Formation of Carbon−Carbon-Bonded Dimers in the Reduction of [Co^II salophen] [salophen = *N,N′-o*-Phenylenebis(salicylideneaminato)]: Their Reactivity with Electrophiles To Form Co−C Bonds

Stefania De Angelis,† Euro Solari,† Emma Gallo,† Carlo Floriani,*,† Angiola Chiesi-Villa,‡ and Corrado Rizzoli‡

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne, CH-1015 Lausanne, Switzerland, and Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy

The reduction of cobalt−Schiff base complexes has been explored as a function of the nature of the ligand. In the case of substituted salen complexes, reduction occurred at the metal with the formation of bifunctional Co-(I)−Na complexes, while for salophen derivatives the reductive coupling of imino groups was observed. Such C−C bonds function as electron shuttles in chemical reductions. Reduction of [Co(MeOsalen)] (**1**) with Na metal in THF led to a monomeric [Co(MeOsalen)Na(THF)$_2$] (**2A**) and a dimeric [{Co(MeOsalen)Na(THF)}$_2$] (**2B**) compound. Compounds **2A** and **2B** exemplify a bifunctional acid−base system with both centers in close proximity. The analogous reduction of [Co(salophen)] (**3**) and [Co(MeOsalophen)] (**5**) led to dimeric cobalt(II) derivatives containing a bridging C−C bond across two units in [Co$_2$(salophen)$_2$Na$_2$(THF)$_6$] (**4**) and [Co$_2$(MeOsalophen)$_2$Na$_2$(THF)$_4$] (**6**), respectively. However, such cobalt(II) centers behave as cobalt(I), since the C−C bond provides a pair of electrons to the metal couple during the chemical reaction. Alkylation at the cobalt has been observed in complexes **4** and **6** with the concomitant formation of a Co(III)−C bond in [Co-(salophen)(Me)] (**9**), [Co(salophen)(COOMe)(THF)] (**10**), [Co(MeOsalophen)(Me)(H$_2$O)] (**11**), and [Co-(MeOsalophen)(COOMe)(H$_2$O)] (**12**). The cleavage and formation of the C−C bond linking the two salophen units have been observed in the reversible reactions of **4** and **6** with carbon dioxide leading to the CO$_2$ adducts [Co(salophen)NaCO$_2$(THF)] (**13**) and [Co(MeOsalophen)NaCO$_2$(THF)] (**14**). Crystallographic data: **2** is triclinic, space group $P\bar{1}$, $a = 14.651(1)$ Å, $b = 15.355(1)$ Å, $c = 11.671(11)$, $\alpha = 105.70(1)°$, $\beta = 102.66(1)°$, $\gamma = 97.65(1)°$, $Z = 2$, and $R = 0.044$; **4** is monoclinic, space group $P2_1/c$, $a = 11.270(2)$ Å, $b = 17.594(3)$ Å, $c = 16.606(3)$ Å, $\alpha = \gamma = 90°$, $\beta = 90.45(2)°$, $Z = 2$, and $R = 0.053$; **6** is triclinic, space group $P\bar{1}$, $a = 11.857(4)$ Å, $b = 12.639(4)$ Å, $c = 10.553(5)$, $\alpha = 106.28(3)°$, $\beta = 101.17(3)°$, $\gamma = 103.04(3)°$, $Z = 1$, and $R = 0.057$.

Introduction

Chemically and electrochemically produced cobalt(I), in a macrocyclic environment, has long been used as a synthetic precursor for making Co(III)−C bonds in the so-called vitamin B$_{12}$ models *via* electrophilic alkylations. However, in many cases, such species have not been characterized.[1] In more recent years, the chemical reduction of cobalt(II)−Schiff base complexes having a square planar N$_2$O$_2$ set of donor atoms led, in the case of alkali metals, to the synthesis of bifunctional Co-(I)−M [M = alkali cation] complexes which contain both a basic and an acidic site in close, geometrical proximity.[2] Such complexes were found to be particularly valuable as reversible

carbon dioxide carriers.[3] They have been characterized in the solid state as cobalt(I)−alkali cation aggregates.[2]

This report will address two major questions which have been left unanswered: (i) Can we produce a monomeric Co(I)−alkali cation bifunctional complex and thus directly correlate the solid and solution state structures? (ii) Is the reduction of cobalt-(II)−Schiff base complexes occurring at the metal or at the ligand,[4] even though the metal reacts as if it was in a reduced form?

In order to reasonably answer these questions, we used the following compounds as starting materials:[5]

* To whom correspondence should be addressed.
† University of Lausanne.
‡ University of Parma.
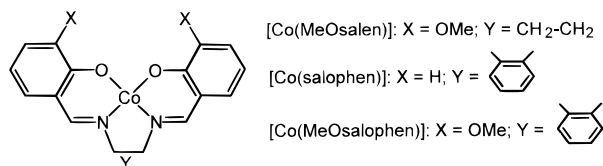⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1996.

(1) (a) Sweany, R. L. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 8, Chapter 1, p 42 and references therein. (b) Calligaris, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987. (c) Pratt, J. M.; Craig, P. J. *Adv. Organomet. Chem.* **1973**, *11*, 404. (d) Calligaris, M.; Nardin, G.; Randaccio, L. *Coord. Chem. Rev.* **1972**, *7*, 385. (e) Bigotto, A.; Costa, G.; Mestroni, G.; Pellizzer, G.; Puxeddu, A.; Reisenhofer, E.; Stefani, L.; Tauzher, G. *Inorg. Chim. Acta* **1970**, *4*, 41. (f) Pattenden, G. *Chem. Soc. Rev.* **1988**, *17*, 361 and references therein. (g) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1. (h) Pratt, J. M.; Craig, P. J. *Adv. Organomet. Chem.* **1973**, *11*, 414. (i) Randaccio, L.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.* **1989**, *18*, 225. (j) Charlaud, J.-P.; Zangrando, E.; Bresciani-Pahor, N.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1993**, *32*, 4256.

(2) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1979**, *18*, 3469.

(3) (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082. (c) Gambarotta, S.; Arena, F.; Floriani, C.; Gaetani-Manfredotti, A. *J. Chem. Soc., Chem. Commun.* **1982**, 835.

(4) (a) Gambarotta, S.; Urso, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 3966. (b) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Zehnder, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1116. (c) Gallo, E.; Solari, E.; De Angelis, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 9850.

(5) (a) Chen, D.; Martell, A. E. *Inorg. Chem.* **1987**, *26*, 1026. (b) Chen, D.; Martell, A. E.; Sun, Y. *Inorg. Chem.* **1989**, *28*, 2647. (c) Marzilli, L. G.; Marzilli, P. A.; Halpern, J. *J. Am. Chem. Soc.* **1971**, *93*, 1374. (d) Avdeef, A.; Schaefer, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 5153. (e) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1969**, 946. (f) Floriani, C.; Fiallo, M.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1987**, 1367. (g) Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Dodic, G.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2478.

[Co(MeOsalen)]: X = OMe; Y = CH$_2$-CH$_2$

[Co(salophen)]: X = H; Y =

[Co(MeOsalophen)]: X = OMe; Y =

We were able to characterize monomeric and dimeric bifunctional cobalt(I)−alkali complexes and to show that, depending on the nature of the ligand, the reduction might occur not at the metal but at the ligand, with the consequent reductive coupling of imino groups to form C−C bonds across two units.[4] These bonds function as electron reservoirs and allow the cobalt-(II) to behave as cobalt(I) in the reactions with CO$_2$ and alkylating agents.

Results and Discussion

The reduction of **1** with Na metal in THF was carried out by following the conventional procedure. This allowed the crystallization, in a 1:1 molar ratio, of a monomeric (A) and a dimeric (B) form of the Co(I)−Na bifunctional complex (eq 1).

[Co(MeOsalen)Na(THF)$_2$], **2A**   [{Co(MeOsalen)Na(THF)}$_2$], **2B**
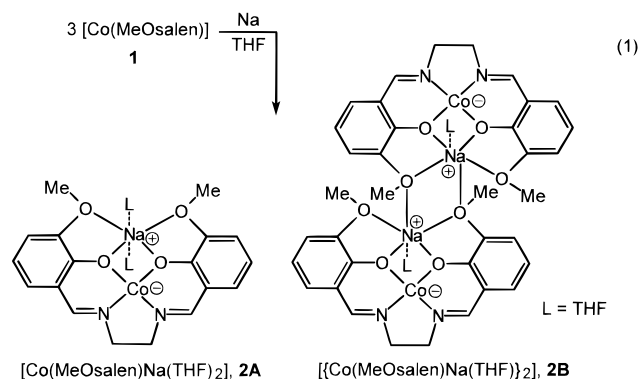
The kinetic lability of Na$^+$ in the solvation and desolvation processes allowed the isolation of both forms of complex **2** in the solid state. The diamagnetism of the complex, based on a d^8 Co(I) configuration, allowed us to record an ^{1}H NMR spectrum, which has never been reported for such complexes. The presence of two different forms in the solid state does not affect the NMR spectrum, since they equilibrate under the solvation conditions. The major structural characteristic of **2** is its topology of a bifunctional unit with a rigid, almost square planar environment for both ions, with a free or weakly-bonded axial position which is available for further reactivity. Further, it has been shown that, in 3-methoxy-substituted salen or salophen, an O$_4$ cage is available for binding a hard cation.[6] Therefore, we have a kind of bifunctional surface.

The structure of complex **2** is shown in Figure 1. In the asymmetric unit of complex **2**, there are two independent
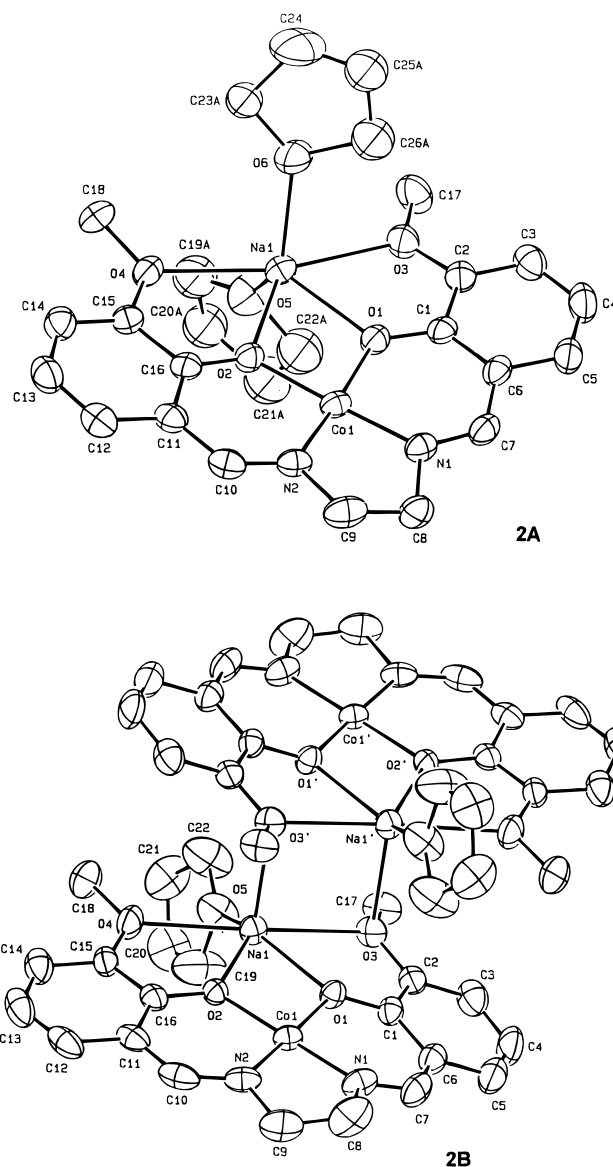
(6) For metal−Schiff base complexes acting as ligands for alkali cations, see: Fenton, D. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 3, Chapter 23, p 16 and references therein. Floriani, C.; Calderazzo, F.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1973**, 384. Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 139. Milburn, H.; Truter, M. R.; Vickery, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 841. Armstrong, L. G.; Lip, H. C.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1771. Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *17*, 3002. Boyce, M.; Clarke, B.; Cunningham, D.; Gallagher, J. F.; Higgins, T.; McArdle, P.; Ni-Cholchuin, M.; O-Gara, M. *J. Organomet. Chem.* **1995**, *498*, 241. Cunningham, D.; Gallagher, J. F.; Higgins, T.; McArdle, P.; McGinley, J. *J. Chem. Soc., Dalton Trans.* **1993**, 2183. Cunningham, D.; McGinley, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1387.

Figure 1. ORTEP views of complexes **2A** (top) and **2B** (bottom) (30% probability ellipsoids). Primes denote a transformation of −x, −y, −z.

molecules, **2A** and **2B**. In both molecules, the anion provides a planar cavity of four oxygen atoms which accommodates a sodium cation. In molecule **2A**, the coordination geometry around sodium is completed by the oxygen atoms from two THF molecules, while in molecule **2B** it is completed by an oxygen atom from a THF molecule and the O3′ methoxy oxygen atom of a second, centrosymmetric molecule which gives rise to a dimer. Bond distances and angles (Table 1) in the two independent [Co(MeOsalen)] anions are very close (values in square brackets refer to molecule **2B**). The statistically significant difference observed in the Co−O distance in molecule **2B** *vs* **2A** could be a consequence of the bridging role of the O3 oxygen atom. In Table 2, the most relevant conformational parameters are compared for the three complexes **2**, **4**, and **6**. The cobalt atoms lie nearly in the plane defined by the N$_2$O$_2$ core of donor atoms, the out-of-plane distances being 0.015(1) [0.026(1)] Å. The salen ligand assumes a flattened "umbrella"[1b,d,7] conformation with the dihedral angles between the two mean planes through O1−C1···C7−N1 and O2−C16···C10−N2 moieties being 168.7(1) [160.2(1)]°. These are nearly coplanar, with the maximum distortion being observed

(7) Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1972**−3, *9*, 311.

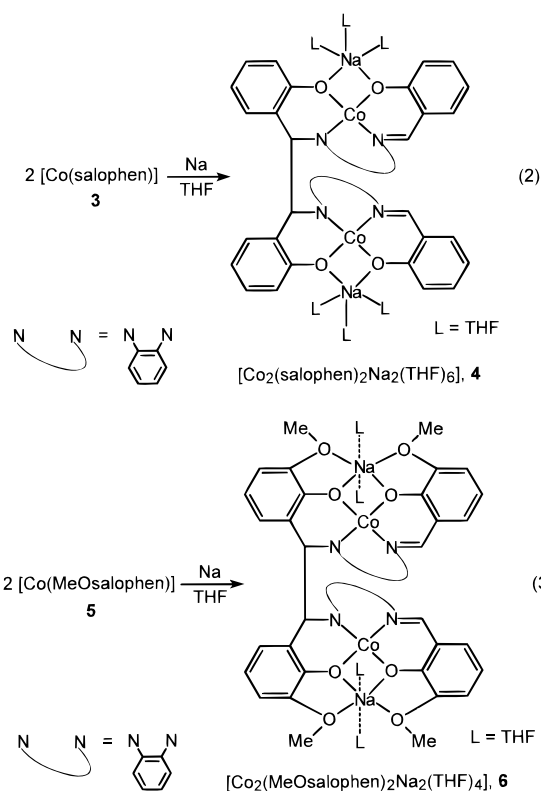**Table 1.** Selected Bond Distances (Å) and Angles (deg) for Complex **2**[a]

	molecule A	molecule B
Co1–O1	1.879(3)	1.894(3)
Co1–O2	1.871(3)	1.863(3)
Co1–N1	1.814(5)	1.802(4)
Co1–N2	1.807(4)	1.808(5)
Na1–O1	2.269(3)	2.304(4)
Na1–O2	2.268(4)	2.273(3)
Na1–O3	2.561(5)	2.660(5)
Na1–O3′		2.546(5)
Na1–O4	2.515(4)	2.544(5)
Na1–O5	2.310(5)	2.339(6)
Na1–O6		2.299(6)
O1–C1	1.313(8)	1.308(8)
O2–C16	1.305(7)	1.322(8)
O3–C2	1.374(7)	1.368(6)
O4–C15	1.372(6)	1.373(7)
N1–C7	1.315(9)	1.307(9)
N1–C8	1.461(7)	1.489(8)
N2–C9	1.492(7)	1.466(9)
N2–C10	1.307(8)	1.311(11)
C1–C2	1.409(7)	1.403(8)
C1–C6	1.402(8)	1.419(7)
C6–C7	1.438(8)	1.400(9)
C8–C9	1.507(10)	1.444(13)
C10–C11	1.412(8)	1.421(10)
C11–C16	1.416(7)	1.404(8)
C15–C16	1.419(8)	1.410(7)
N1–Co1–N2	88.2(2)	87.5(2)
O2–Co1–N2	94.4(2)	94.9(2)
O2–Co1–N1	177.4(2)	176.8(2)
O1–Co1–N2	176.7(2)	178.0(2)
O1–Co1–N1	94.6(2)	94.2(2)
O1–Co1–O2	82.8(1)	83.4(1)
O3–Na1–O4	164.7(1)	164.5(1)
O2–Na1–O4	65.1(1)	64.5(1)
O1–Na1–O3	63.9(1)	62.6(1)
TO1–Na1–O2	66.3(1)	66.2(1)
O3–Na1–O5	82.5(2)	83.2(2)
O4–Na1–O5	90.0(2)	81.3(2)
O5–Na1–O6	124.5(2)	
O5–Na1–O3′		112.0(2)
Na1–O3–Na1′		85.1(1)
Co1–N1–C8	114.7(4)	113.5(4)
Co1–N1–C7	128.4(4)	128.0(4)
C7–N1–C8	116.9(5)	118.5(5)
Co1–N2–C10	128.1(4)	127.8(5)
Co1–N2–C9	115.1(4)	115.0(4)
C9–N2–C10	116.7(5)	117.0(5)
O1–C1–C6	124.1(5)	123.7(5)
O1–C1–C2	118.0(5)	118.0(5)
O3–C2–C1	113.2(5)	114.9(5)
C1–C6–C7	122.3(5)	122.0(5)
N1–C7–C6	123.4(5)	124.7(5)
N1–C8–C9	109.8(5)	109.6(6)
N2–C9–C8	108.3(5)	110.0(6)
N2–C10–C11	125.0(5)	125.0(6)
C10–C11–C16	121.3(5)	121.0(6)
O4–C15–C16	113.9(5)	113.8(5)
O2–C16–C15	117.5(5)	117.7(5)
O2–C16–C11	123.8(5)	124.6(5)

[a] Prime = −x, −y, −z.

for C7 [0.065(8) Å]. The five-membered chelate ring has the usual gauche conformation in molecule **2A**, with C8 and C9 on opposite sides of the N1–Co–N2 plane, while they are on the same side in molecule **2B**. In molecule **2A**, the coordination around sodium is mainly imposed by the conformation of the Schiff base behaving as a tetradentate ligand. The four oxygen atoms [O1, O2, O3, O4] define a coordination plane containing the sodium cation (maximum displacement from mean plane through the five atoms: 0.036(5) Å for O3). The O5 and O6 oxygen atoms from the THF molecules are

symmetrically arranged on opposite sides with respect to that plane. There are significant differences among the Na–O distances, according to their chemical nature (Table 1). In molecule **2B**, the sodium cation is significantly displaced from the oxygen plane by 0.163(3) Å toward the O3′ oxygen atom. The O5 and O3′ atoms are asymmetrically out of that plane by 0.0964(6) and −2.690(5) Å, respectively. So, the coordination polyhedron could be best described as a distorted pentagonal pyramid having the O1, O2, O3, O4, and O5 atoms at the base and the O3′ atom at the apex, the dihedral angle formed between the Na–O3′ line and the normal to the mean coordination plane (including O5) being 178.0(1)°. The bridging role of the O3 atom gives rise to a square Na$_2$O$_2$ inner core which is planar for symmetry requirements. The O3 atom behaves as an asymmetrical bridge; the two Na–O3 and Na–O3′ bond distances are significantly different (Table 1).

Changing the Schiff base around cobalt led to completely different results in the reduction of [Co(salophen)], **3**[8] (eq 2), and [Co(MeOsalophen)], **5** (eq 3).

$$2\ [Co(salophen)] \xrightarrow[\text{THF}]{\text{Na}} \qquad (2)$$

N⌒N = N⌒N

[Co$_2$(salophen)$_2$Na$_2$(THF)$_6$], **4**

$$2\ [Co(MeOsalophen)] \xrightarrow[\text{THF}]{\text{Na}} \qquad (3)$$

N⌒N = N⌒N

L = THF

[Co$_2$(MeOsalophen)$_2$Na$_2$(THF)$_4$], **6**

Both reactions 2 and 3 give rise to reductive coupling of the two imino groups, which in turn leads to C–C bond bridging of the two Schiff base units. The major difference between **4** and **6** concerns the coordination sphere of the sodium cation. In the latter case, MeOsalophen behaves as a compartmental ligand having an N$_2$O$_2$ donor set for the cobalt and an O$_4$ for the Na$^+$ cation, both in a nearly square planar geometry. This is an interesting example of a bifunctional complex.[2–5] We should emphasize, however, that in **4** and **6** reduction does not affect the oxidation state of the metal (remaining cobalt(II)) but, rather, the ligand. The metal is paramagnetic [μ_{eff} = 2.21 and 2.23 μ_B at 293 K for **4** and **6**, respectively]. These values are very close to those of the starting complexes **3** and **5** [2.30 and 2.35 μ_B at 293 K, respectively]. The formation of a C–C bond converts the dianionic salophen into a trianionic ligand, where one of the nitrogen atoms becomes an amido donor atom.

(8) Isse, A. A.; Gennaro, A.; Vianello, E.; Floriani, C. *J. Mol. Catal.* **1991**, *70*, 197 and references therein.

Table 2. Comparison of Structural Parameters within the Co(salen) and Co(salophen) Units for Complexes **2**, **4**, and **6**

	2^a		4	6
dist of atoms from the N$_2$O$_2$ core, Å				
O1	0.009(3)	[0.005(3)]	0.018(4)	0.020(5)
O2	−0.009(3)	[−0.005(3)]	−0.018(4)	−0.021(5)
N1	−0.019(5)	[−0.010(5)]	−0.040(5)	−0.023(6)
N2	0.019(5)	[0.011(5)]	0.039(5)	0.022(6)
Co1	−0.015(1)	[0.026(1)]	0.010(1)	−0.008(2)
folding^b along the N1···O1 line, deg	5.5(2)	[11.6(2)]	21.8(2)	14.6(3)
folding along the N2···O2 line, deg	3.3(2)	[3.2(2)]	2.7(2)	3.0(3)
angle between Co1−N1−O1 and Co1−N2−O2 planes, deg	1.8(2)	[2.5(2)]	2.6(2)	1.9(2)
angle between the mean OC$_3$N planes, deg	10.3(2)	[17.1(2)]	19.3(2)	18.7(3)
torsion angle N1−C8−C9−N2, deg	20.6(7)	[−21.0(9)]		
torsion angle N1−C8−C13−N2, deg			0.0(7)	0.6(10)
dist of atoms from the Co1−N1−N2 plane, Å				
C8	0.239(6)	[0.298(11)]	0.057(6)	0.035(7)
C9	−0.057(6)	[0.006(8)]		
C13			0.058(5)	0.043(8)

^{a} Molecule B values in square brackets. ^{b} The folding is defined as the dihedral angle between the Co,N,O and OC$_3$N planes of a six-membered chelation ring.
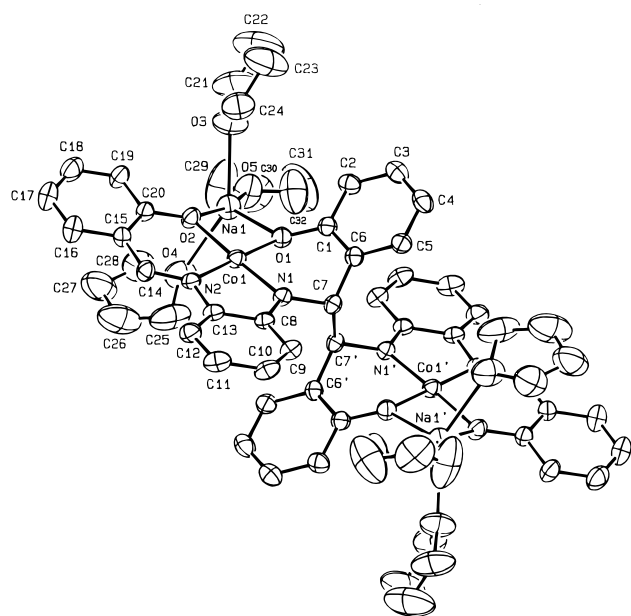
Figure 2. ORTEP view (30% probability ellipsoids) of the dimer in complex **4**. Primes denote a transformation of $1 - x, -y, -z$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 4^a

Co1−O1	1.894(5)	N1−C7	1.464(7)
Co1−O2	1.852(4)	N1−C8	1.382(8)
Co1−N1	1.824(5)	N2−C13	1.418(7)
Co1−N2	1.852(5)	N2−C14	1.306(8)
Na1−O1	2.269(5)	C1−C6	1.404(9)
Na1−O2	2.302(5)	C6−C7	1.519(8)
Na1−O3	2.357(7)	C7−C7′	1.544(7)
Na1−O4	2.417(8)	C8−C13	1.415(8)
Na1−O5	2.352(8)	C14−C15	1.441(10)
O1−C1	1.336(8)	C15−C20	1.394(10)
O2−C20	1.328(8)		
N1−Co1−N2	87.0(2)	Co1−N1−C8	114.0(4)
O2−Co1−N2	94.2(2)	Co1−N1−C7	125.5(4)
O2−Co1−N1	177.4(2)	C7−N1−C8	120.5(5)
O1−Co1−N2	178.8(2)	Co1−N2−C14	127.9(4)
O1−Co1−N1	93.1(2)	Co1−N2−C13	112.0(3)
O1−Co1−O2	85.8(2)	C13−N2−C14	120.0(5)
O1−Na1−O2	67.8(2)	O1−C1−C6	121.6(5)
O4−Na1−O5	87.6(3)	C1−C6−C7	119.7(5)
O3−Na1−O5	88.2(3)	N1−C7−C6	109.6(5)
O2−Na1−O4	86.5(2)	C6−C7−C7′	111.0(4)
O2−Na1−O3	89.7(2)	N1−C7−C7′	111.1(4)
Na1−O1−C1	133.9(4)	N1−C8−C13	113.9(5)
Co1−O1−C1	119.1(4)	N2−C13−C8	113.0(5)
Co1−O1−Na1	100.4(2)	N2−C14−C15	123.4(5)
Na1−O2−C20	127.5(4)	C14−C15−C20	122.9(6)
Co1−O2−C20	128.0(4)	O2−C20−C15	123.4(6)
Co1−O2−Na1	100.6(2)		

^{a} Prime = $1 - x, -y, -z$.

The structure of **4** consists of [Co(salophen)] units linked in centrosymmetric dimers through a C(sp^3)−C(sp^3) (C7−C7′) bond between the imine carbon atoms of the original salophen molecules (Figure 2) and dioxane molecules of crystallization in a dimer/dioxane molar ratio of 1/1. The compound is isostructural with the analogous nickel derivative.^{4a} One sodium cation for each [Co(salophen)] unit interacts with the oxygen atoms of the Schiff base and three THF molecules, resulting in a distorted square pyramidal coordination about the sodium atom with the O1 oxygen at the apex. The dihedral angle between the Na1−O1 line and the normal to the mean plane through O2, O3, O4, and O5, from which Na1 is displaced by 0.443(3) Å, is 31.3(1)°. Coordination around cobalt is almost planar, with the metal lying in the mean plane through the N$_2$O$_2$ core, and shows small but significant tetrahedral distortions (Table 2). The formation of dimers markedly influences the conformation of the ligand. In fact, the six-membered chelation ring not involved in the interligand C−C bond remains almost planar, as indicated by the folding angles quoted in Table 2. The chelate ring containing the tetrahedral C7 carbon assumes a conformation which could be better described as a boat rather

than by the folding angle given in Table 2. O1 and C7 are displaced by 0.567(4) and 0.483(5) Å, respectively, from the mean plane through Co1, N1, C1, C6, with the dihedral angle between the two mean planes through O1, Co1, N1, C7 and O1, C1, C6, C7 being 43.2(2)°. The asymmetry of the ligand causes an asymmetry in its coordination, the Co−O and Co−N bond distances being little, but significantly, different from each other (Table 3). The value of 1.464(7) Å for N1−C7 is for an N−C(sp^3) single bond.

The structure of complex **6** consists of [Co(MeOsalophen)] units linked in centrosymmetric dimers through a C(sp^3)−C(sp^3) bond provided by a reduced imino carbon (C7) of the Schiff base (Figure 3). The structural parameters are listed in Table 4. One sodium cation for each [Co(MeOsalophen)] unit coordinates to the four oxygen atoms of the ligand and two THF molecules. So this complex contains characteristics of both compounds **2** and **4**. Cobalt exhibits the usual square
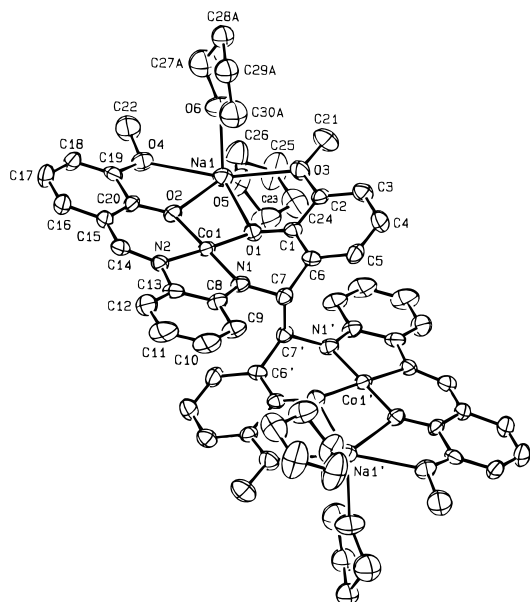
Figure 3. ORTEP view (30% probability ellipsoids) of the dimer in complex **6**. Primes denote a transformation of −x, −y, −z.

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for Complex **6**^{a}

Co1−O1	1.896(4)	O4−C19	1.371(9)
Co1−O2	1.869(6)	N1−C7	1.459(8)
Co1−N1	1.849(7)	N1−C8	1.375(9)
Co1−N2	1.866(5)	N2−C13	1.422(11)
Na1−O1	2.319(6)	N2−C14	1.320(10)
Na1−O2	2.289(6)	C1−C6	1.406(11)
Na1−O3	2.420(6)	C6−C7	1.521(11)
Na1−O4	2.559(7)	C7−C7′	1.572(9)
Na1−O5	2.339(5)	C8−C13	1.378(11)
Na1−O6	2.381(7)	C14−C15	1.404(13)
O1−C1	1.322(9)	C15−C20	1.417(10)
O2−C20	1.313(9)	C19−C20	1.432(13)
O3−C2	1.373(9)		
N1−Co1−N2	86.2(3)	Co1−N1−C8	112.9(5)
O2−Co1−N2	95.1(3)	Co1−N1−C7	123.2(5)
O2−Co1−N1	178.4(3)	C7−N1−C8	123.4(6)
O1−Co1−N2	178.2(3)	Co1−N2−C14	125.0(5)
O1−Co1−N1	94.4(3)	Co1−N2−C13	111.9(4)
O1−Co1−O2	84.3(2)	C13−N2−C14	122.8(6)
O5−Na1−O6	117.0(3)	O1−C1−C6	125.2(6)
O3−Na1−O4	163.5(2)	O1−C1−C2	118.2(6)
O4−Na1−O5	91.0(2)	O3−C2−C1	113.2(6)
O3−Na1−O5	86.6(2)	C5−C6−C7	121.7(7)
O2−Na1−O4	63.6(2)	N1−C7−C6	112.3(6)
O1−Na1−O3	66.3(2)	C6−C7−C7′	112.3(6)
O1−Na1−O2	66.5(2)	N1−C7−C7′	110.3(6)
Co1−O1−Na1	102.7(2)	N1−C8−C13	115.9(7)
Na1−O1−C1	121.7(4)	N2−C13−C8	113.0(7)
Co1−O1−C1	121.1(4)	N2−C14−C15	126.5(7)
Co1−O2−Na1	104.8(3)	C14−C15−C20	121.8(8)
Na1−O2−C20	126.2(5)	O4−C19−C20	112.6(7)
Co1−O2−C20	126.9(5)	O2−C20−C15	124.4(8)
Na1−O3−C2	118.9(4)	O2−C20−C19	117.3(7)
Na1−O4−C19	116.3(5)		

^{a} Prime = −x, −y, −z.

planar coordination, lying in the mean plane through the N$_2$O$_2$ core, and shows small but significant tetrahedral distortions (Table 2). The presence of the methoxy substituents in the salophen ligand does not severely modify the conformation of the dimer if compared with that of complex **4**, since it is mainly determined by the formation of the interligand C−C bond. One of the six-membered chelate rings (O2···N2) is nearly planar (maximum displacement 0.031(6) Å for N2) (Table 2), while the other containing the tetrahedral C7 carbon is bent by 36.6-

(3)° along the O1···C7 line. As observed in **4**, this chelate ring assumes a boat conformation, the displacements from the mean plane through Co1, N1, C1, C6 being 0.410(5) and 0.509(7) Å for O1 and C7, respectively. The Na$^+$ cation is accomodated in the cavity provided by the four oxygen atoms of the Schiff b−1ase,[6] completing the coordination through the oxygen atoms from two THF molecules in a way similar to that observed in compound **2A**. However, a significant difference concerns the system of the four oxygen atoms which is no longer planar and shows tetrahedral distortions ranging from −0.244(5) Å for O2 to 0.223(5) Å for O1. Sodium is displaced by 0.163(3) Å from the mean plane. The two O5 and O6 atoms are almost symmetrically arranged with respect to the oxygen plane, being displaced by 2.102(7) and −1.907(7) Å.

The major objective at this point is to find a structural relationship between the solid and the solution state for such dimers. Could we show that these dimers remain intact in solution or would we expect an equilibrium between C−C-bonded dimers and the corresponding free radical or cobalt(I) monomers?
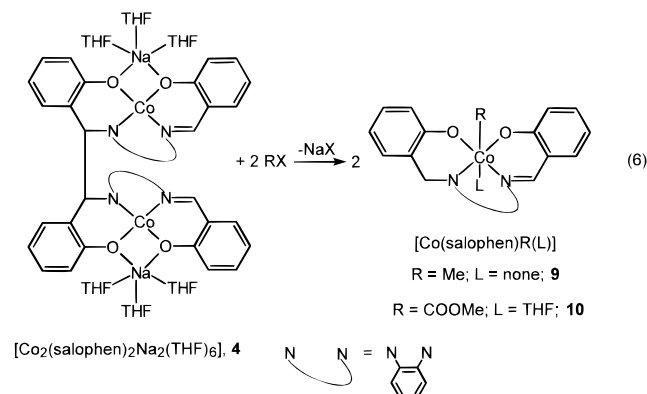

[Co$_2$(salophen)$_2$Na$_2$(THF)$_6$], **4**
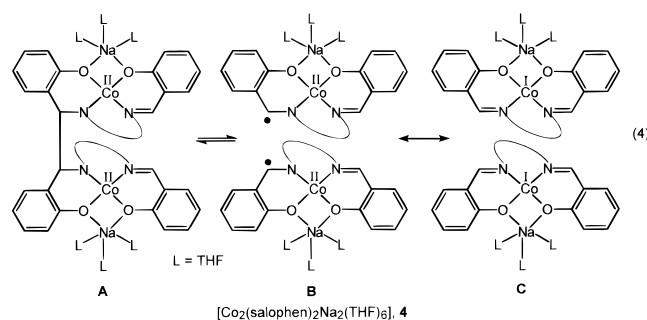
The distinct characteristics of the cobalt(I) *vs* the cobalt(II) derivative, namely **2** *vs* **1**, is the appearance of an intense charge-transfer band at 696 nm, which is peculiar for cobalt(I)−Schiff base complexes. Such a band is completely absent for **4** and **6**, while their spectra are similar to those of the starting compounds **3** and **5**. The ESR spectra of **4** and **6**, though very poorly informative, are neither silent (form **C**) nor indicative of any paramagnetic species (form **B**) in addition to the cobalt-(II) pattern. This is in agreement with what has been observed for the corresponding C−C bonded [Ni(salophen)] dimers.[4a] For such compounds, we did not observe any paramagnetic species in the solid state or in solution, and typical diamagnetic ^{1}H NMR spectra have been observed.

Complexes **2**, **4**, and **6** demonstrate an interesting comparison in their reactions with carbon dioxide and, in general, with electrophiles. The reaction of **2** with alkylating agents such as MeI and ClCOOMe gave rise, as expected, to the corresponding Co−C-containing derivatives (eq 5).

R = Me, L = none, **7**
R = COOMe, L = H$_2$O, **8**
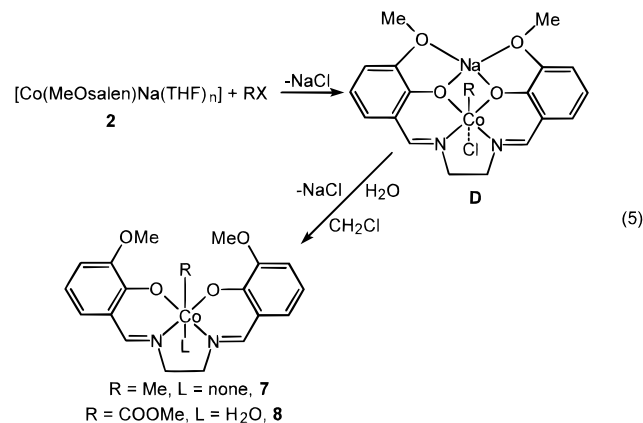
This class of compounds (see Experimental Section) has been extensively mentioned in the literature, although with other, substituted salen-type ligands.[1a,c−j] The elimination of NaCl was, however, particularly difficult because of the tight complexation of Na^+ by the O_4 cage in the intermediate species **D**;[6] thus it remains soluble even in hydrocarbon solvents. It can be removed from the molecule only in water.

Usually reaction 5 has been described as an attack on the RX electrophilic carbon by the Co(I) nucleophile.[1] However, it would be much more difficult to maintain the same mechanism in the case of **4** and **6**, which contain a cobalt(II), although the synthetic result is quite similar (see reaction 6).

$$[Co_2(salophen)_2Na_2(THF)_6], \mathbf{4}$$

$$+ 2 RX \xrightarrow{-NaX} 2$$

$$(6)$$

$$[Co(salophen)R(L)]$$

R = Me; L = none; **9**

R = COOMe; L = THF; **10**

The same results have been obtained in the reaction of **6** with RX leading to the corresponding complexes [Co(MeOsalophen)-(Me)(H₂O)] (**11**) and [Co(MeOsalophen)(COOMe)(H₂O)] (**12**). These compounds (see the Experimental Section) have been characterized using conventional methods, and their structure and properties do not deserve any particular comment. We should emphasize, however, that **3** and **5** do not undergo any alkylation reaction under the same conditions, even in the presence of NaBPh₄.[6]

Reactions leading to **9**−**12** are quite unusual, since the metal behaves as a nucleophile using the electrons stored at the C−C bond, but the C−C bond has never been involved in the reactions with electrophiles. This kind of reactivity requires a long-range electron transfer from the C−C bond to the met. Here, we emphasize some of the peculiarities of the system: (i) the C−C bond functions as a shuttle of two electrons, and such a functionality can be used for storing and releasing electrons;[9] (ii) the C−C bond fragment can be used for masking nucleophilic sites at the metal; (iii) the electron transfer can occur from the C−C bond to the utilization site; (iv) the C−C bond is never involved in the reactivity. This result undoubtedly gives further support to the absence of any equilibrium as shown in eq 4.

Such properties of the [C−C] fragment has been confirmed in the reaction of **4** and **6** with carbon dioxide. The reaction of **2** with CO₂, as expected, does not differ from that of other substituted salen complexes.[3] However, the reaction of **4** and **6** with CO₂ emphasizes the peculiarities mentioned above of the C−C-containing cobalt(II)−Schiff base complexes. Carbon dioxide fixation occurs with both **4** and **6** leading to [Co-(salophen)NaCO₂(THF)]ₙ, **13**, and [Co(MeOsalophen)NaCO₂-

(THF)], **14**, respectively, shown by reaction 7 for the case of **6**.

$$[Co_2(MeOsalophen)_2Na_2(THF)_4], \mathbf{6}$$

L = THF

$$+ 2 CO_2 \rightleftharpoons 2$$

$$(7)$$

$$[Co(MeOsalophen)NaCO_2(THF)], \mathbf{14}$$
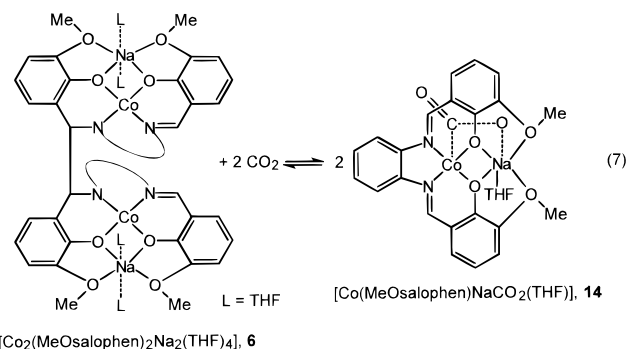
Carbon dioxide fixation by **2** is markedly different from that achieved using **4** or **6**. In the former case, a direct metal to CO₂ electron transfer is conceivable, while, in the latter case, one electron comes from the metal and the other from the C−C bond. Thus, the metal behaves as d^8 cobalt(I) rather than d^7 cobalt(II). What is even more surprising is that the reaction with CO₂ is reversible. This implies that the cleavage and formation of the C−C bond across the two [Co(salophen)] units are reversible. The C−C bond behaves as a two-electron shuttle, and complexes **4** and **6** are in effect a type of molecular battery for chemical transformations.

Conclusions

The formation and cleavage of a carbon−carbon bond can be used for storing and releasing a pair of electrons. These electrons are available far from the C−C unit, the long-range electron transfer being assisted by a transition met. A transition metal in combination with the C−C bonds can be used as a molecular battery in chemical transformations. These principles have been put into practice in the reduction of cobalt(II)−salophen-type complexes and in the use of reduced forms directed toward the formation of cobalt−carbon bonds. In particular, we explored (i) reactions with alkylating agents, where the C−C bond allows a d^7 cobalt(II) free radical-type system to behave as a d^8 carbanion-type one, and (ii) the reversible cleavage and formation of a C−C bond in the reversible reaction with carbon dioxide.

Experimental Section

General Procedure. All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. ¹H NMR, IR, UV−vis, and EPR spectra were recorded on Bruker 200-AC, Perkin-Elmer 883, Hewlett Packard 8452A, and Bruker ESP 300E instruments, respectively. Magnetic measurements were made on a MPMS5 SQUID susceptometer (Quantum Design Inc.).

The syntheses of **1**, **3**, and **5** have not been performed as previously reported,[5] but under rigorously aprotic conditions, as given below.

Preparation of 1. NaH (2.9 g, 120 mmol) was added slowly (*ca.* 3 min) to a yellow suspension of MeOsalenH₂ (15.6 g, 47.4 mmol) in THF (600 mL). Immediate gas evolution was observed. The resultant clear yellow suspension was stirred at room temperature until gas evolution stopped and then refluxed for 2 h. The excess NaH was removed by extraction and CoCl₂(THF)₁.₅ (11.3 g, 47.4 mmol) added to the yellow suspension. A red suspension was obtained, which was refluxed overnight. After removal of NaCl, the solution was taken to dryness and the dark-red solid collected and dried (7.8 g, 40%). The solid cocrystallized with a small amount of NaCl. Anal. Calcd for [Co(MeOsalen)](NaCl)₀.₅, C₁₈H₁₈CoN₂O₄(NaCl)₀.₅: C, 52.16; H, 4.38; N, 6.76. Found: C, 52.40; H, 4.82; N, 6.64. $\mu_{eff} = 3.58 \mu_B$ at 295 K. UV−vis (THF, 2.2 × 10⁻⁴ M): λ =208 nm (ϵ 83 004 cm⁻¹ M⁻¹), 242 (99 836), 280 (37 067), 364 (26 338), 422 (27 531), 488 (6608).

(9) For recent examples of C−C bonds behaving as electron shuttles, see: De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1994**, *116*, 5691, 5702. Floriani, C. In *Transition Metals in Supramolecular Chemistry*; Fabbrizzi. L., Poggi, A., Eds.; Nato ASI Series; Kluwer: Dordrecht, The Netherlands, 1994, *448*, 191.

Preparation of 2. **1** (3.7 g, 8.9 mmol) was suspended in THF (200 mL) and the resulting red suspension reacted with sodium sand (0.5 g, 21 mmol). After 1 h of stirring, a bright green solution was obtained. The excess Na was filtered off, and *n*-heptane (30 mL) added dropwise. A dichroic, red−green crystalline solid precipitated, which was collected and dried (46%). Anal. Calcd for **2**, [Co$_2$(MeOsalen)$_2$Na$_2$(THF)$_3$], C$_{48}$H$_{60}$Co$_2$N$_4$Na$_2$O$_{11}$: C, 55.82; H, 5.86; N, 5.42. Found: C, 55.34; H, 5.27; N, 5.80. ^{1}H NMR (THF-d^8, 298 K): δ 8.91 (s, 2H), 7.20 (m, 2H), 6.90 (m, 2H), 6.20 (m, 2H), 3.77 (s, 6H), 3.77 (m, THF), 2.41 (s, 4H), 1.88 (m, THF). UV−vis (THF, 2.18 × 10^{-4} M): λ = 208 nm (ϵ 36069 cm^{-1} M^{-1}), 234 (39 944), 264 (17 495), 316 (12 608), 376 (5749), 696 (20 435).

Preparation of 3. NaH (1.0 g, 41.7 mmol) was added slowly (*ca.* 3 min), without stirring, to an orange THF (300 ml) solution of salophenH$_2$ (6.0 g, 19.0 mmol). Gas evolution was immediately observed. A yellow suspension was obtained, which was stirred at room temperature until gas evolution stopped (*ca* 10 min.) and then heated under reflux for 3 h. The NaH excess was filtered off, and CoCl$_2$(THF)$_{1.5}$ (4.5 g, 19.0 mmol) was added. A red suspension was obtained, which was refluxed overnight and extracted to eliminate NaCl. The red crystalline product was collected and dried (5.3 g, 75 %). Anal. Calcd for [Co(salophen)], C$_{20}$H$_{14}$CoN$_2$O$_2$: C, 64.35; H, 3.78; N, 7.50. Found: C, 64.53; H, 3.99; N, 7.45. IR (Nujol ν_{max}/cm^{-1}): 1640 (s), 1605 (s), 1560 (s), 1400 (s), 1300 (w), 1275 (w), 1240 (s), 1185 (m), 1160 (w), 990 (w), 795 (s). μ_{eff} = 3.00 μ_B at 295 K. UV−vis (THF, 8.51 × 10^{-4} M): λ = 208 nm (ϵ 11 924 cm^{-1} M^{-1}), 248 (11 890), 290 (7977), 334 (4793), 386 (6549), 422 (5158), 526 (1485), 604 (707), 688 (225).

Preparation of 4. Sodium sand (1.0 g, 43.5 mmol) was added to a stirred suspension of **3** (10 g, 27 mmol) in THF (350 mL). After 4 h, a deep-green solution was observed, from which the excess Na was filtered. The solution was evaporated to dryness, and the residue was triturated with *n*-heptane, to give a green crystalline solid, which was then collected and dried (65%). Anal. Calcd for **4**·2THF, [Co$_2$-(salophen)$_2$Na$_2$(THF)$_6$]·2C$_4$H$_8$O, C$_{72}$H$_{92}$Co$_2$N$_4$Na$_2$O$_{12}$: C, 63.15; H, 6.77, N, 4.09. Found: C, 62.75; H, 7.02; N, 4.35. IR (Nujol, ν_{max}/cm^{-1}): 1586 (s), 1520 (s), 1287 (s), 1148 (s), 924 (m), 903 (m), 743 (s), 645 (w). μ_{eff} =1.68 μ_B at 295 K. Recrystallization of the product from THF/heptane/dioxane gave crystals suitable for X-ray analysis. UV−vis (THF, 2.04 × 10^{-4} M): λ = 208 nm (ϵ 49 831 cm^{-1} M^{-1}), 236 (30 568), 292 (22 392), 322 (28 871), 416 (14 449), 440 (12 631), 560 (3098), 678 (3186).

Preparation of 5. A red suspension of MeOsalophenH$_2$ (49.0 g, 0.13 mol) in THF (450 ml) was reacted with [Co(MeCOO)$_2$] (23.0 g, 0.13 mol) and the red mixture stirred at room temperature overnight. A red solid formed, which was collected by filtration and dried *in vacuo* (47.3 g, 84%). Anal. Calcd for [Co(MeOsalophen)], C$_{22}$H$_{18}$CoN$_2$O$_4$: C, 60.89; H, 4.19; N, 6.46. Found: C, 60.95; H, 4.97; N, 6.32. μ_{eff} = 2.3 μ_B at 295 K. IR (Nujol, ν_{max}/cm^{-1}): 1610 (s), 1600 (m), 1580 (s), 1540 (s), 1500 (m), 1250 (s), 1200 (s), 1180 (m), 1110 (m), 1090 (m), 980 (m), 900 (w), 880 (w), 740 (s), 580 (w), 540 (m).

Preparation of 6. Sodium sand (0.6 g, 26 mmol) was added to a stirred red suspension of **5** (4.8 g, 11 mmol) in THF (300 mL). After 4 h, a deep-green solution was obtained. The excess Na was filtered off, and the filtrate was taken to dryness. Trituration of the solid with *n*-heptane gave a green product, which was collected and dried (83%). Recrystallization from THF/heptane (2:5) gave crystals suitable for X-ray analysis. Anal. Calcd for **6**, [Co$_2$(MeOsalophen)$_2$Na$_2$(THF)$_4$], C$_{60}$H$_{68}$Co$_2$N$_4$Na$_2$O$_{12}$: C, 60.00; H, 5.71; N, 4.66. Found: C, 60.10; H, 5.80; N, 4.57. IR (Nujol, ν_{max}/cm^{-1}): 1585 (s), 1570 (s), 1378 (m), 1341 (s), 1273 (s), 1236 (s), 1174 (s), 1153 (s), 1100 (s), 1079 (s), 1052 (s), 979 (m), 956 (m), 870 (m), 728 (s), 660 (m). μ_{eff} = 1.91 μ_B at 295 K.

Preparation of 7. A freshly distilled solution of MeI (0.2 mL, 3.2 mmol) in THF (20 mL) was added dropwise, at −30°C, to a THF (100 mL) solution of **2** (1.35 g, 2.6 mmol). A rapid reaction took place, resulting in a color change from green to red. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, the red residue was dissolved in CH$_2$-Cl$_2$, and the solution was poured into water. All attempts to crystallize the solid from organic solvents (avoiding the use of water) gave a material containing complexed NaCl. The organic phase was collected

and the water eliminated by azeotropic distillation. After 1 day at −20 °C, a red crystalline solid was obtained and collected (55%). ^{1}H NMR (DMSO-d$_6$, 298 K): δ 7.90 (s, 2H), 6.72 (m, 4H), 6.26 (t, 2H), 5.76 (s, 2H, CH$_2$Cl$_2$), 3.72 (s, 6H), 3.36 (s, 4H), 2.14 (s, 3H, Me). Anal. Calcd for **7**·CH$_2$Cl$_2$, [Co(MeOsalen)(Me)]·CH$_2$Cl$_2$, C$_{20}$H$_{23}$Cl$_2$CoN$_2$O$_4$: C, 49.50; H, 4.78; N, 5.77. Found: C, 49.14; H, 4.50; N, 5.86.

Preparation of 8. A solution of freshly distilled methyl chloroformate (0.1 mL, 1.2 mmol) in THF (40 mL) was added dropwise to a THF (100 mL) solution of **2** (0.65 g, 1.3 mmol) at −30 °C. A rapid reaction took place, resulting in a color change from green to red. The mixture was allowed to warm to room temperature and then stirred for 3 h. After removal of the solvent, the solid was dissolved in CH$_2$Cl$_2$ and the solution was poured into water. All attempts to crystallize the solid from organic solvents (avoiding the use of water) gave a material containing complexed NaCl. The organic phase was collected and the water eliminated by azeotropic distillation. After 1 day at −20 °C, a red crystalline solid was obtained from the organic phase which was collected and dried *in vacuo* (70%). Recrystallization from CH$_3$CN gave crystals suitable for an X-ray analysis. ^{1}H NMR (DMSO-d$_6$, 308 K): δ 7.94 (s, 2H), 6.85 (dd, 2H), 6.70 (dd, 2H), 6.30 (t, 2H), 3.75 (s, 6H), 3.47 (s, 3H, CO$_2$Me), 3.33 (s, 2H, H$_2$O). IR (ν_{max}/cm^{-1}): 3397 (br, s), 1671 (s), 1636 (s), 1606 (s), 1547 (m), 1245 (s), 1226 (s), 1088 (s), 1044 (s), 996 (m), 733 (s). Anal. Calcd for **8**, [Co(MeOsalen)-(COOMe)(H$_2$O)], C$_{20}$H$_{23}$CoN$_2$O$_7$: C, 51.96; H, 5.01; N, 6.06. Found: C, 51.44; H, 5.20; N, 6.08.

Preparation of 9. A freshly distilled solution of MeI (0.3 mL, 4.8 mmol) in THF (30 mL) was added dropwise to a stirred solution of **4**·2THF (1.84 g, 1.34 mmol) in THF (150 mL) at −50 °C. An immediate color change to red was observed. The mixture was allowed to warm to room temperature, resulting in a dark red solution from which solvent was removed; the residual solid was dissolved in CH$_2$-Cl$_2$ and the resultant solution poured into water. The organic phase was collected, and the water was eliminated by azeotropic distillation. After 1 day at −4 °C, a purple crystalline solid (78%) was obtained. ^{1}H NMR (DMSO-d$_6$, 298 K): δ 8.75 (s, 2H), 8.21 (m, 2H), 7.48 (d, 2H), 7.30 (m, 2H), 7.20 (t, 2H), 6.93 (d, 2H), 6.48 (t, 2H), 5.76 (s, 2H, CH$_2$Cl$_2$), 1.96 (s, 3H, Me). Anal. Calcd for **9**·CH$_2$Cl$_2$, [Co(salophen)-(Me)]·CH$_2$Cl$_2$, C$_{22}$H$_{19}$Cl$_2$CoN$_2$O$_2$: C, 55.84; H, 4.05; N, 5.92. Found: C, 55.77; H, 4.28; N, 5.92. IR (Nujol, ν_{max}/cm^{-1}): 1608 (s), 1578 (s), 1527 (s), 1194 (s), 1145 (s), 1027 (w), 952 (w), 928 (m), 800 (w), 762 (s), 723 (s).

Preparation of 10. A freshly distilled solution of ClCOOMe (0.2 mL, 2.6 mmol) in THF (70 mL) was added dropwise to a stirred solution of **4**·2THF (1.70 g, 1.24 mmol) in THF (70 mL) at −30 °C. A rapid color change from green to red was observed. The mixture was allowed to warm to room temperature, NaCl was extracted, and the resultant solution left for 1 day at −4 °C to yield a red crystalline solid, which was collected (69%). ^{1}H NMR (DMSO-d$_6$, 298 K) δ 8.84 (s, 2H), 8.20 (m, 2H), 7.55 (d, 2H), 7.28 (m, 4H), 7.00 (d, 2H), 6.55 (t, 2H), 3.80 (m, 4H, THF), 3.34 (s, 3H, CO$_2$Me), 1.73 (m, 4H, THF). Anal. Calcd for **10**, [Co(salophen)(COOMe)(THF)], C$_{26}$H$_{25}$CoN$_2$O$_5$: C, 61.91; H, 5.00; N, 5.55. Found: C, 62.28; H, 4.76; N, 6.04. IR (ν_{max}/cm^{-1}): 1680 (s), 1608 (s), 1522 (s), 1193 (s), 1147 (s), 1070 (s), 752 (s).

Preparation of 11. A freshly distilled solution of MeI (0.2 mL, 3.2 mmol) in THF (50 mL) was added dropwise to a THF (100 mL) solution of **6** (1.54 g, 2.6 mmol) at −30°C. A rapid color change of green to red was observed. The mixture was allowed to warm to room temperature, and stirred for 2 h, and the solvent was removed. The resulting red residue was dissolved in CH$_2$Cl$_2$, and the solution was poured into water. The organic phase was collected, and the water was eliminated by azeotropic distillation. After 1 day at −20 °C, a red crystalline solid formed, which was collected and dried (53%). ^{1}H NMR (DMSO-d$_6$, 298 K): δ 8.69 (s, 2H), 8.14 (m, 2H), 7.27 (m, 2H), 7.06 (d, 2H), 6.74 (d, 2H), 6.40 (t, 2H), 5.76 (s, 1H, CH$_2$Cl$_2$), 3.80 (s, 6H), 3.27 (s, 2H, H$_2$O), 2.03 (s, 3H, Me). Anal. Calcd for **11**·0.5CH$_2$-Cl$_2$, [Co(MeOsalophen)(Me)(H$_2$O)]·CH$_2$Cl$_2$, C$_{23.5}$H$_{24}$ClCoN$_2$O$_5$: C, 55.47; H, 4.75; N, 5.51. Found: C, 55.19; H, 4.98; N, 5.50. IR (ν_{max}/cm^{-1}): 3405 (br), 1611 (s), 1583 (s), 1540 (s), 1245 (s), 1194 (s), 1100 (w), 1080 (w), 980 (w), 800 (w), 729 (s).

Preparation of 12. A freshly distilled solution of ClCOOMe (0.3 mL, 3.9 mmol) in THF (50 mL) was added dropwise to a THF (100 mL) solution of **6** (1.14 g, 1.0 mmol) at −30 °C. A rapid color change

Table 5. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **2**, **4**, and **6**

	2	**4**	**6**
empirical formula	$C_{26}H_{34}CoN_2NaO_6 \cdot 0.5C_{44}H_{52}Co_2N_4Na_2O_{10}$	$C_{64}H_{76}Co_2N_4Na_2O_{10} \cdot C_4H_8O_2$	$C_{60}H_{68}Co_2N_4Na_2O_{12}$
a, Å	14.651(1)	11.270(2)	11.857(4)
b, Å	15.355(1)	17.594(3)	12.639(4)
c, Å	11.671(1)	16.606(3)	10.553(5)
α, deg	105.70(1)	90	106.28(3)
β, deg	102.66(1)	90.45(2)	101.17(3)
γ, deg	97.65(1)	90	103.04(3)
V, Å^3	2413.9(4)	3292.6(10)	1422.0(10)
Z	2	2	1
fw	1032.9	1313.3	1201.1
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
t, °C	22	22	22
λ, Å	0.710 69	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.421	1.325	1.403
μ, cm^{-1}	7.63	5.75	6.59
transm coeff	0.914−1.000	0.955−1.000	0.940−1.000
no. of unique total data	8590	4597	5145
no. of unique obsd data	4752	2636	1524
R^a	0.044	0.053	0.057
wR2^b	0.130	0.129	0.162
GOF^c	1.058	1.031	0.815

^{a} $R = \sum|\Delta F|/\sum|F_o|$ (calculated for the unique observed data [$I>2\sigma(I)$] for all complexes). ^{b} wR2 $= [\sum(w\Delta F^2)^2/\sum(wF_o^2)^2]^{1/2}$ (calculated for the unique observed data for complexes **2** and **4** and for the unique total data for complex **6**). ^{c} GOF $= [\sum(w\Delta F^2)^2/(NO - NV)]^{1/2}$.

of green to red was observed. The mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed, the resulting solid was dissolved in CH_2Cl_2, and the solution was poured into water. The organic phase was collected and the water eliminated by azeotropic distillation. The organic phase was left at −20°C for 1 day, which gave rise to a red crystalline solid (84%). ^{1}H NMR (DMSO-d_6, 308 K): δ 8.99 (s, 2H), 8.33 (m, 2H), 7.38 (m, 2H), 7.24 (d, 2H), 6.92 (d, 2H), 6.60 (t, 2H), 5.73 (s,1H, CH_2Cl_2), 3.88 (s, 6H), 3.34 (s, 3H, CO_2Me), 3.29 (s, 3H, H_2O). Anal. Calcd for **12**·0.5CH$_2$-Cl$_2$·0.5(H$_2$O), [Co(MeOsalophen)(COOMe)(H$_2$O)]·0.5CH$_2$Cl$_2$·0.5(H$_2$O), $C_{24.5}H_{25}ClCoN_2O_{7.5}$: C, 52.37; H, 4.48; N, 4.99. Found: C, 52.07; H, 4.19; N, 5.21. IR (Nujol, ν_{max}/cm^{-1}): 3405 (br, s); 1661 (s), 1609 (s), 1582 (s), 1541 (s), 1341 (m), 1243 (s), 1197 (s), 1048 (s), 987 (m), 881 (m), 728 (s).

Preparation of 13. A reaction vessel containing a green solution of **4**·2THF (1.50 g, 1.10 mmol) in THF (50 mL) was evacuated, and CO_2 was then bubbled into the solution. A violet solid formed after 30 min. The mixture was then left to stand for 1 day and gave 1.0 g (93%) of microcrystalline solid. Anal. Calcd for **13**, [Co(salophen)-NaCO$_2$(THF)], $C_{25}H_{22}CoN_2NaO_5$: C, 58.60; H, 4.33; N, 5.47. Found: C, 58.35; H, 3.98; N, 5.79. IR (Nujol, ν_{max}/cm^{-1}): 1689 (s), 1612 (s), 1584 (m), 1533 (s), 1515 (m), 1326 (s), 1206 (s), 1151 (m), 925 (w), 746 (s). $\mu_{eff} = 1.09$ μ_B at 295 K.

Preparation of 14. A reaction vessel containing a green solution of **6** (1.9 g, 1.58 mmol) in THF (100 mL) was evacuated, and CO_2 was bubbled into the solution. After 30 min of stirring, a brown solid formed. The mixture was stirred at room temperature for 1 day, and then the brown solid was collected and dried (0.70 g). IR (Nujol, ν_{max}/cm^{-1}): 1883 (br, w), 1608 (s), 1582 (s), 1233 (s), 1193 (s), 1107 (m), 1075 (m), 979 (m), 860 (m), 735 (s). Anal. Calcd for **14**, [Co-(MeOsalophen)NaCO$_2$(THF)], $C_{27}H_{26}CoN_2NaO_7$: C, 56.65; H, 4.58; N, 4.89. Found: C, 56.98; H, 4.46; N, 4.80. Complex **14** is diamagnetic.

X-ray Crystallography for Complexes 2, 4, and 6. Suitable single crystals of complexes **2**, **4**, and **6** were mounted in glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[10] Crystal data and details associated with data collection are given in Tables 5 and S1 (Supporting Information). Data were collected at room temperature (295 K) on a single-crystal diffractometer. For intensities and background, individual reflection profiles were analyzed.[11] The structure amplitudes were obtained after the usual

Lorentz and polarization corrections[12] and the absolute scale was established by the Wilson method.[13] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. Data were corrected for absorption using the program ABSORB[14] for complex **4** and a semiempirical method[15] for complexes **2** and **6**. The function minimized during the least-squares refinement was $\sum w|\Delta F^2|^2$. Weights were applied according to the scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ with $P = (F_o^2 + 2F_c^2)/3$ and $a = 0.0766$, 0.0825, and 0.0571 for **2**, **4**, and **6**, respectively. Anomalous scattering corrections were included in all structure factor calculations.[16b] Scattering factors for neutral atoms were taken from ref 16a for non-hydrogen atoms and from ref 17 for H. Among the low-angle reflections, no correction for secondary extinction was deemed necessary.

All the structures were solved with SHELX86.[18] The refinement of the structures was carried out with SHELX92[19] and was based on the observed data for **2** and **4** and on the total data for **6**.

Refinements were done first isotropically and then anisotropically for non-H atoms, except those affected by disorder. The two THF molecules of molecule A in complex **2** were found to be affected by disorder and were solved by considering the C19−C22 and C23, C25, C26 carbon atoms distributed over two positions (A and C) isotropically refined with the site occupation factors given in Table S2 (Supporting Information). In complex **4**, the X-ray analysis revealed a dioxane solvent molecule of crystallization having the gravity center on a center of symmetry with the oxygen atoms statistically distributed over two positions (A and C) and refined with site occupation factors of 0.6 and 0.4, respectively. All the atoms of the dioxane molecule were isotropically refined. In complex **6**, one THF molecule (O6, C27−C30) was found to be affected by disorder and was solved by considering the carbon atoms distributed over two positions (A and B) isotropically refined with site occupation factors of 0.6 and 0.4, respectively. During the refinement, the C−O and C−C bond distances

(10) Lawton, S. L.; Jacobson, R. A. *TRACER, a cell reduction program*; Ames Laboratory, Iowa State University of Science and Technology: Ames, IA, 1965.

(11) Lehmann, M .S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(12) Data reduction, structure solution, and refinement were carried out on an Iμ_B PS2 personal computer and on an Encore 91 computer.

(13) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151.

(14) Ugozzoli, F. ABSORB. A program for F_o absorption correction. *Comput. Chem.* **1987**, *11*, 109.

(15) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

(16) International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 149.

(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(18) Sheldrick, G. *SHELX-86, Program for the solution of crystal structures*; University of Göttingen: Göttingen, Germany, 1986.

(19) Sheldrick, G. M. *SHELXL-92, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1992.

involving the disordered carbon and oxygen atoms in all complexes were constrained to be 1.48(1) and 1.54(1) Å, respectively.

For all of the complexes, all of the hydrogen atoms, except for those which were ignored because of their association with the disordered THF molecules in **2** and **6** and with the dioxane molecule in **4**, were located from difference Fourier maps. They were introduced into the subsequent refinements as fixed atom contributions with isotropic U's fixed at 0.10 Å^2.

The final difference maps showed no unusual features, with no significant peak above the general background.

Final atomic coordinates are listed in Tables S2−S4 for non-H atoms and in Tables S5−S7 for hydrogens. Thermal parameters are given in Tables S8−10, and bond distances and angles, in Tables S11−S13.[20]

Supporting Information Available: Tables giving crystal data and details of the structure determination, fractional atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (21 pages). Ordering information is given on any current masthead page.

IC951661D

(20) See the paragraph at the end of the paper regarding the Supporting Information.