283	1.168
0.609	0.631
$2.06 \le \theta \le$	$0.84 \le \theta \le$
26.21	25.00
$-17 \le h \le 15$	$-8 \le h \le 10$
$-11 \le k \le 13$	$-57 \le k \le 57$
$-24 \le l \le 23$	$-9 \le l \le 8$
16088	15559
0.0369	0.0421
6025	5456
6025/6/385	5456/54/335
1.090	1.178
$R_1 = 0.0512$	$R_1 = 0.0668$
$wR_2 = 0.1359$	$wR_2 = 0.1291$
$R_1 = 0.0765$	$R_1 = 0.0874$
$wR_2 = 0.1544$	$wR_2 = 0.1373$
	$\begin{array}{c} C_{29}H_{34}CoN_{3}O_{6.5}\\ 587.52\\ dark green\\ orthorhombic\\ Pna2(1)\\ 13.7090(16)\\ 11.2224(13)\\ 19.773(2)\\ 90\\ 3042.0(6)\\ 4\\ 1.283\\ 0.609\\ 2.06 \leq \theta \leq \\ 26.21\\ -17 \leq h \leq 15\\ -11 \leq k \leq 13\\ -24 \leq l \leq 23\\ 16088\\ 0.0369\\ 6025\\ 6025/6/385\\ 1.090\\ R_{1} = 0.0512\\ wR_{2} = 0.1359\\ R_{1} = 0.0765\\ wR_{2} = 0.1544 \end{array}$

CCDC-607934 and CCDC-607935 for **13** and **15** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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