Inorg. Chem. **2003**, *42*, 6805–6811

Inorganic Chemistry
Article

New β Cis Folded Organocobalt Derivatives with a Salen-Type Ligand

Renata Dreos,* Giorgio Nardin, Lucio Randaccio,* Patrizia Siega, Giovanni Tauzher, and Višnja Vrdoljak[†]

Dipartimento di Scienze Chimiche, Università di Trieste, via Licio Giorgieri 1,
34127 Trieste, Italy

Received January 27, 2003

The reduction of $[Co^{III}(tmsalen)py_2]^+ClO_4^-$, where tmsalen = 4,4′,7,7′-tetramethylsalen, with $NaBH_4/PdCl_2$ in alkaline methanolic solution, followed by the oxidative addition of CH_2ClI, leads to the expected trans organometallic dimeric species **1**, $[CH_2ClCo(tmsalen)]_2$, provided that the product is recovered from the reaction mixture immediately after the completion of the reaction. If **1** is left for longer time in contact with the reaction mixture, the intramolecular reaction of the axial chloromethyl group with the equatorial chelate leads to the formation of the monocationic complex **2**, containing a seven-membered ring. In this complex the novel tetradentate ligand coordinates Co in a cis fashion, the other two positions being occupied by one py and one water molecule. The resulting complex is chiral, even if the reaction product is a racemic compound. The unidentate ligands of **2** have been exchanged quantitatively for *N*-MeIm, and the resulting complex **3** still maintains the β cis geometry. Therefore, **2** may be considered the precursor of a new class of organocobalt derivatives with a folded tetradentate ligand and two adjacent exchangeable sites. On the basis of the geometry of the tetradentate Schiff bases in complexes, where they adopt a planar geometry, it was suggested that there is a significant electron density delocalization involving the metal center over the two chemically equivalent moieties of Co(chel). Comparison of the geometry of the planar salicylaldiminate (sal) moiety with that of the cyclized methoxy–iminate one (imi) in **2** and **3** strongly supports that the delocalization, still present in sal, is essentially either lost or strongly reduced in imi.

Introduction

In recent years the metal complexes with tetradentate Schiff base ligands derived from salicylaldehyde and diamines (salen-type ligands) have received new attention in connection with a number of possible applications, which range from asymmetric catalysis[1] to material sciences.[2] In the complexes of the salen-type ligands, the Schiff base preferentially adopts a planar geometry, with the four donor atoms nearly coplanar.[3] However, there are some examples of metal complexes in which the “salen-like” ligands have a β cis configuration. Generally, this folded configuration is induced either by a bidentate ligand[4] which occupies two cis sites in the coordination sphere or by the bonding nature of the two unidentate ligands, which strongly demand a cis coordination.[5] A lengthening of the polymethylenic chain bridging the two imine nitrogen atoms[6] and an increase of the size of the central metal atom[7] may also favor a strained nonplanar configuration.

We have recently reported the synthesis and the characterization of several organometallic derivatives RCo(tmsalen), where tmsalen = 4,4′,7,7′-tetramethylsalen (Chart 1), in view

---

* To whom correspondence should be addressed. E-mail: dreos@univ.trieste.it (R.D.); randaccio@univ.trieste.it (L.R.).

[†] Current address: Laboratory of General and Inorganic Chemistry, Chemistry Department, Faculty of Science, University of Zagreb, Ul. Kralja Zvonimira 8, 10000 Zagreb, Croatia.

(1) (a) Canali, L.; Sherrington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85. (b) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189.

(2) For instance: (a) Hoshino, N. *Coord. Chem. Rev.* **1998**, *174*, 77. (b) Di Bella, S.; Fragalà, I.; Ledoux, I.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 9481.

(3) (a) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem Rev.* **1972**, *7*, 385. (b) Yamada, S. *Coord. Chem. Rev.* **1999**, *190*, 537.

(4) (a) Carroll, K. M.; Schwartz, J.; Ho, D. M. *Inorg. Chem.* **1994**, *33*, 2707. (b) Calligaris, M.;. Manzini, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton. Trans.* **1979**, 729. (c) Kushi, Y.; Tada, T.; Fujii, Y.; Yoneda, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1834 and references therein.

(5) (a) Yamanouchi, K.; Yamada, S. *Inorg. Chim. Acta* **1974**, *9*, 161. (b) Cilla, A. C.; Goghi, L.; Manfredotti, A. G.; Guastini, G. *Cryst. Struct. Commun.* **1974**, *3*, 551. (c) Thornback, J. R.; Wilkinson, G. *J. Chem. Soc., Dalton. Trans.* **1978**, 110. (d) Motevalli, M.; Parkin, B.; Ramnauth, R.; Sullivan, A. *Chem. Commun.* **2000**, 2661.

(6) (a) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1991**, *189*, 97. (b) Gatehouse, B. M.; Reichert, B. E.; West, B. *Acta Crystallogr., Sect. B* **1976**, *32*, 30.

(7) Corden, J. P.; Errington, W.; Moore, P.; Wallbridge, M. G. H. *Chem. Commun.* **1999**, 323.

10.1021/ic034085r CCC: $25.00

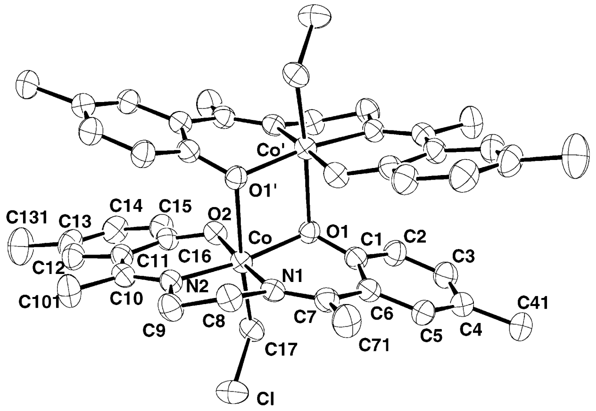


Figure 1. ORTEP drawing with the numbering scheme for the non-hydrogen atoms of **1**.

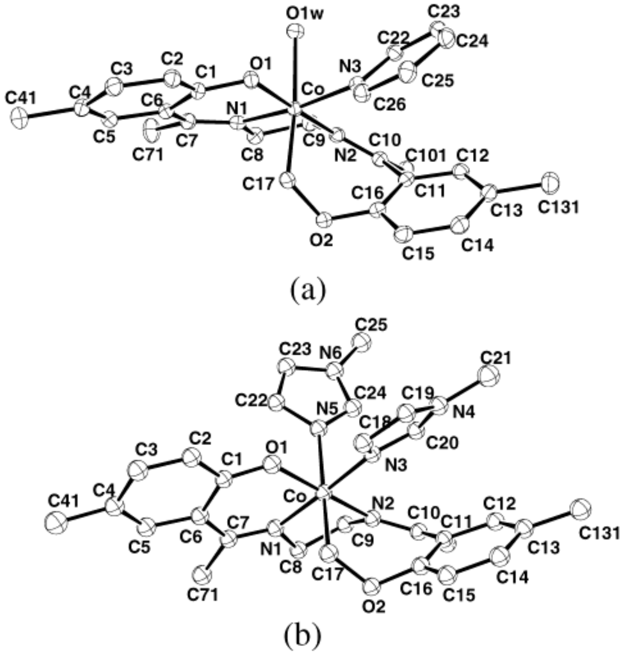
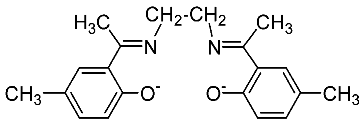


Figure 2. ORTEP drawing with the numbering scheme for the non-hydrogen atoms of the cations of (a) **2** and (b) **3**.

Chart 1



tmsalen = 4,4',7,7' tetramethylsalen

of their interest as vitamin B$_{12}$ models.[8] Available structural data showed that the RCo(tmsalen) complexes may exhibit both six and five coordination in the solid state, but they invariably adopt a planar trans geometry. The attempts to synthesize in a similar way the derivative with R = CH$_2$Cl led, beside the expected trans organometallic species **1** (Figure 1), to a β cis organometallic derivative **2** (Figure 2a), by intramolecular reaction of the axial chloromethyl group with the equatorial chelate.

Modifications of the equatorial ligand have been observed in organocobaloxime-type complexes as a consequence of the reaction between the axial alkyl group and the equatorial ligand moiety.[9,10] In some cases,[9] the reaction is induced by the Co−C bond cleavage and the subsequent migration of the alkyl group to a site of the equatorial ligand. In other cases[10] the reaction in CH$_2$X−Co (X = halogen) derivatives is induced by the deprotonation of the equatorial ligand in alkaline medium and the subsequent nucleophilic attack of an equatorial N donor to the axial CH$_2$ group with formation of a stable N−Co−C three-membered ring.

With this Schiff base complex a new kind of reaction occurs leading to compound **2** (Figure 2a).

The unidentate ligands of **2** have been exchanged quantitatively for *N*-MeIm, and the resulting complex **3** still maintains the β cis geometry (Figure 2b). Therefore, **2** may be considered the precursor of a new class of organocobalt derivatives with a folded tetradentate ligand and two adjacent exchangeable sites.

Experimental Section

General Details. All the manipulations were performed in the dark. [Co^{III}(tmsalen)py$_2$]$^+$ClO$_4^-$ was synthesized as previously described.[8] All other reagents were analytical grade and used without further purification. NMR spectra were recorded on a JEOL EX-400 (^{1}H at 400 MHz and ^{13}C at 100.4 MHz). Electrospray mass spectra were recorded in positive mode by using an API 1 mass spectrometer (Perkin-Elmer).

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.*

Synthesis of [CH$_2$ClCo(tmsalen)]$_2$, 1. [Co^{III}(tmsalen)py$_2$]$^+$-ClO$_4^-$ (0.5 g, 0.8 mmol) was suspended in methanol (50 mL), and the suspension was deaerated several times with continuous stirring. NaBH$_4$ (0.035 g, 1 mmol) in H$_2$O (0.5 mL) was added to the suspension under nitrogen, followed by the addition of few drops of an aqueous 10% PdCl$_2$ solution. A very fast reduction occurred, evidenced by the instantaneous change of the suspension color from light brown to red. CH$_2$ClI (1 mL) was added, and the stirring was continued for 1.5 h, until a red solution was obtained. After filtration, 100 mL of water was added drop by drop to the solution and the precipitate was collected by filtration, washed with water, and dried in air. X-ray-quality crystals were obtained by slow evaporation from a saturated methanolic solution at 4 °C. Yield: 0.30 g (89%). Anal. Calcd for C$_{42}$H$_{48}$Cl$_2$Co$_2$N$_4$O$_4$ (M_r = 861.6): C, 58.55; H, 5.62; N, 6.50. Found: C, 58.1; H, 5.49; N, 6.31. ESI-MS (90 V, CH$_3$OH; $m/z+$): calcd for [RCo(tmsalen)]$_2$, 861.6; found, 861.5 (92%). Further peaks: 825.5 (−1 Cl, 68%), 811.5 (−1

---

(8) Dreos, R.; Nardin, G.; Randaccio, L.; Siega, P.; Tauzher, G.; Vrdoljak, V. *Inorg. Chim. Acta* **2003**, *349*, 239.

(9) (a) Shi, S.; Babac, A.; Espenson, J. H. *Inorg. Chem.* **1991**, *30*, 3410. (b) Daikh, B. E.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 4160.

(10) (a) Polson, S. M.; Hansen, L.; Marzilli, L. G. *J. Am. Chem. Soc.* **1996**, *118*, 4804. (b) Marzilli, L. G.; Polson, S. M.; Hansen, L.; Moore, S. J. *Inorg. Chem.* **1997**, *36*, 3851. (c) Dreos, R.; Felluga, A.; Nardin, G.; Randaccio, L.; Siega, P.; Tauzher, G. *Inorg. Chem.* **2001**, *40*, 5541.

CH$_2$Cl, 60%), 463.0 (CH$_2$ClCo(tmsalen)CH$_3$OH, 40%), 431.0 (CH$_2$ClCo(tmsalen), 40%), 395.5 (CH$_2$ClCo(tmsalen) − Cl, 100%), 381.5 (Co(tmsalen), 48%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, TMS): δ (ppm) = 2.10 (s, 6H, C*H*$_3$Ph), 2.34 (s, 6H, C*H*$_3$C═N), 3.68 (m, 2H, C*H*$_2$C*H*$_2$), 4.18 (m, 2H, C*H*$_2$C*H*$_2$) 5.16 (s, 2H, C*H*$_2$Cl) 6.65(d, 2H, *H*-C2), 6.83 (d, 2H, *H*-C3), 6.96 (s, 2H, *H*-C5). ^{1}H NMR (400 MHz, CD$_3$OD, TMS): δ (ppm) = 2.20 (s, 6H, C*H*$_3$Ph), 2.53 (s, 6H, C*H*$_3$C═N), 3.81 (m, 2H, C*H*$_2$C*H*$_2$), 3.91 (m, 2H, C*H*$_2$C*H*$_2$), 5.26 (s, 2H, C*H*$_2$Cl), 6.95 (m, 4H, *H*-C2, *H*-C3), 7.31 (s, 2H, *H*-C5). ^{13}C{^{1}H} NMR (100.4 MHz, CD$_2$Cl$_2$, TMS): δ = 18.71 (*C*H$_3$C═N), 20.21 (*C*H$_3$Ph), 53.84 (*C*H$_2$*C*H$_2$), 123.42 (C2), 124.69 (quaternary carbon), 129.01 (C5), 131.93 (C3), 162.56 (quaternary carbon), 170.00 (C═N).

Synthesis of 2. The reduction of [Co^{III}(tmsalen)(py)$_2$]$^+$ClO$_4^-$ and the successive oxidative alkylation were carried out as for **1.** After the filtration of the red solution and the addition of 10 mL of water, the solution was covered to prevent evaporation and left aside for 3 days. After this time, the solvent was evaporated at ambient pressure. Dark red crystals of **2** were collected by filtration, washed with water, and dried over P$_2$O$_5$. X-ray-quality crystals of **2** were obtained by slow evaporation from a solution of the complex in CD$_2$Cl$_2$. Yield: 0.32 g (72%). Anal. Calcd for C$_{26}$H$_{31}$ClCoN$_3$O$_7$ (M_r = 591.9): C, 52.7; H, 5.28; N, 7.10. Found: C, 52.5; H, 5.08; N, 6.90. ESI-MS (60 V, CH$_2$Cl$_2$; m/z^+): calcd for the cation of **2**, 492.5; found, 474.5 (cation of **2** − H$_2$O, 100%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ (ppm) = 1.95 (s, 3H, H−C131), 2.23 (s, 3H, H−C41), 2.31 (s, 3H, H−C71), 2.48 (s, 3H, H−C101), 3.43 (m, 1H, CH$_2$CH$_2$), 4.06 (m, 2H, CH$_2$CH$_2$), 5.10 (m, 1H, CH$_2$CH$_2$), 6.10 (s, 1H, H−C17), 6.59 (s, 1H, H−C12), 6.78 (bm, 3H, H−C14, H−C15 and H−C17), 6.82 (d, 1H, H−C2), 6.94 (d, 1H, H−C3), 7.08 (m, 2H, *meta* py), 7.13 (s, 1H, H−C5), 7.51 (m, 1H, *para* py), 8.08 (d, 2H, *ortho* py). ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, TMS): δ (ppm) = 18.53 (C71), 20.25 (C131), 20.55 (C41), 24.26 (C101), 55.88 (CH$_2$CH$_2$), 56.72 (CH$_2$CH$_2$), 76.69 (C17), 121.31 (C15), 122.36, 122.91 (C2), 124.28 (*meta* py), 124.81, 129.02 (C5), 129.67 (C12), 131.89, 132.40 (C14), 133.67 (C3), 134.19, 136.69 (*para* py), 152.24 (*ortho* py), 159.91, 179.96.

Synthesis of 3. *N*-MeIm (0.13 g, 1.6 mmol) was added to a solution of **2** (0.094 g, 0.16 mmol) in CH$_2$Cl$_2$ (6 mL). The solution color changed quickly from dark red to dark orange. *i*-C$_3$H$_7$OH (2 mL) was added, and the solution was set aside for crystallization. After partial evaporation of the solvent, an orange solid precipitated from the solution, which was collected by filtration and dried over P$_2$O$_5$. X-ray-quality crystals of **3** were obtained from a solution of the complex in CD$_2$Cl$_2$/*n*-heptane by diffusion. Yield: 0.07 g (65%). Anal. Calcd for C$_{29}$H$_{36}$ClCoN$_6$O$_6$ (M_r = 659.0): C, 52.8; H, 5.59; N, 12.7. Found: C, 51.9; H, 5.94; N, 12.4. ESI-MS (60 V, CH$_2$Cl$_2$; m/z^+): calcd for the cation of **3**, 559.6; found, 477.8 (cation of **3** − *N*-MeIm, 100%). ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 2.24 (s, 3H, H−C41), 2.25 (s, 3H, H−C131), 2.48 (s, 3H, H−C71), 2.58 (s, 3H, H−C101), 3.45(m, 1H, CH$_2$–CH$_2$), 3.55 (s, 3H, H−C21), 3.74 (s, 3H, H−C25), 3.84 (m, 2H, CH$_2$CH$_2$), 4.52 (m, 1H, CH$_2$CH$_2$), 6.35 (s, 1H, H−C19), 6.54 (s, 1H; H−C18), 6.59 (s, 1H, H−C17), 6.69 (d, 2H; H−C2), 6.82 (d, 1H; H−C15), 6.90 (bm, 3H; H−C3, H−C14, and H−C22), 7.05 (bs, 1H, H of the axial *N*-MeIm), 7.18 (s, 1H; H−C17), 7.27 (bs, 2H, H−C5 and H−C12),), 7.78 (s, 1H, H−C20), 8.16 (bs, 1H, H of the axial *N*-MeIm). ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$, TMS): δ (ppm) = 18.49 (C71), 20.64 (C41), 20.83 (C131), 25.58 (C101), 34.23 (C21 and C25), 55.81 (CH$_2$CH$_2$), 56.98 (CH$_2$CH$_2$), 87.79 (C17), 119.70 (C19), 121.34, 121.89 (C15), 123.49 (C2), 127.72 (C18), 129.31, 130.04, 132.13, 132.81, 133.70, 133.94, 141.34 (C20), 152.88, 162.13, 169.29, 181.07.

^{1}H NMR Evaluation of the Cyclization Rate. In a typical experiment **1** (7.2 mg, 13.5 mmol) was dissolved in CD$_3$OD (3 mL), and the solution was filtered. The stock solution was divided into three batches, and each batch was poured in a NMR tube protected with aluminum foil. The pD of the three samples was adjusted at 3.9 (concentrated HClO$_4$), 7.7, and 11.2 (NaOD), respectively. Spectra were acquired at different times at the room temperature.

Structure Determination of 1−3. Single crystals, suitable for X-ray data collection, were obtained as already reported in the Experimental Section. The diffraction data were collected with a Nonius DIP 1030 H system, using graphite-monochromated Mo Kα radiation. For all the structures a total of 30 frames were collected, using the xpress program,[11] over a hemisphere of reciprocal space with rotation of 6° about the φ axis. A MAC Science image plate (diameter = 300 mm) was used, and the crystal-to-plate distance was fixed at 90 mm. The determination of unit-cell parameters, integration of reflection intensities, and data scaling were performed using MOSFLM and SCALA from the CCP4 program suite.[12] Reflections, which were measured on previous and following frames, were used to scale the frames on each other, a procedure that partially eliminated absorption effects, taking into account also any crystal decay. The structures were solved with direct methods,[13] followed by Fourier syntheses, and refined by full-matrix least-squares (on F^2) cycles.[14] Compound **1** crystallized with a molecule of MeOH, while **2** cocrystallized with a molecule of CH$_2$Cl$_2$. The solvent molecules were fully ordered and refined anisotropically without restraint. The H atoms were not refined but included at calculated positions, in the final refinements. A suite of programs[15] was also used in the geometrical and final calculation. Crystal and refinement data are given in Table 1.

Computational Details. All the calculations were carried out with the Gaussian-98 program, using the 6-31g* (for H, C, N, and O) and Ahlrichs' VTZ (for Co) basis sets.

---

(11) Schierbeek, B. *Xpress*; Nonius: Delft, The Netherlands, 1998.

(12) Collaborative Computational Project, Number 4. *Acta Crystallogr.* **1990**, *46A*, 467.

(13) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. SIR92-A program for crystal structure solution. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(14) Sheldrick, G. M. *SHELXL97-Programs for Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1998.

(15) Farrugia, L. J. *Appl. Crystallogr.* **1999**, *32*, 837.

Table 1. Crystal Data and Structure Refinement for **1**−**3**

Compound	**1**	**2**	**3**
empirical formula	$C_{22}H_{28}ClCoN_2O_3$	$C_{27}H_{33}Cl_3CoN_3O_7$	$C_{29}H_{36}ClCoN_6O_6$
fw	462.84	676.84	659.02
T, K	293(2)	150(2)	150
λ, Å	0.710 69	0.710 69	0.710 69
cryst system, s.g.	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	9.508(3)	11.387(4)	7.472(5)
b, Å	10.676(9)	11.922(4)	12.981(6)
c, Å	12.101(5)	12.036(4)	16.716(6)
α, deg	99.05(2)	106.75(2)	72.90(2)
β, deg	104.95(2)	110.02(2)	80.73(2)
γ, deg	108.59(2)	82.16(2)	72.49(2)
V, Å^3	1085.6(11)	1468.8(9)	1473.2(13)
Z	2	2	2
ρ_{calcd}, g cm^{-3}	1.416	1.530	1.486
μ, mm^{-1}	0.939	0.907	0.727
final R indices [$I > 2\sigma(I)$]	$R_1{}^a = 0.0600$, $wR_2{}^b = 0.1623$	$R_1 = 0.0538$, $wR_2 = 0.1422$	$R_1 = 0.0656$, $wR_2 = 0.1699$
R indices (all data)	$R_1 = 0.0820$, $wR_2 = 0.1923$	$R_1 = 0.0719$, $wR_2 = 0.1580$	$R_1 = 0.0901$, $wR_2 = 0.1957$

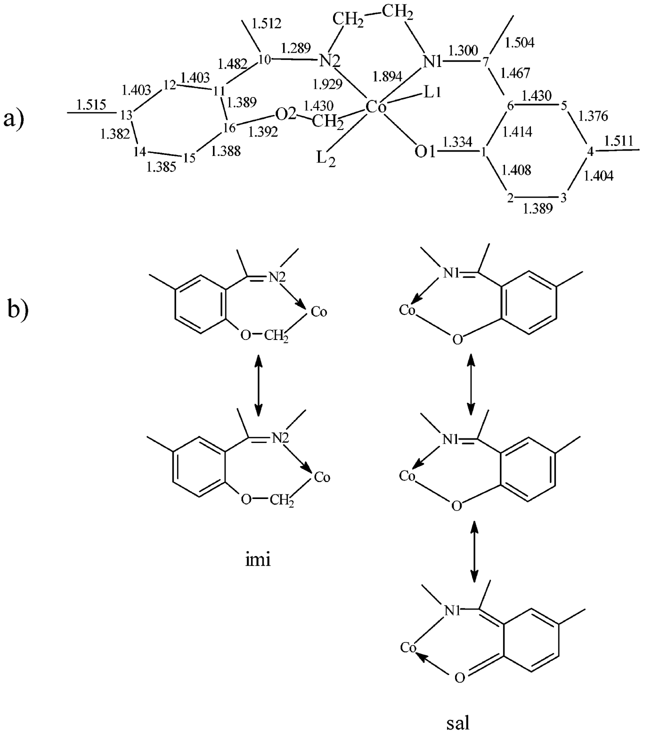
^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o{}^2|^2]^{1/2}$.

Results and Discussion

Syntheses. A quite common way to obtain the organometallic derivatives of the cobalt Schiff base complexes involves the "in situ" generation of a Co(I) species by reduction with $NaBH_4/PdCl_2$ in alkaline methanolic solution, followed by the oxidative addition of the appropriate alkyl halide. This procedure allowed us to isolate a series of organometallic RCo(tmsalen) complexes,[8] all having the Schiff base in a planar geometry. The trans geometry of **1** is clearly demonstrated by the X-ray structure in solid state (Figure 1) and by the ^{1}H and ^{13}C NMR spectra in solution. Indeed, the ^{1}H NMR spectra in both CD_2Cl_2 and CD_3OD show a singlet of the methyls bound to C4, a singlet of the methyls on C7, two symmetrical multiplets (AA′BB′ system) of the ethylenic protons, a quartet of the protons on C2 and C3 (AB system), and a singlet of the proton on C5. The number and the sharpness of the signals indicate that the complex **1**, as the previously described $[RCo(tmsalen)]_2$ derivatives,[8] is monomeric in solution. Indeed, the dimerization should increase the complexity of the spectra, owing to the loss of symmetry consequent to the formation of the dinuclear species.[16]

If **1** is left for longer time in contact with the reaction mixture, a further process occurs, which leads to the formation of **2**. In the complex **2** the tetradentate ligand assumes a β cis configuration, with the formation of a seven-membered ring, the other two positions being occupied by one py and one water molecule (Figure 2a). The resulting complex is chiral, even if the reaction product is a racemic compound. The complex **2**, once formed, is very stable in solution. It is not light sensitive, even in aerobic conditions, in contrast to **1** and to the other complexes of the RCo(tmsalen) series.[8]

Scheme 1



In the ^{1}H NMR spectrum of **2**, the protons belonging to the same half of the equatorial ligand can be easily identified, but assigning the signals to the planar half of the equatorial ligand (sal) or to the cyclizated one (imi) (Scheme 1) is not straightforward. A tentative assignment has been made starting from the observation that in the ^{13}C spectrum of **2** one $CH_3C{=}N$ methyl (18.53 ppm) resonates very close to the $CH_3C{=}N$ methyl in the ^{13}C spectrum of **1** (18.71 ppm), whereas the other is strongly deshielded (24.26 ppm). Therefore, the former resonance has been assigned to the methyl carbon of the sal moiety. The bonded protons have been picked out through an HETCOR experiment, and the complete assignment has been performed through COSY and NOESY experiments.

The two unidentate ligands of **2** can be easily replaced by *N*-MeIm. The addition of a 1:1 amount of *N*-MeIm to a solution of **2** causes the almost complete replacement of pyridine, whereas in the presence of a 10-fold excess of *N*-MeIm both the unidentate ligands are replaced. The resulting complex **3** maintains the β cis geometry (Figure 2b). The ^{1}H NMR spectrum of **3** in $CDCl_3$ at the room temperature shows broad signals for the *N*-MeIm in axial position, suggesting that this ligand is involved in a relatively fast exchange process. The lability of the *N*-MeIm parallels the longer Co−N5 bond found in the solid state (see below) and is presumably due to the strong trans effect of the residual CH_2 group.

Factors Affecting the Cyclization Rate in 1. The cyclization reaction of **1** in CD_3OD can be easily monitored by ^{1}H NMR spectroscopy, because the loss of symmetry

---

(16) The peaks corresponding to dimeric species in the ESI-MS spectrum at 60 V in methanol are likely due to species generated in the source during the ionization process. The formation of polynuclear aggregates during the electrospray ionization process is well recognized in applications of ESI-MS in organometallic chemistry. (For instance: Henderson, W.; Nicholson, B. K.; McCaffrey, L. J. *Polyhedron* **1998**, *17*, 4291.) Several examples of polynuclear aggregates generated in situ have been reported. (For some relevant examples: Chipperfield, J. R.; Clayton, J.; Khan, S. A.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **2000**, 1087. Dinger, M. B.; Henderson, W.; *J. Organomet. Chem.* **1998**, *560*, 233. Cardwell, T. J.; Colton, R.; Mitchell, S.; Traeger, J. C. *Inorg. Chim. Acta* **1994**, *216*, 75.) This hypothesis is supported by the dependence of the peaks intensity on the ESI MS conditions, the intensity of the peaks corresponding to dimeric species decreasing at higher cone voltages.

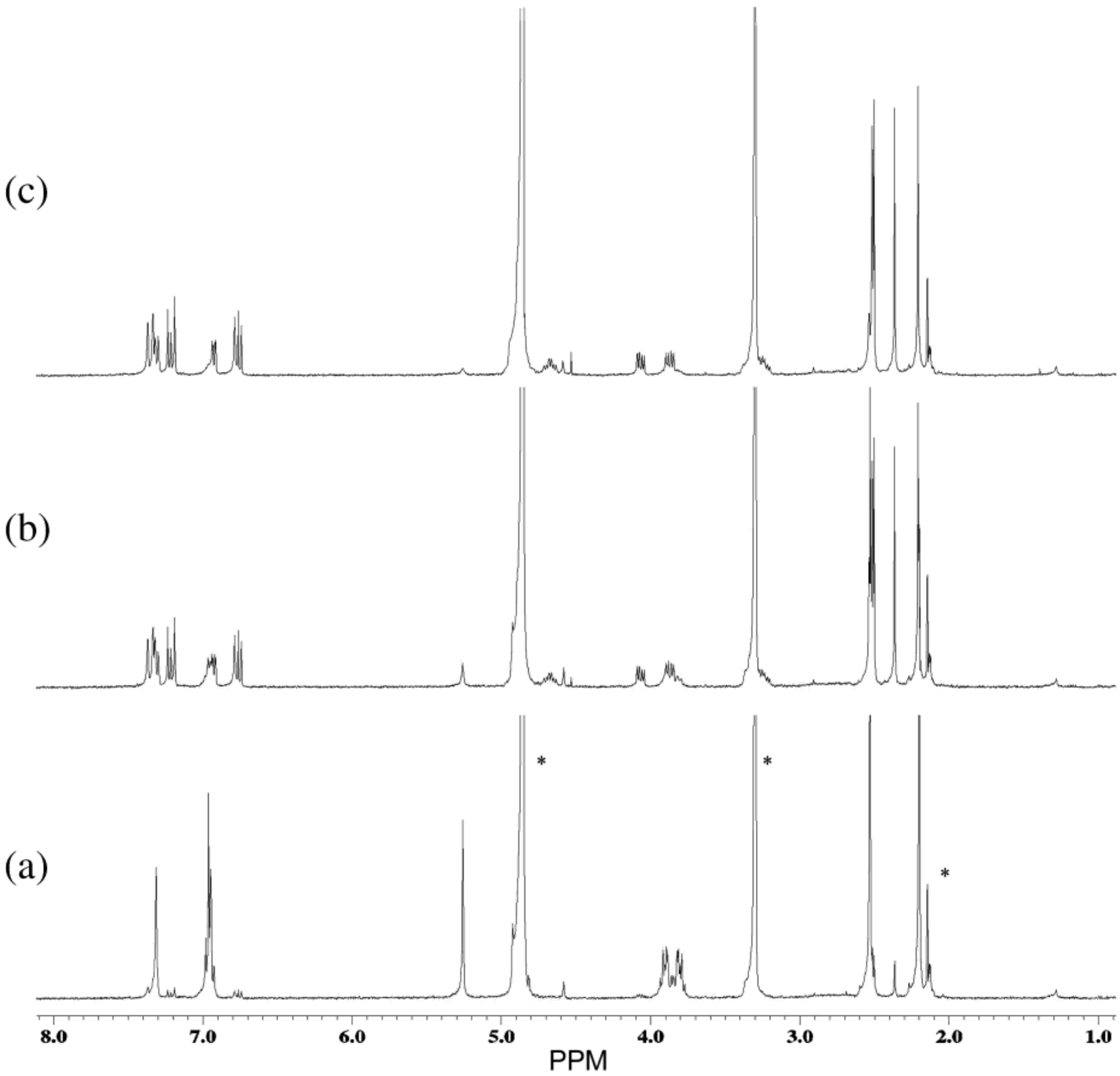


Figure 3. (a) ^{1}H NMR spectra of **1** immediately after the dissolution in CD_3OD at pD 7.7, (b) after 1 day, and (c) after 2 days. The peaks of the solvent and the impurities are marked with asterisks.

causes a doubling of the number of signals arising from the macrocycle (Figure 3). The reaction rate has been qualitatively evaluated in the pH range 4.0−11.0 in the dark, and in all cases the cyclization was almost complete within about 2 days. It is noteworthy that the product of the cyclization of **1**, which presumably contains two solvent molecules as unidentate ligands, is not stable in methanolic solution, and further reactions occur after the cyclization is complete. On the contrary, **2**, which contains pyridine in equatorial position, is stable in methanolic solution. The different behavior may be ascribed to the stabilizing effect of the nitrogen ligand.

The cyclization reaction requires a coordinating solvent: in $CDCl_3$ the complex **1** decomposes slowly in the dark, presumably through a radicalic pathway, leading to the formation of paramagnetic Co(II) species, revealed by the appearance of the ^{1}H NMR spectra. The homolytic dissociation of the Co−C bond is competitive with the cyclization reaction in CD_3OD, if the reaction is carried out in the presence of the light.

The above results suggest that the formation of **2** from the trans derivative involves the attack of the negatively charged oxygen of the equatorial ligand on the axial chloromethyl group and the loss of a chloride from the latter, with formation of the monocationic complex containing a seven-membered ring. Previous examples of intramolecular reaction of CH_2X axial groups (X = Cl, Br, I) with imino−oxime or amino−oxime equatorial ligands have been described.[10] In both cases the generation of an equatorial negatively charged nitrogen is required and therefore the reaction occurs in basic medium. In the present case the negative charge present on the oxygen atom makes it prone to a nucleophilic attack on the CH_2 group, so that the cyclization occurs also in neutral medium. More detailed studies regarding kinetics and mechanism of the cyclization reaction are in progress and will be reported elsewhere.

It is noteworthy that most of the Schiff bases complexes that adopt a cis geometry are forced in this configuration by steric constraints, such as a polymethylenic chain[6] or bulky substituents on the diamine,[6] or by the necessity to accommodate a bidentate ligand.[4] In the present case the driving force of the reaction is the high reactivity of the axial chloromethyl group together with the relative flexibility of the tetradentate ligand.

X-ray Structures. The ORTEP drawing of **1** with the atom numbering scheme is depicted in Figure 1. Crystals of **1** are built up by neutral dimeric units, $[CH_2ClCo(tmsalen)]_2$, arranged on a crystallographic symmetry center and by methanol molecules in the ratio 1:1. The O1′ atom of one $CH_2ClCo(tmsalen)$ unit coordinates to Co of the other unit, and both the Co atoms are hexacoordinated. The conformation of the equatorial ligand has an asymmetric umbrella shape with α and β angles of 26.5 and 9.5°, where α and β are the dihedral angles between the O2N2 equatorial donor plane and the salycilaldiminate planes, respectively. The equatorial donors around the Co are nearly coplanar, being displaced from their mean plane of ± 0.002 Å, whereas the dimerization causes a lengthening of the Co−O1 distance (1.905 Å), with respect to Co−O2 (1.870(3) Å). The two axial bond lengths Co−C and Co−O1′ are 1.934(5) and 2.295(3) Å, respectively. The Co−O1′ distance in **1** is significantly longer than that of 2.209(2) Å in $[CH_3Co(tmsalen)]_2$ and 2.199(2) Å in $[CF_3CH_2Co(tmsalen)]_2$.[8] This is very surprising, since the CH_2Cl group is less electron-donating than the methyl and is expected to lengthen the Co−O1′ trans bond less than CH_3. The Co−C17−Cl plane nearly bisects the five membered cycle, with a dihedral angle N1CoC17Cl of 46.2°. This orientation is similar to that found in the analogue $[CF_3CH_2Co(tmsalen)]_2$. The compound **1** crystallizes with an independent methanol molecule. The OH group of the solvent molecules are H-bonded to the O2 atom ($-x + 1$, $-y$, $-z + 2$) with a O···O distance of 2.89 Å.

The ORTEP drawing of the cations of **2** and **3** are depicted in Figure 2a,b. Crystals of **2** and **3** are built up by the two enantiomeric units arranged on a crystallographic symmetry center. The novel tetradentate ligand coordinates Co in a cis fashion, the other two positions being occupied by one py and one water molecule in **2** and by two *N*-MeIm molecules in **3**. The boatlike conformation of the seven-membered metallacycle is very similar in the two cations and brings the fused phenyl ring approximately parallel to the py plane in **2** (interplanar angle of 25°) and to the N3 imidazole plane in **3** (interplanar angle of 32°) (Figure 2a,b).

The coordination bond lengths and angles are given in Table 2. The angles about Co are only few degrees different from the ideal values of 90 and 180°. The Co−C distance of 1.965(4) Å in **2** and 1.964(6) Å in **3** are very close to those of 1.951(2)[8] and 1.963(7) Å[17] found in the $[MeCo(chel)]_2$ dimeric species, where chel = Schiff base.

The water molecule trans to OCH_2 undergoes the strong trans influence of the latter, with a long Co−O bond of 2.213(3) Å in **2**. O1W is also H-bonded (O1W···O = 2.733 Å) to the O1 atom of the centrosymmetric molecule at $-x$, $1 - y$, $-z$ and to the oxygen of the ClO_4^- anion (O1W···O4 = 2.986 Å).

Table 2. Coordination Bond Distances (Å) for **2** and **3**

sal				imi			
	2	**3**	**3** (calcd)		**2**	**3**	**3** (calcd)
O1−C1	1.334(4)	1.304(6)	1.308	O2−C16	1.392(4)	1.391(6)	1.367
C1−C2	1.408(5)	1.418(9)	1.423	C16−C15	1.388(5)	1.359(8)	1.398
C1−C6	1.414(5)	1.435(8)	1.432	C16−C11	1.389(5)	1.402(8)	1.407
C2−C3	1.389(5)	1.380(8)	1.377	C15−C14	1.385(5)	1.400(8)	1.390
C3−C4	1.404(5)	1.391(9)	1.415	C14−C13	1.382(5)	1.392(8)	1.406
C4−C5	1.376(5)	1.380(9)	1.381	C13−C12	1.403(5)	1.383(8)	1.395
C4−C41	1.511(5)	1.515(8)	1.510	C13−C131	1.515(5)	1.505(8)	1.511
C5−C6	1.430(5)	1.428(8)	1.426	C12−C11	1.403(5)	1.416(7)	1.410
C6−C7	1.467(5)	1.467(9)	1.456	C11−C10	1.482(5)	1.467(8)	1.480
C7−C71	1.504(5)	1.516(8)	1.519	C10−C101	1.512(5)	1.514(8)	1.520
C7−N1	1.300(5)	1.302(7)	1.312	C10−N2	1.289(5)	1.303(7)	1.298
Co−N1	1.894(3)	1.919(5)	1.935	Co−N2	1.929(3)	1.929(7)	2.007
				O2−C17	1.430(4)	1.423(8)	1.425

The trans influence of the OCH_2 group can be appreciated in **3**, where the Co−N trans to the latter group is 2.129(9) Å, whereas that trans to iminic N1 donor is 1.958(9) Å.

On the basis of the geometry of the tetradentate Schiff bases in complexes, where they adopt a planar geometry, it was suggested that there is a significant electron density delocalization involving the metal center over the two chemically equivalent moieties of Co(chel).[3,12] Comparison (Scheme 1a) of the geometry of the salicylaldiminate (sal) moiety with that of methoxy−iminate one (imi) in **2** strongly supports that the delocalization, still present in sal, is essentially either lost or strongly reduced in imi. This is suggested by the shortening of the C−N bond and the lengthening of the C−O and C−CN bonds in imi with respect to the corresponding bonds in sal, as well as by the change observed in the phenyl ring distances (Scheme 1a).

Examination of the main resonance structures in the two moieties of **2** (Scheme 1b) easily interprets the observed variations in bond lengths between sal and imi. In fact, the C−C−N fragment has some degree of delocalization in sal, due to the contribution of the ketonic resonance structure, not resonating in imi. Thus, the C7−N1 bond is longer than the C10−N2 bond. Analogously, the contribution to the resonance of the cationic form in sal allows one to interpret the change in the phenyl ring distances in imi and sal, respectively. Furthermore, the comparison of the resonance schemes in imi and sal suggests that the Co−N2 distance should be longer than the Co−N1 one. Indeed, the former is found to be 1.929(5) Å and the latter is 1.894(5) Å. The trend of the bond lengths in **2** is also approximately followed in the less accurate structure of **3,** as shown by data reported in Table 2.

To confirm the above qualitative interpretation, theoretical calculations by the density functional method (DFT) have been carried out on complex **3**. The minimized distances are compared in Table 2 with the experimental ones. The trend of the latter in the imi and the sal moiety is fairly well reproduced, including the Co−N distances.

Acknowledgment. This work was supported by the MIUR (Grant PRIN MM03185591) and by the CNR,

---

(17) Marzilli, L. G.; Summers, M. F.; Bresciani-Pahor, N.; Zangrando, E.; Charland, J. P.; Randaccio, L. *J. Am. Chem. Soc.* **1985**, *107*, 6880.

Agenzia 2000 (Rome). V.V is grateful to the Consorzio per lo Sviluppo Internazionale dell'Università di Trieste for the Alpe Adria fellowship. We thank Prof. Vinicio Galasso for performing theoretical calculations and Dr. Fabio Hollan for recording mass spectra.

Supporting Information Available: Three X-ray crystallographic files in CIF format and 1D and 2D NMR spectra of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034085R