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Bridged (β-alkoxyalkyl)Co^{III}(salen) complexes by intramolecular alkoxycobaltation of unactivated alkenes: new models for coenzyme B_{12}

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Co^{II}(salen) derivatives (salen = {*N*,*N′*-ethylenebis[salicylideneaminato]}) whose ethanediyl moiety carries an alkenyl side-chain R [R = prop-2-en-1-yl (**6a**), 2-methylprop-2-en-1-yl (**6b**), but-2-en-1-yl (**6c**), but-3-en-1-yl (**6d**)] react with oxygen and alcohols to give organocobalt(III) complexes containing a β-alkoxy-substituted three- or four-carbon bridge between cobalt and the equatorial ligand. NMR and UV–VIS spectroscopic studies show that product formation is a three-stage process involving (1) oxidation of cobalt(II) to produce an (alkoxo)cobalt(III) complex, (2) intramolecular interaction of cobalt(III) with the alkenyl double bond to yield a carbocationic intermediate, and (3) nucleophilic attack by the alcohol. In the case of cobalt(II) complex **6e** (R = 3-methylbut-3-en-1-yl), the major product is bridged β-methylene organocobalt(III) complex **10**, demonstrating that proton loss competes with addition of alcohols when the intermediate organocobalt(III) species has a substantial degree of tertiary carbocation character. Application of the alkoxycobaltation reaction to **6d** and ethane-1,2-diol afforded bridged [β-(2-hydroxyethoxy)alkyl]Co(salen) complex **20**, a simple model for coenzyme B_{12} with a built-in substrate. The molecular structure of **20** has been determined by X-ray diffraction methods.

Introduction

For more than three decades now, the chemistry of coenzyme B_{12}-dependent (B_{12} = 5′-deoxyadenosylcobalamin) enzymatic 1,2-rearrangements has fascinated researchers in many fields of chemistry. It is generally accepted that substrate rearrangement is initiated by H-abstraction to give a substrate radical, followed by the intramolecular migration of an electronegative group to a neighbouring carbon atom and recapture of a hydrogen atom. The role that cobalt–substrate interactions may play in the actual mechanism of this migration is poorly understood. A potentially useful strategy to study the importance of such interactions is to force substrates, or models thereof, to stay in close proximity to cobalt in order to see whether reactivity can be induced which is otherwise not, or rarely, observed. Recent studies by Murakami *et al.* have shown that the efficiency of substrate rearrangement can be enhanced during photolysis of a hydrophobic organocobalamin derivative by enclosing it in a single-walled vesicle that acts as an artificial holoenzyme.[1] Keese *et al.* found that rearrangement of methylmalonyl-CoA in a protic solvent becomes an efficient process when both the vitamin B_{12}-derived catalyst and the substrate carry a long alkyl chain.[2] A considerable amount of methylsuccinic acid was isolated by Rétey *et al.* after photolysis and saponification of a methylmalonate bridged cobaloxime.[3] These studies demonstrate that one of the important functions of the holoenzyme may be to keep the substrate close to the cobalt centre of the coenzyme during reaction, thereby moderating the reactivity of radical intermediates and allowing cobalt to assist in group migration. Indeed, recent EPR studies of the B_{12}-dependent carbon skeleton rearrangement of glutamate to methylaspartate have demonstrated ‘communication’ between Co^{II} and the 4-glutamyl radical over a distance of *ca.* 6 Å.[4] This accords with the finding that distances from Co to the putative radical centres on the substrate or substrate analogues in crystal structures of methylmalonyl-CoA mutase range from 6 to 7 Å.[5]

We are interested in the formation and subsequent cleavage of the cobalt–carbon bond in model complexes[6] for B_{12} in which an alkenyl substituent is attached to the equatorial ligand and thus forced to stay in close proximity to the cobalt centre during reactions. The reaction of cobalt species with unactivated alkenes is very unusual in the chemistry of B_{12} and structural models thereof. Generally, only alkenes with activating substituents are reactive towards cobalt(I), cobalt(II), or cobalt(III) complexes to give, depending on the reaction conditions, α- or β-substituted organocobalt derivatives[7] or oxidation products such as ketones and secondary alcohols.[8] On the other hand, alkenes are often formed by β-hydrogen elimination after Co–C bond homolysis or heterolysis of B_{12} and derivatives. Furthermore, alkenes, whether or not interacting with Co species, have recently regained interest as potentially important intermediates in B_{12}-catalysed rearrangements.[4,9] In order to investigate whether the presence of cobalt in close proximity to a C=C double bond enhances their mutual reactivity, we have synthesized Co^{II}(salen) derivatives whose ethanediyl moiety carries an alkenyl side-chain. Here, we describe the ability of these complexes to form cobalt–carbon bonds upon aeration in alcoholic media. The products, bridged (β-alkoxyalkyl)-Co^{III}(salen) complexes, are structural mimics of coenzyme B_{12}. Synthetic, structural, as well as mechanistic details will be presented. A preliminary report of part of this work has been published.[10]

Results and discussion

Preparation of Co^{II}(salen) complexes 6a–e with a pendant alkenyl arm

H_2salen ligands required for the synthesis of Co^{II}(salen) deriv-

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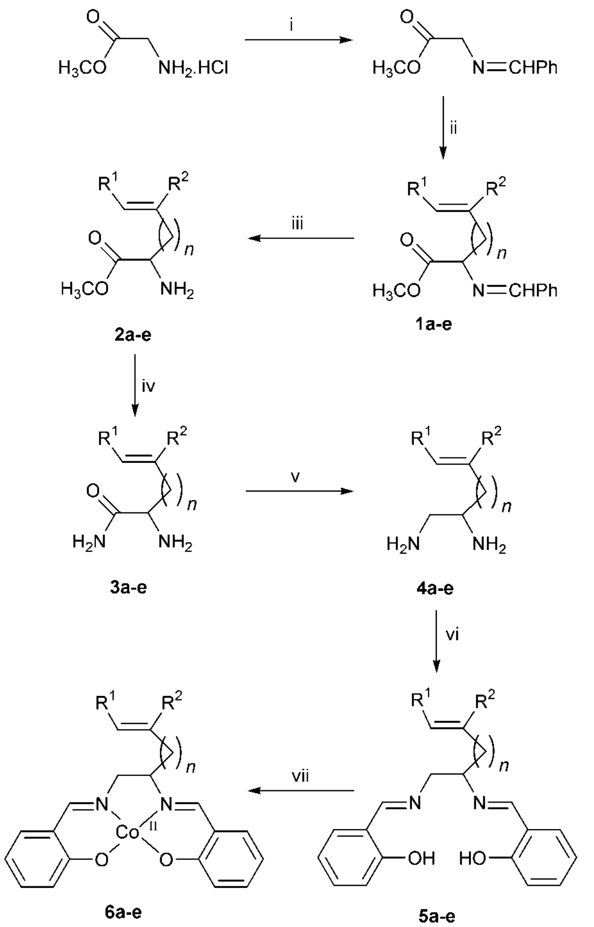

a: n=1, R^1= R^2=H
b: n=1, R^1=H, R^2=CH_3
c: n=1, R^1=CH_3, R^2=H
d: n=2, R^1= R^2=H
e: n=2, R^1=H, R^2=CH_3

Scheme 1 *Reagents and conditions*: i, PhCHO, Et_3N, CH_2Cl_2, $MgSO_4$; ii, Method I (**a**, **b**): $R^1CH{=}CHR^2CH_2OC(O)OEt$, $(Ph_3P)_4Pd(0)$, THF; Method II (**c**, **d**, **e**): 1) LiN(*i*-Pr)$_2$, THF, HMPA, −60 °C, 2) $R^1CH{=}CHR^2(CH_2)_nBr$, RT; iii, 1.5 M HCl; iv, NH_3, MeOH; v, $LiAlH_4$, THF, 55 °C; vi, salicylaldehyde, EtOH, 60 °C; vii, $Co(OAc)_2$, THF, 60 °C.

atives are generally prepared by condensation of salicylaldehyde with the appropriate vicinal diamines, which, in their turn, are available *via* several routes. 1,2-Diaminoalkenes **4** used for the construction of Co^{II}(salen) complexes **6** are conveniently prepared in a five-step procedure (without purification of the intermediates) in which alkylation of methyl *N*-benzylideneglycinate, either by Pd(0)-catalysed reaction with allyl carbonates[11] (→**6a**,**b**) or by reaction of the (LDA-generated) lithium enolate with bromoalkenes[12] (→**6c**,**d**,**e**), is the crucial step (Scheme 1). The crude alkylation products **1** (which in the case of **1c**,**d**,**e** contained varying amounts of dialkylation products)† were hydrolysed to aminoesters **2** and then converted to amino amides **3** by NH_3–MeOH. Reduction with a large excess of $LiAlH_4$ in THF[13] afforded the 1,2-diamines **4**, which could easily be purified by distillation. Heating of **4** with two equivalents of salicylaldehyde in ethanol[14] gave H_2salen ligands **5** as very viscous liquids in high yield and reasonable purity. Since purification by chromatography often led to partial decomposition, the crude products were used in the final conversion of **5** to the desired Co^{II}(salen) complexes **6** by reaction with $Co(OAc)_2$ in hot deaerated THF.‡ Evaporation of the solvent and repeated washings with deaerated water and diethyl ether, respectively, furnished **6a**–**e** as air-sensitive red-brown paramagnetic solids which were identified by the ^{1}H NMR spectra of the corresponding diamagnetic iodocobalt(III) derivatives after *in situ* conversion with I_2 in DMSO-d_6 or pyridine-d_5.§

Oxygenation of cobalt(III) complexes 6a–e in alcohols

Red solutions of Co^{II}(salen) derivatives **6a**–**e** in methanol quickly turn brown upon exposure to air. Further changes then follow, the course of which depends on the structure of the alkenyl side chain. For **6a**–**d**, the brown solutions eventually turn dark red. UV–VIS spectral changes that accompany the oxidation process are quite similar in shape and extinction, and indicate the rapid conversion of a Co^{II}(salen) into a transient Co^{III}(salen) species, followed by a further slower reaction that eventually leads to the spectrum characteristic of (alkyl)-Co^{III}(salen) compounds.[15] Starting material has disappeared completely after *ca.* 3 hours (**6a**), 14 days (**6b**,**c**) or 8 hours (**6d**), respectively.

Red diamagnetic solids were obtained after solvent evaporation and purification by column chromatography (Al_2O_3, 10% MeOH in CH_2Cl_2) or preparative TLC (silica, 5% MeOH in $CHCl_3$). In non-coordinating solvents like chloroform or dichloromethane, these red products dissolve to give an intense green colour and display UV–VIS absorption at *ca.* 650 nm (CH_2Cl_2, $\varepsilon = 1.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}) which is characteristic for five-coordinate (alkyl)Co^{III}(salen) complexes.[6,15] The green solids, obtained after extensive drying of the red products *in vacuo*, were dissolved in $CDCl_3$ and identified by correlated NMR spectroscopic techniques as bridged (β-methoxyalkyl)-Co^{III}(salen) complexes **7**–**9** (Scheme 2).

Interestingly, no signals of diastereomers are observed in the NMR spectra of any of the bridged complexes except **7b**, indicating that the addition of cobalt and a methoxy group to the C=C double bond (methoxycobaltation) is a stereospecific process. For complex **7b**, two diastereomers **I** and **II** (Fig. 1) are formed in a *ca.* 1 : 2 ratio.

In order to determine the bridge conformations of the complexes **7a**–**c**, the Karplus equation was applied to the vicinal coupling constants of H(9) with H(17a) and H(17b), respectively (Fig. 1). From the scalar values of the coupling constants it was concluded that compounds **7a**, **7b(I)**, and **7c** have a geometry in which the Co–N–C(9)–C(17)–C(18)–C(19) ring adopts a chair-like conformation, while the corresponding six-membered ring in diastereomer **II** of **7b** has a boat-like conformation. NOE experiments were carried out to reveal the configuration around the β-carbon atom of the bridge. In complexes **7a** and **7c**, the OCH_3 substituent occupies the *pseudo*-equatorial position *i.e.* OCH_3 is antiperiplanar with respect to cobalt. By contrast, it is the methyl group that takes this position in **7b(I)** and **7b(II)**. In both **I** and **II**, the OCH_3 substituent is proximal to the equatorial salen ligand, probably because the OCH_3-oxygen atom is less bulky than the CH_3 substituent. This assignment is further corroborated by the anisotropic highfield shift of the OCH_3-protons (δ 2.67 and 2.68 ppm for **I** and **II**, respectively) compared to those of **7a** and **7c** (δ 3.33 and 3.17

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† Preparation of **1c** was also tried *via* Pd(0)-catalysed alkylation, but in that case also a considerable amount of an isomer that was difficult to separate was formed by reaction at C-3 of the but-2-en-1-yl moiety of the starting material.

‡ Previously,[6,10] we had used DMF, which was difficult to remove. Solubility of $Co(OAc)_2$ is sufficiently high in boiling THF to accomplish complete complexation.

§ Although, in principle, the formation of two diastereomeric ICo^{III}-(salen) derivatives is expected in this reaction, the *in situ* ^{1}H NMR spectra in DMSO-d_6 and pyridine-d_5 show the presence of only one species, probably because of extensive dissociation of the Co–I bond in these solvents. In chloroform-d_1, the complexes are paramagnetic. However, after evaporation of this solvent and dissolution in DMSO-d_6 or pyridine-d_5, the original spectra are restored (*cf.* **18** and **19** in Scheme 6 and accompanying text).

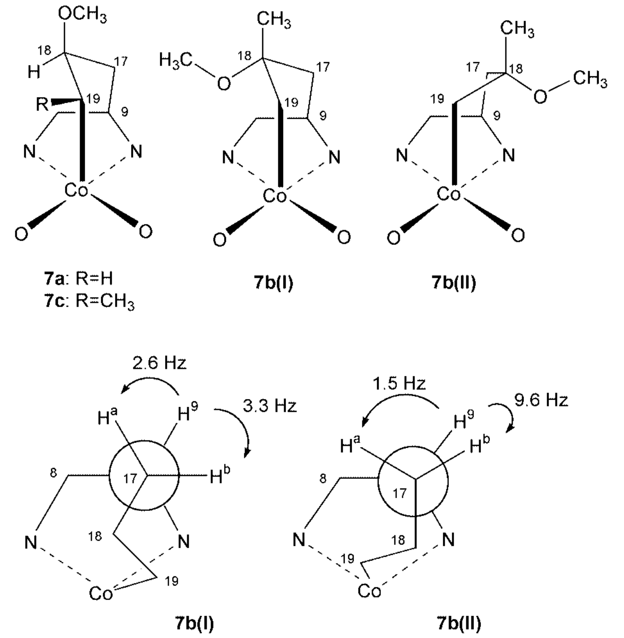
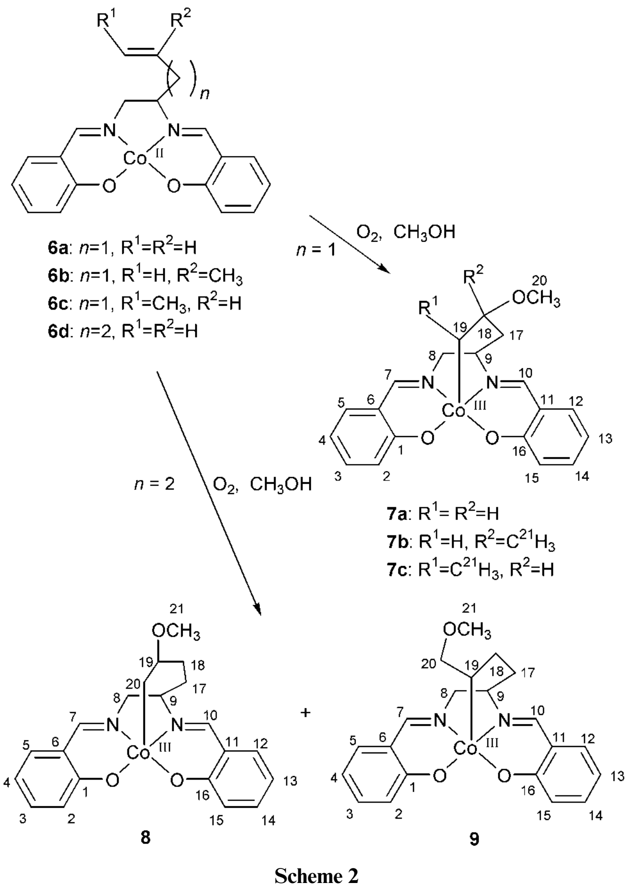


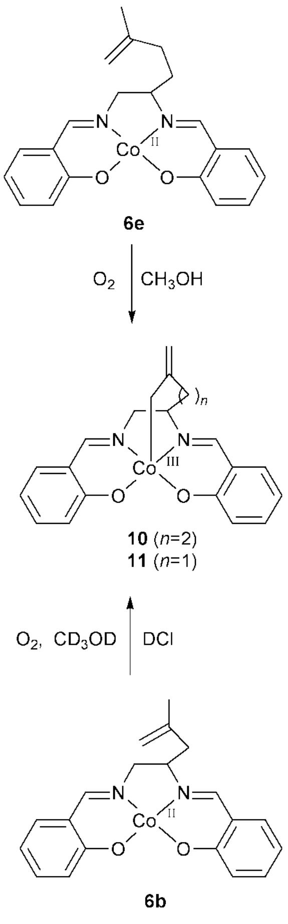
Fig. 1 Presentations of parts of **7a–c** showing bridge conformations and configurations around C(18), Newman projections along C(17)–C(9) and vicinal coupling constants of **7b(I)** and **7b(II)** (CH_3 and OCH_3 are omitted for clarity).



Scheme 2

ppm, respectively). Ring current effects cause the H(18)-signal of **7a** and **7c** to be shifted to higher field (δ 3.25 and 2.82 ppm, respectively). For complex **8**, separated from its isomer **9** by chromatography (**8**:**9** *ca.* 2:1), the antiperiplanar orientation of the β-OCH_3 substituent and cobalt, and a zigzag bridge conformation is confirmed by its crystal structure reported earlier.[10] The exact geometry of complex **9** was not determined; however, in view of the results mentioned above, a structure with a chair-like conformation of the Co–N–C(9)–C(17)–C(18)–C(19) ring with a *pseudo*-equatorial methoxymethyl group and a zigzag orientation from C(17) to C(20) is considered most likely. Its ^1H NMR spectrum displays a specific highfield signal at −0.46 ppm, similar to the signal at −0.49 ppm reported for an (alkyl)-Co(salen) complex with a trimethylene bridge,[6] and assigned unambiguously by NOE experiments to the *pseudo*-equatorial β-proton of the bridge [H(18)] which is antiperiplanar with respect to cobalt.

Oxidation of cobalt(II) complex **6e** in methanol follows a somewhat different course. During the reaction a green-brown precipitate forms as the major product which was identified by NMR (see Experimental section) as bridged (β-methylenebutyl)Co(salen) complex **10** (Scheme 3). Minor amounts of one or more bridged (β-methoxyalkyl)cobalt(III) complexes are also formed, as suggested by characteristic signals in the ^1H NMR spectrum (for instance, a signal at −0.42 ppm, indicative of a bridged (α-methoxymethylalkyl)cobalt(III) derivative similar to **9**). The formation of **10** demonstrates that proton loss can compete with methanol addition.



Scheme 3

Initially, it was assumed that a similar product would not be formed upon oxidation of **6b** because of too much strain. However, when **6b** was oxidised in methanol-d_4 containing a small amount of deuterium chloride ($[D^+] = 10^{-5}$ M), a precipitate slowly formed, which was separated by filtration and identified by NMR as bridged (β-methylenepropyl)Co(salen) complex **11** (Scheme 3). The filtrate contained the two diastereomers **7b(I)** and **(II)**.

The intramolecular alkoxycobaltation is not limited to methanol; (β-oxyalkyl)cobalt(III)salen complexes with a bridge geometry similar to **7a** are obtained when **6a** is oxidised in *e.g.* ethanol, phenol (20 equiv. in THF), water (H_2O–THF = 1:1), or ethane-1,2-diol (50% in THF, *vide infra*). Unidentified

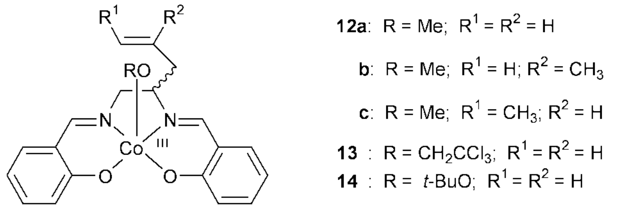


Fig. 2

paramagnetic material was obtained when propan-2-ol or *tert*-butyl alcohol were used as reaction solvents.¶

Mechanistic observations

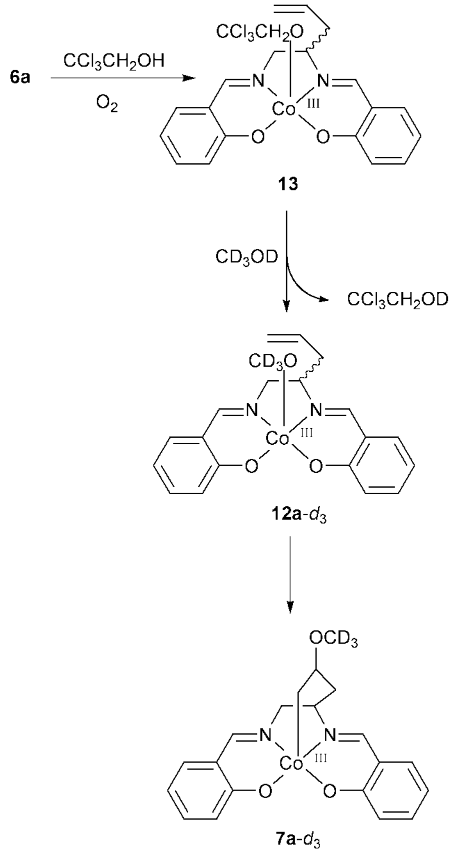
Mechanistic experiments mainly focused on the methoxycobaltation of **6a**, since this reaction is sufficiently fast and furnishes only one intramolecularly bridged product (**7a**) in high yield.

Analogous to the oxygenation of Co^{II}(salen), the first step of the reaction of **6a** with O_2 is very probably the formation of the corresponding μ-peroxo- and/or superoxocobalt(III) complex. This type of reaction is known to be rapid and reversible,[16] and several monomeric and dimeric cobalt–dioxygen complexes of Co^{II}(salen) and derivatives have been isolated.[17] In coordinating solvents such as pyridine, DMSO or DMF, aeration of Co^{II}(salen) leads to precipitation of diamagnetic $[(L)Co^{III}(salen)]_2O_2$ complexes (L = solvent).[16a] These complexes, when dissolved in alcohols, are irreversibly transformed into the corresponding alkoxocobalt(III) derivatives.[18]

Probably because of higher solubility, no precipitate was formed when air was bubbled through solutions of **6a** in these solvents. Furthermore, the solid obtained by evaporation of the solvent in a stream of air was found to be paramagnetic in pyridine-d_5 or DMSO-d_6 solution. On the other hand, as described before, aeration of **6a** in methanol *initially* induces UV–VIS spectral changes which are very similar under these conditions to those characterizing the conversion of Co^{II}(salen) into (methoxo)Co^{III}(salen) *via* the corresponding peroxo complexes.[18b] However, further, slower changes are observed for **6a** until eventually the spectrum of **7a** is obtained. Similarly, when the oxidation of **6a** in methanol-d_4 was followed by ^1H NMR spectroscopy, a diamagnetic Co^{III}-intermediate was observed initially whose carbon–carbon double bond is still intact. This intermediate spectrum (which already contained signals of **7a**-d_3) then changed further to give the spectrum of **7a**-d_3 only.

These results indicate that the first detectable Co^{III}-intermediate in the methoxycobaltation of **6a** is the corresponding methoxocobalt(III) complex **12a** (Fig. 2). However, its isolation proved to be cumbersome. Concentration of a methanol solution of **6a** after short exposure to air was shown by ^1H NMR spectroscopy in DMSO-d_6 to furnish a mixture of **7a** and paramagnetic material. The precipitate isolated after addition of diethyl ether to a saturated solution of oxidised **6a** in methanol turned out to be a similar mixture. Apparently, equilibria are involved which make it difficult to isolate intermediates.

When **6a** was oxidised in the presence of the weakly nucleophilic 2,2,2-trichloroethanol (20 equiv. in dichloromethane), only (2,2,2-trichloroethoxo)cobalt(III)salen derivative **13** (Fig. 2) was isolated and identified by NMR spectroscopy as a mixture of two diastereomers (ratio *ca.* 1 : 1). It is the *end-product* of the reaction, *i.e.*, no subsequent cobalt–carbon bond formation occurred. Trichloroethoxo complex **13** reacts *anaerobically* when dissolved in methanol-d_4 (monitored by ^1H NMR spectroscopy) to form bridged product **7a**-d_3 and one equivalent of 2,2,2-trichloroethanol-d_1. Very probably, the trichloroethoxy group of **13** is rapidly exchanged by methoxy to give **12a** which then cyclises to **7a** (Scheme 4).



Scheme 4

Like trichloroethoxo complex **13**, *tert*-butylperoxo complex **14** (Fig. 2) (prepared in the same way as (*tert*-butylperoxo)-Co^{III}(salen))[19] reacts in deaerated methanol to give **7a**. It was not investigated whether formation of **7a** from **14** involves fast replacement of the *tert*-BuOO moiety by a MeO group to give **12a** followed by methoxycobaltation, or more complicated alkyl peroxide decomposition pathways are followed.

In methanol, the rate of formation of **7a** from **6a** is about 100 times faster at pH 4 than at pH 7, suggesting that protonated species are involved in the rate-determining step. The pH–rate profile of the reaction of **6a** in buffered 9 : 1 methanol–water mixtures follows a titration curve and gives a pK_a value (of the conjugate acid of **6a**) of 7.6.[10] In alkaline solutions formation of **7a** is very slow. Thus, when air was admitted to a solution of **6a** in methanol-d_4 containing a small amount of a solution of NaOD (40%) in D_2O such that $[OD^-]$ is 10^{-2} M, fast oxidation to $(CD_3O)Co^{III}$(salen) derivative **12a**-d_3 was observed by ^1H NMR spectroscopy. Further reaction to give **7a**-d_3 was slowed down dramatically by the presence of the base. In a control experiment, **7a** was shown to be stable in alkaline methanol-d_4, ruling out the possibility that **7a** cannot exist in basic solution. In an attempt to observe a resonance for the cobalt-bound methoxy group of **12a** by ^{13}C NMR spectroscopy, the above experiment was repeated in an alkaline mixture of CH_3OH and CD_3OD (4 : 1). However, even at −75 °C, such a signal was not found. Since an analogous signal was also not present in spectra of (MeO)Co^{III}(salen), it is concluded that exchange of the axial methoxo ligand by CH_3OH is too fast to be observed on the NMR time scale. In DMSO-d_6, however, the resonance of the methoxo ligand of (MeO)Co^{III}(salen) is clearly present (δ ^{13}C = 51.9 and δ ^1H = 1.21 ppm).

Methoxocobalt(III) complexes **12b** and **12c** (Fig. 2) are certainly intermediates in the oxidation of **6b** and **6c**, respect-

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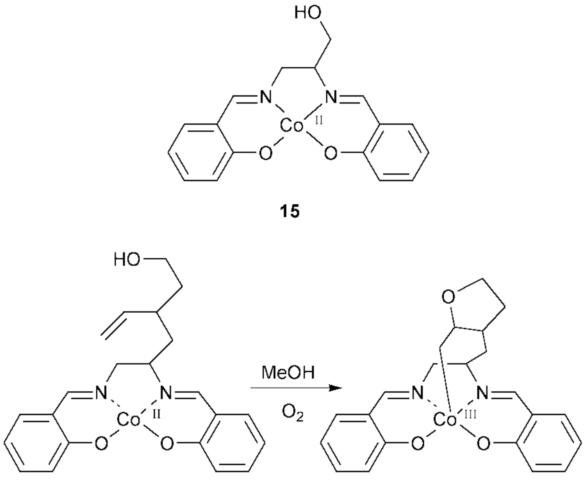
¶ Recently we found that the expected β-isopropoxy- and *tert*-butoxy-substituted intramolecularly alkylated salen derivatives are formed when cationic complex **19** (Scheme 6) is dissolved in propan-2-ol and *tert*-butyl alcohol, respectively.

ively. Because oxidation is fast whilst Co–C bond formation is very slow, they could be isolated (although contaminated with small amounts of **7b** and **7c**, respectively) and characterised by ^{1}H NMR spectroscopy in DMSO-d_6 as mixtures of two diastereomers (**12b**: ratio *ca.* 2 : 1; **12c**: ratio *ca.* 1 : 1). However, these complexes are rather unstable and decompose to paramagnetic material at room temperature.

Co^{II}(salen) was found not to react with (a large excess of) hex-1-ene in methanol. The only cobalt(III) product isolated after two weeks was (MeO)Co^{III}(salen). Similarly, Co^{II}(salen) complex **15** with a hydroxymethyl group attached to the equatorial ligand (Scheme 5) did not furnish an alkoxycobaltation product when exposed to hex-1-ene in aerated methanol. In contrast, we recently reported that **16**, provided with both a pendant alkenyl and an ω-hydroxyalkyl side-chain, undergoes a very fast reaction to give **17** when dissolved in aerated methanol.[20] The intramolecular presence or close proximity of the unactivated C=C double bond, therefore, seems to be essential for Co–C bond formation to occur by alkoxycobaltation.



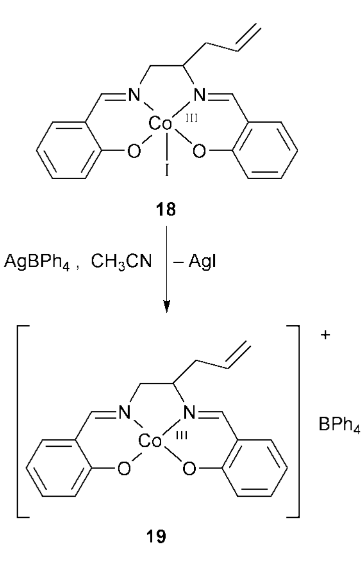
15

16

17

Scheme 5

A bonding interaction between a C=C group and Co(III) in salen derivatives carrying an alkenyl side-chain can only be established and detected if free coordination sites on Co(III) are available. Hence, we synthesized cationic Co^{III}(salen) derivative **19** neutralized by the large counterion tetraphenylborate (Scheme 6). The starting material, iodocobalt(III) complex **18**, was prepared by reaction of iodine with **6a** in THF. Upon addition of a solution of **18** in acetonitrile to a solution of silver tetraphenylborate in the same solvent, a yellowish precipitate and a green-brown solution formed. Removal of the solid (AgI) and concentration of the filtrate gave **19** as a green-brown solid, identified by its ^{1}H NMR spectrum in DMSO-d_6. Because the spectrum of **19** is fully identical to that of **18** (except for the aromatic signals of the anion) and because no diastereomers were detected, we conclude that both compounds are extensively ionized in DMSO (and in pyridine).



18

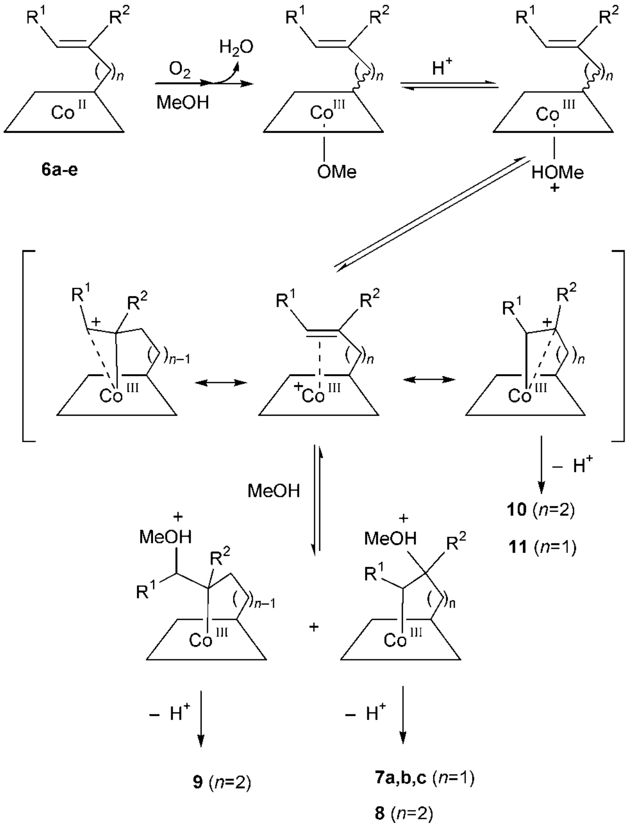
19

Scheme 6

In strongly coordinating solvents like DMSO and pyridine, an interaction between the C=C double bond and Co(III) is not expected due to full occupation of the coordination sites.[21] This is in accord with the fact that **19** undergoes fast *anaerobic* methoxycobaltation to give **7a** when dissolved in methanol, whereas (similar to **6a**) neither **18** nor **19** cyclizes to **7a** in mixtures of methanol and DMSO (or pyridine). On the other hand, in non-coordinating solvents like dichloromethane and chloroform, both **18** and **19** appear to be paramagnetic. With the exception of the aromatic region, only very broad indistinct NMR signals are observed. Decomposition can be excluded, since removal of the chlorinated solvent and dissolution in DMSO-d_6 (or pyridine-d_5) results in restoration of the original NMR spectra found for diamagnetic **18** and **19**. A possible explanation is that, in non-coordinating solvents, both **18** and **19** have a geometry in which one of the coordinating oxygens of the salen ligand is displaced from the equatorial plane to an axial position causing transition from a low-spin to a high-spin state. Attempts to crystallize **19**, in order to observe a possible Co(III)–olefin interaction in the solid state, have so far been unsuccessful.

Mechanism of intramolecular alkoxycobaltation

In our preliminary account[10] we proposed the mechanism given in Scheme 7 for the methoxycobaltation of **6a** and **6d**. The results of the present work provide additional support for this mechanism which also explains the results obtained with **6b**, **6c**, and **6e**, and thus may be general for these reactions.



Scheme 7

The first step in this mechanism is most likely identical to the oxygenation of the parent unsubstituted Co^{II}(salen) in methanol and produces methoxocobalt(III) derivatives *via* (transient) μ-peroxo-, superoxo- and hydroxocobalt(III) intermediates.[18] As described above for **6b** and **6c**, the methoxocobalt(III) complexes **12b** and **12c** could be isolated and identified by NMR due to the fact that subsequent steps in the reaction sequence are much slower.

The following step is probably the acid-catalyzed dissociation of the methoxo ligand to yield a cationic organocobalt(III) intermediate. This is evidenced by the fact that methoxycobaltation is more rapid in mildly acidic solution (optimum at *ca.* pH = 4), whereas in alkaline medium the reaction essentially stalls after formation of the methoxocobalt(III) complex. Moreover, cationic salen derivative **19** is rapidly converted (*anaerobically!*) to **7a** on dissolution in methanol.

The nature and fate of this cationic organocobalt(III) intermediate may be rather similar to those of several related intermediates of reactions in the B_{12} field. These include the addition of vinyl ethers to cob(III)alamin and cob(III)aloximes, respectively, in alcohols to give (2,2-dialkoxyalkyl)cobalt(III) complexes,[22] and the acid-catalysed Co–C bond heterolysis of coenzyme B_{12},[23] of (β-hydroxyalkyl)- and (β-alkoxyalkyl)-cobalamins and -cobinamides,[24] and of (β-hydroxyalkyl)- and (β-alkoxyalkyl)cobaloximes[25] to give Co(III), alkene, and alcohol or water.

Mechanisms that have been proposed for these reactions involve Co(III)–olefin π-cations,[22,25] β-cobaltoethyl cations stabilised by cobalt–carbon hyperconjugation,[25] and a concerted elimination of alcohol or water and cobalt(III).[24] More recently, cobaloxime π-cations have also been suggested as intermediates in the reaction of (β-hydroxyalkyl)cobaloximes with nucleophiles[26] and in cobalt-mediated carbocyclic ring constructions.[27] Considering these proposals, it seems that a structure-dependent mechanistic continuum exists, similar to that implied for the solvomercuration–demercuration reaction for which arguments in favour and against bridged mercurinium and unsymmetrical mercury-stabilised carbocations, respectively, have been advanced.[28] Depending on the substitution pattern of the alkenyl side-chain of the starting Co^{II}(salen) derivative, delocalization of the positive charge in the cationic intermediate over Co and the C=C bond will be more or less unsymmetrical. In the intermediates derived from **6b** and **6e**, the methyl bearing carbon atom may have, to a large degree, the characteristics of a tertiary carbocation.

An alternative mechanism for the formation of alkoxycobaltation products in which the alkene inserts directly into the Co–O bond of the intermediate alkoxocobalt(III) complex, without formation of a cationic intermediate, can be ruled out since it would lead to a *syn*-relation between cobalt and the alkoxy substituent, whereas the actual arrangement is *anti*.[10]

The last essential step in the alkoxycobaltation is nucleophilic attack of an alcohol on the cationic intermediate. The fact that 2,2,2-trichloroethanol, a weak nucleophile, does react with alkenyl-substituted Co^{II}(salen) complexes and oxygen to produce (trichloroethoxo)Co^{III}(salen) derivatives but does not react further to give alkoxycobaltation products, demonstrates that the nucleophilicity of the alcohol is an important factor in Co–C bond formation.

In view of the stereospecificity of the reaction it seems likely that the incipient carbon-bridges in the transition states have already adopted their favoured chair-like conformations (**A**, **B** and **C** in Fig. 3) while methanol approaches the electrophilic carbon centre on a stereoelectronically controlled path *anti* to the final Co–C bond. The presumably planar structure of the tertiary carbocationic part of the intermediate derived from **6b** allows methanol to close in from either side to furnish both **7b(I)** and **(II)** (**D** in Fig. 3); alternatively, a proton is released to give **11** (Scheme 3). The same applies to **6e** which, on aeration in methanol, mainly produces methylene-substituted bridged compound **10** (Scheme 3).

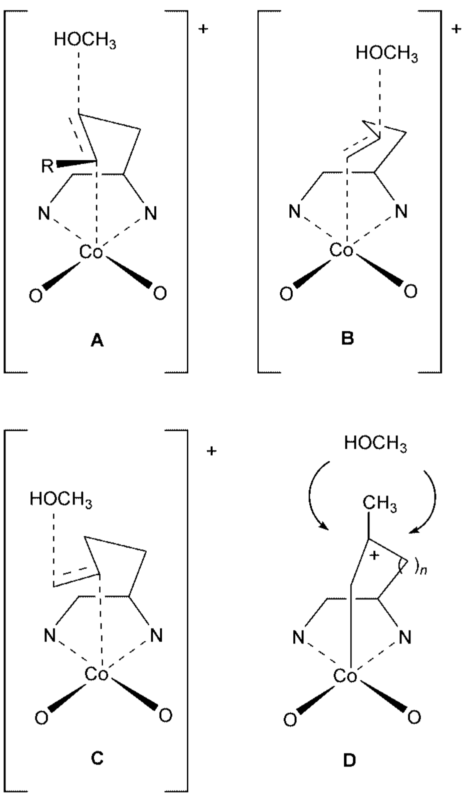


Fig. 3 Proposed transition state structures for formation of **7a** (**A**, R = H), **7c** (**A**, R = CH$_3$), **8** (**B**), **9** (**C**), and intermediate **D** for formation of **7b** (**I** and **II**) (n = 1), **10** (n = 2), and **11** (n = 1).

In principle, intramolecular alkoxycobaltation of **6a**–**e** can take place in two regioisomeric ways (*cf.* transition state structures **B** and **C** in Fig. 3). Indeed, for **6d** both isomers are found of which the major component **8** has a four-carbon bridge with a β-methoxy substituent and the minor constituent **9** a three-carbon bridge with an α-methoxymethyl substituent. For **6a**–**c**, bond formation between Co(III) and the internal sp^2-carbon would lead to a Co^{III}(salen) derivative with a two-carbon bridge which is too strained to exist as a stable compound.[6]

Application of intramolecular alkoxycobaltation to prepare a bridged [β-(2-hydroxy)ethoxyalkyl]Co^{III}(salen) complex: a simple model of coenzyme B_{12} with a built-in substrate

B_{12}-Model complexes to which a substrate (or model thereof) is connected, can be used to test for the possible occurrence of cobalt–substrate interactions in coenzyme B_{12}-dependent enzymatic rearrangements. In that vein, intramolecular alkoxycobaltation was used to prepare a bridged Co^{III}(salen) complex with a built-in glycol unit positioned in such a way that, after homolysis of the Co–C bond, a 1,5-H shift could initiate a 1,2-radical rearrangement.[29] Thus, but-3-en-1-yl-substituted Co^{II}-(salen) complex **6d** was aerated in a 1 : 1 mixture of ethylene glycol and THF. After stirring for five days in the dark, a green solid was obtained, which was shown by NMR spectroscopy to consist of a *ca.* 3 : 1 mixture of the bridged organocobalt isomers **20** and **21** (Scheme 8). The desired isomer **20** (whose four-carbon bridge is expected to undergo homolysis more easily than the three-carbon bridge of **21**)[30] is less soluble in dichloromethane than **21**, enabling the selective isolation of crystals of **20** suitable for X-ray analysis.

The molecular structure and atom numbering of **20** are shown in Fig. 4. Selected bond lengths and angles are shown in Table 1 and details of the X-ray structure determination are described in the Experimental section. In the solid state, compound **20** is a centrosymmetric dimer, half of which

Table 1 Selected bond lengths (Å) and bond angles (°) for bridged [β-(2-hydroxyethoxy)butyl]Co^{III}(salen) complex **20**

Co(1)–C(20)	1.964(6)	C(18)–C(19)	1.514(10)
Co(1)–O(1)	1.914(3)	C(19)–C(20)	1.516(9)
Co(1)–O(2)	1.887(4)	C(19)–O(3)	1.457(8)
Co(1)–N(1)	1.867(6)	C(7)–N(1)	1.274(11)
Co(1)–N(2)	1.863(5)	C(10)–N(2)	1.293(10)
Co(1)–O(1′) (dimer)	2.360(5)		
Co(1)–C(20)–C(19)	120.2(4)	C(20)–Co(1)–N(1)	90.7(3)
C(17)–C(18)–C(19)	116.3(7)	C(20)–Co(1)–N(2)	93.8(2)
C(18)–C(19)–C(20)	114.3(6)	O(3)–C(19)–C(20)	109.0(5)
C(20)–Co(1)–O(1)	92.9(2)	O(3)–C(19)–C(18)	106.4(6)
C(20)–Co(1)–O(2)	91.2(2)		

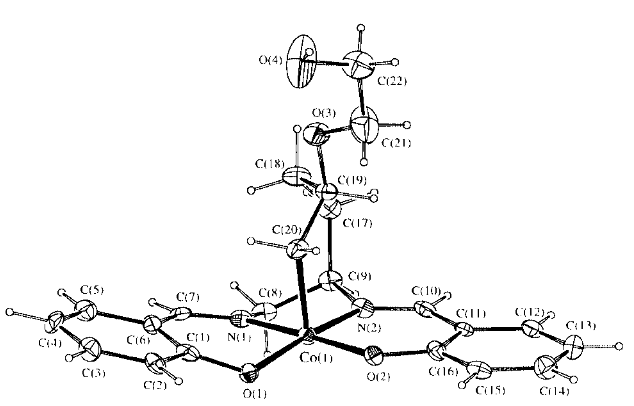
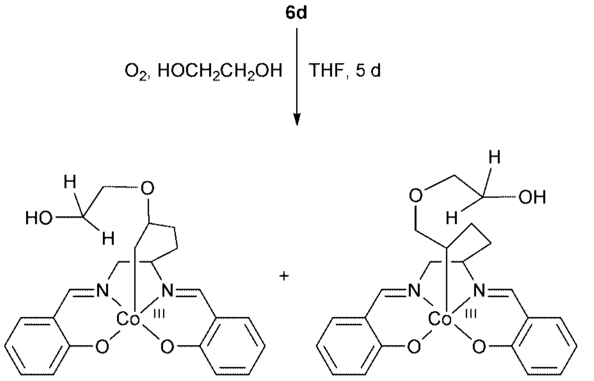


Fig. 4 ORTEP diagram drawn at 50% probability level and atom numbering scheme of half a dimer of **20**. Solvent molecules have been omitted for clarity.



20 **21**

Scheme 8

(for reasons of clarity) is shown in Fig. 4. The cobalt atom of each molecule contained in the dimer is bonded to the salen-O(1) atom of its enantiomeric partner (Co–O′ = 2.360(5) Å). This way of establishing hexacoordination of cobalt is not uncommon; of the few examples of (alkyl)Co^{III}(salen) complexes that have been structurally characterised, [(ethyl)-Co(salen)]$_2$[31] and two of the intramolecularly bridged organocobalt(salen) complexes recently reported by us[6] have the same feature. The Co–C bond length of 1.964(6) Å lies in the range usually found for (alkyl)Co^{III}(salen) complexes.[6,10,20,32] The length of the C(20)–C(19) bond is 1.516(9) Å, similar to the corresponding bond in coenzyme B$_{12}$.[33] The C(19)–O(3) bond is slightly longer than in the coenzyme (1.457(8) Å *vs.* 1.427 Å). The Co–C–C angle of 120.2°, although not as large as in B$_{12}$ (122.5°), deviates strongly from the ideal tetrahedral geometry. This can be explained by the fact that the metal-bonded C(20) has considerable sp^2-character. A conspicuous feature is that, like in other bridged (alkyl)Co(salen) compounds, the C–C–C angles in the carbon bridge are quite large, probably because of steric constraints. The zigzag conformation of the four-carbon bridge and the antiperiplanar arrangement of Co and O(3) are almost identical with those found in the solid state structures of other bridged (β-alkoxyalkyl)Co(salen) complexes.[10,20]

Product formation after homolysis of the Co–C bond of **20** and related (β-alkoxyalkyl)Co(salen) complexes will be reported separately.

Conclusions

Intramolecularly bridged (β-alkoxyalkyl)Co^{III}(salen) complexes are formed when Co^{II}(salen) derivatives carrying an alkenyl side-chain are oxidised in alcoholic media. Mechanistic studies indicate that this reaction has three main separate stages: 1) fast oxidation of cobalt(II) to give an (alkoxo)Co^{III}(salen) derivative, 2) acid-catalyzed dissociation of the alkoxo ligand enabling intramolecular interaction of Co(III) with the alkenyl double bond to yield a carbocationic intermediate and 3) nucleophilic attack by alcohol. Whether the intermediate in the second stage is better described as a Co(salen) π-cation than as a β-cobaltoethyl cation stabilised by cobalt–carbon hyperconjugation depends on the substitution pattern of the C=C bond. The exclusive *anti*-arrangement of cobalt and the alkoxy substituent found in most complexes, and the fact that, in most cases, the bridge in the organocobalt(III) products adopts the favourable chair-like conformation, point to a mechanism that proceeds *via* a product-like transition state in the third stage. In cases where a methyl substituent enables formation of a tertiary carbocation, addition of an alcohol can occur at either side of the tertiary carbocation. Alternatively, a proton is released from the neighbouring methyl group to give a methylene-substituted bridged compound.

Co–C bond formation between cobalt(III) and unactivated alkenes is highly unusual under such mild conditions, and seems limited to cases where the reactants are formed or forced to stay in close proximity. The present intramolecular alkoxycobaltation gives access to (β-alkoxyalkyl)Co^{III}(salen) complexes which are applicable as simple models for coenzyme B$_{12}$.

Experimental

General

NMR spectra were obtained using a Bruker AC 200 (^{1}H NMR: 200.1 MHz; ^{13}C NMR: 50.29 MHz) or a Bruker MSL 400 spectrometer (^{1}H NMR: 400.1 MHz; ^{13}C NMR: 100.63 MHz). Chemical shifts (δ) are reported in ppm relative to tetramethylsilane using the solvent signal as internal reference; J values are quoted in Hz. Mass spectra were measured on a Finnigan MAT 90 spectrometer. Two ionization methods were used: Electron Impact (EI) (70 eV ionization energy, source temperature 200 °C) and Fast Atom Bombardment (FAB) (8 keV xenon and *m*-nitrobenzyl alcohol as matrix). UV–VIS spectra were recorded on a Beckman DU-70 spectrophotometer. THF was distilled from NaH and, subsequently, from sodium benzophenone ketyl. Et$_2$O was distilled from NaH. Other solvents were dried over molecular sieves (3 or 4 Å).

All reactions were performed under a nitrogen atmosphere, unless stated otherwise. In order to prevent cleavage of the cobalt–carbon bond, all organocobalt complexes were handled with minimal exposure to light.

Methyl *N*-benzylideneglycinate,[34] allyl ethyl carbonate,[35] ethyl 2-methylprop-2-enyl carbonate,[35] 4-bromo-2-methylbut-2-ene,[36] 4-bromobutene,[37] and (MeO)Co(salen)[18b] were prepared according to published procedures.

Methyl 2-(benzylideneamino)pent-4-enoate 1a (Method I)

To a solution of methyl *N*-benzylideneglycinate (33.2 g, 0.19 mol) and allyl ethyl carbonate (51.0 g, 0.39 mol) in dry THF (190 cm^3) was added (Ph$_3$P)$_4$Pd (9.16 g, 7.9 mmol). After stirring at room temperature for five hours, the mixture was poured into diethyl ether (800 cm^3) and filtered through Celite. The filtrate was concentrated *in vacuo* at 30 °C. ^{1}H NMR analysis of the resulting oil (48.0 g) showed that **1a** had been formed almost quantitatively, but was contaminated with a small amount of Ph_3P which was removed in the next step; δ_H (200 MHz; $CDCl_3$) 8.20 (1 H, s, CH=N), 7.72 (2 H, m, arom-H), 7.48 (3 H, m, arom-H), 5.70 (1 H, m, CH=), 5.10 (2 H, m, CH_2=), 4.00 (1 H, dd, CHN), 3.65 (3 H, s, OCH_3), 2.70 (2 H, m, CH_2).

Methyl 2-(benzylideneamino)-4-methylpent-4-enoate 1b

Compound **1b** was prepared in almost quantitative yield from methyl *N*-benzylideneglycinate and ethyl methallyl carbonate similar to the method used for **1a**; δ_H (200 MHz; $CDCl_3$) 8.17 (1 H, s, CH=N), 7.75–7.30 (5 H, m, arom-H), 4.78 (1 H, s, C*H*H=), 4.14 (1 H, dd, CHN), 3.73 (3 H, s, OCH_3), 2.65 (2 H, m, CH_2), 1.73 (3 H, s, CH_3).

Methyl (*E*)-2-(benzylideneamino)hex-4-enoate 1c (Method II)

A solution of $(^iPr)_2NH$ (8.5 cm^3, 62 mmol) in dry THF (240 cm^3) and HMPT (27 cm^3) was cooled to 0 °C. A hexane solution of ^{n}BuLi (37.5 cm^3, 1.6 M, 60 mmol) was added in 10 min *via* a syringe. The cooling bath was removed and the mixture was stirred for 30 min at room temperature. After cooling to −60 °C, methyl *N*-benzylideneglycinate (10.6 g, 60.0 mmol) was added dropwise in 30 min and the mixture stirred for 1 h at −60 °C. The orange solution was then transferred within 2 h *via* a stainless steel tube to a vigorously stirred solution of 4-bromobut-2-ene (14.2 g, 90 mmol) in dry THF (55 cm^3) at room temperature and stirred overnight. The orange mixture was poured into a stirred mixture of diethyl ether (250 cm^3) and a saturated NH_4Cl solution (500 cm^3). The organic layer was washed with water and brine, dried over $MgSO_4$ and concentrated *in vacuo* at 30 °C. ^{1}H NMR analysis of the resulting oil (15.4 g) showed that **1c** had been formed but was contaminated with the dialkylated product (35%) which was removed in the final step of the reaction sequence; δ_H (200 MHz; $CDCl_3$) 8.20 (1 H, s, CH=N), 7.75 (2 H, m, arom-H), 7.38 (3 H, m, arom-H), 5.45 (2 H, m, CH=CH), 3.98 (1 H, dd, CHN), 3.72 (3 H, s, OCH_3), 2.62 (2 H, m, CH_2), 1.61 (3 H, d, CH_3).

Methyl 2-(benzylideneamino)hex-5-enoate 1d

Compound **1d** (contaminated with *ca.* 5% of the dialkylated product) was prepared from methyl *N*-benzylideneglycinate and 4-bromobutene, similar to the method used for **1c** (yield *ca.* 90%); δ_H (200 MHz; $CDCl_3$) 8.20 (1 H, s, CH=N), 7.70 (2 H, m, arom-H), 7.49 (3 H, m, arom-H), 5.70 (1 H, m, CH=), 4.95 (2 H, m, CH_2=), 4.00 (1 H, dd, CH), 3.70 (3 H, s, OCH_3), 2.00 (4 H, m, CH_2).

Methyl 2-(benzylideneamino)-5-methylhex-5-enoate 1e

Compound **1e** (contaminated with *ca.* 5% of the dialkylated product) was prepared from methyl *N*-benzylideneglycinate and 4-bromo-2-methylbutene, similar to the method used for **1c** (yield *ca.* 90%); δ_H (200 MHz; $CDCl_3$) 8.25 (1 H, s, CH=N), 7.41 (2 H, m, arom-H), 7.26 (3 H, m, arom-H), 4.72 (1H, s, =C*H*H), 4.65 (1H, s, =CH*H*), 3.98 (1H, dd, CHN), 3.72 (3H, s, OCH_3), 2.10 (4H, br m, CH_2CH_2), 1.71 (3H, s, CH_3).

General procedure for the preparation of methyl 2-aminoalkenoates 2a–e

Compound **1** (1 equiv.) was stirred for 2 h with 1.5 M HCl (2 equiv.) at room temperature. After washing with Et_2O (to remove benzaldehyde), solid $NaHCO_3$ was added to the aqueous phase until pH 8 was reached. After saturation with solid NaCl, extraction with $CHCl_3$ (3×), drying over $MgSO_4$ and removal of the solvent *in vacuo* at <30 °C, crude **2a**–**e** were obtained as yellow oils (75–90% yield) which were used as such in the following step.

Methyl 2-aminopent-4-enoate 2a. δ_H (200 MHz; $CDCl_3$) 5.68 (1 H, m, CH=), 5.61 (2 H, m, =CH_2), 3.70 (3 H, s, OCH_3), 3.51 (1 H, dd, CHN), 2.38 (2 H, m, CH_2), 1.52 (2 H, br s, NH_2).

Methyl 2-amino-4-methylpent-4-enoate 2b. δ_H (200 MHz; $CDCl_3$) 4.82 (1 H, s, C*H*H=), 4.72 (1 H, s, CH*H*=), 3.67 (3 H, s, OCH_3), 3.57 (1 H, dd, CHN), 2.44 (1 H, dd, C*H*H), 2.23 (1 H, dd, CH*H*), 1.70 (3 H, s, CH_3), 1.51 (2 H, br s, NH_2).

Methyl (*E*)-2-aminohex-4-enoate 2c. δ_H (200 MHz; $CDCl_3$) 5.68–5.16 (2 H, m, CH=CH), 3.68 (3 H, s, OCH_3), 3.45 (1 H, dd, CHN), 2.50–2.05 (2 H, m, CH_2), 1.6 (5 H, m, CH_3/NH_2).

Methyl 2-aminohex-5-enoate 2d. δ_H (200 MHz; $CDCl_3$) 5.75 (1 H, m, CH=), 4.98 (2 H, m, CH_2=), 3.66 (3 H, s, OCH_3), 3.40 (1 H, dd, CH), 2.11 (2 H, m, CH_2), 1.9–1.45 (4 H, m, CH_2/NH_2).

Methyl 2-amino-5-methylhex-5-enoate 2e. δ_H (200 MHz; $CDCl_3$) 4.72 (1 H, s, =C*H*H), 4.69 (1 H, s =CH*H*), 3.70 (3 H, s, OCH_3), 3.44 (1 H, dd, CHN), 2.09 (2 H, m, CH_2), 1.87 (1 H, m, C*H*H), 1.71 (4 H, s/m, C*H*$_3$/CH*H*), 1.61 (2 H, br s, NH_2).

General procedure for the synthesis of 2-aminoalkenamides 3a–e

A solution of **2** in MeOH (2.3 cm^3 per mmol of **2**) was cooled to 0 °C and saturated with NH_3. The resulting mixture was stirred for 3 days at room temperature, repeating saturation at 0 °C every 24 h. Removal of the solvent *in vacuo* gave **3a**–**e** as yellow semi-solids (*ca.* 90% yield) which were used as such in the following step.

2-Aminopent-4-enamide 3a. δ_H (200 MHz; $CDCl_3$) 7.16 (1 H, br s, N*H*HCO), 5.91 (1 H, br s, NH*H*CO), 5.74 (1 H, m, CH=), 5.11 (2 H, m, =CH_2), 3.45 (3 H, s, OCH_3), 3.40 (1 H, dd, CHN), 2.52 (1 H, m, C*H*H), 2.22 (1 H, m, CH*H*), 1.61 (2 H, br s, NH_2).

2-Amino-4-methylpent-4-enamide 3b. δ_H (200 MHz; $CDCl_3$) 6.70 (1 H, br s, N*H*HCO), 5.50 (1 H, br s, NH*H*CO), 4.86 (1 H, s, C*H*H=), 4.75 (1 H, s, CH*H*), 3.45 (1 H, dd, CHN), 2.61 (1 H, dd, C*H*H), 2.07 (1 H, dd, CH*H*), 1.69 (3 H, s, CH_3), 1.62 (2 H, br s, NH_2).

(*E*)-2-Aminohex-4-enamide 3c. δ_H (200 MHz; $CDCl_3$) 7.10 (1 H, br s, N*H*HCO), 5.63–5.15 (3 H, m, C*H*=C*H*/NH*H*CO), 3.35 (1 H, dd, CHN), 2.48 (1 H, m, C*H*H), 2.18 (1 H, m, CH*H*), 1.70–1.45 (5 H, m, C*H*$_3$/N*H*$_2$).

2-Aminohex-5-enamide 3d. δ_H (200 MHz; $CDCl_3$) 7.05 (1 H, br s, N*H*HCO), 5.80 (2 H, m, NH*H*CO/C*H*=), 5.01 (2 H, m, =CH_2), 3.35 (1 H, dd, CHN), 2.15 (2 H, m, CH_2), 1.94 (1 H, m, C*H*H), 1.58 (1 H, m, CH*H*), 1.45 (2 H, br s, NH_2).

2-Amino-5-methylhex-5-enamide 3e. δ_H (200 MHz; $CDCl_3$) 7.05 (1 H, br s, N*H*HCO), 5.62 (1 H, br s, NH*H*CO), 4.71 (1 H, s, =C*H*H), 4.69 (1 H, s, =CH*H*), 3.33 (1 H, dd, CHN), 2.10 (2 H, m, CH_2), 2.00 (1 H, m, C*H*H), 1.72 (3 H, s, CH_3), 1.60 (1 H, m, CH*H*), 1.44 (2 H, br s, NH_2).

General procedure for the preparation of 1,2-diaminoalkenes 4a–e

Compound **3** (10 mmol) was added in small portions to a mixture of $LiAlH_4$ (30 mmol) in dry THF (2.0 cm^3 per mmol of **3**) at room temperature. The mixture was vigorously stirred at 55 °C for 20 h, followed by cooling in an ice-bath and slow addition of H_2O (0.08 cm^3 per cm^3 of THF), a 15% NaOH solution (0.08 cm^3 per cm^3 of THF) and H_2O (0.16 cm^3 per cm^3

of THF), respectively. After vigorous stirring, the white suspension was filtered, the residue extracted with boiling THF, and the combined THF fractions dried over $MgSO_4$ and concentrated using a 30 cm Vigreux column. Crude **4** was purified by short path distillation under reduced pressure to give **4a**–**e** as colourless liquids (30–40% yield). For analytical purposes, small portions of **4a**–**e** were converted into the corresponding dipicrates (**4a′**–**e′**).

1,2-Diaminopent-4-ene 4a. Collected at a bath temperature of 40–45 °C at 15 mmHg; δ_H (200 MHz; $CDCl_3$) 5.80 (1 H, m CH=), 5.07 (2 H, m, $=CH_2$), 2.85–2.70 (3 H, m, CH_2N/CHN), 2.20 (2 H, m, CH_2), 1.40 (4 H, s, 2 × NH_2). **4a′** (Found: C, 36.9; H, 3.35; N, 19.9. Calc for $C_{17}H_{18}N_8O_{14}$: C, 36.6; H, 3.25; N, 20.1%).

1,2-Diamino-4-methylpent-4-ene 4b. Collected at a bath temperature of 50–55 °C at 15 mmHg; δ_H (200 MHz; $CDCl_3$) 4.79 (1 H, s, C*H*H=), 4.71 (1 H, s, CH*H*=), 2.87 (1 H, m, CHN), 2.71 (1 H, dd, C*H*HN), 2.47 (1 H, dd, CH*H*N), 2.12 (1 H, dd, C*H*H), 1.88 (1 H, dd, CH*H*), 1.69 (3 H, s, CH_3), 1.27 (4 H, br s, 2 × NH_2). **4b′** (Found: C, 37.8; H, 3.3; N, 19.6. Calc for $C_{18}H_{20}N_8O_{14}$: C, 37.75; H, 3.5; N, 19.6%).

(*E*)-1,2-Diaminohex-4-ene 4c. Collected at a bath temperature of 50–60 °C at 15 mmHg; δ_H (200 MHz; $CDCl_3$) 5.60–5.26 (2 H, m, CH=CH), 2.75–2.58 (2 H, m, C*H*N/C*H*HN), 2.45 (1 H, m, CH*H*N), 2.10 (1 H, m, C*H*H), 1.86 (1 H, m, CH*H*), 1.63 (3 H, d, CH_3), 1.22 (4 H, br s, 2 × NH_2). **4c′** (Found: C, 37.7; H, 3.4; N, 19.7. Calc for $C_{18}H_{20}N_8O_{14}$: C, 37.75; H, 3.5; N, 19.6%).

1,2-Diaminohex-5-ene 4d. Collected at a bath temperature of 50–55 °C at 15 mmHg; δ_H (200 MHz; $CDCl_3$) 5.80 (1 H, m, CH=), 5.00 (2 H, m, $=CH_2$), 2.75–2.40 (3 H, m, CH_2N/CHN), 2.20 (2 H, m, CH_2), 1.40 (6 H, m, CH_2/2 × NH_2). **4d′** (Found: C, 37.8; H, 3.3; N, 19.6. Calc for $C_{18}H_{20}N_8O_{14}$: C, 37.75; H, 3.5; N, 19.6%).

1,2-Diamino-5-methylhex-5-ene 4e. Collected at a bath temperature of 65–70 °C at 15 mmHg; δ_H (200 MHz; $CDCl_3$) 4.65 (2 H, br s, CH_2=), 2.79–2.55 (2H, m, C*H*N/C*H*HN), 2.44 (1 H, dd, CH*H*N), 2.09 (2 H, m, CH_2), 1.69 (3 H, s, CH_3), 1.58 (1 H, m, C*H*H), 1.39 (1 H, m, CH*H*), 1.22 (4 H, br s, 2 × NH_2). **4e′** (Found: C, 38.6; H, 3.7; N, 19.2. Calc for $C_{19}H_{22}N_8O_{14}$: C, 38.9; H, 3.8; N, 19.1%).

General procedure for the synthesis of H_2salen ligands 5a–e

At 60 °C, salicylaldehyde (2.1 mmol) was added to a stirred solution of diamine **4** (1 mmol) in EtOH (3.5 cm^3 per mmol of **4**). After stirring for 2 h, the yellow solution was concentrated and excess salicylaldehyde was removed *in vacuo* at 50 °C/10^{-3} mmHg during 3 h. The crude ligands were obtained as viscous yellow oils in quantitative yield and used directly in the next step.

2,2′-[(1-Prop-2-enylethane-1,2-diyl)bis(nitrilomethylidyne)]-diphenol 5a. This compound crystallized on prolonged standing, mp 70–75 °C (from hexane-ethanol) (Found: C, 74.1; H, 6.4; N, 9.0. Calc for $C_{19}H_{20}N_2O_2$: C, 74.0; H, 6.55; N, 9.1%); δ_H (200 MHz; $CDCl_3$) 13.60 (2 H, br s, 2 × OH), 8.25 (2 H, s, 2 × CH=N), 7.20 (4 H, m, arom-H), 6.90 (4 H, m, arom-H), 5.80 (1 H, m, CH=), 5.10 (2 H, m, $=CH_2$), 3.90 (1 H, m, CHN), 3.70 (2 H, m, CH_2N), 2.50 (2 H, m, CH_2).

2,2′-{[1-(2-Methylprop-2-enyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol 5b. δ_H (200 MHz; $CDCl_3$) 13.18 (2 H, br s, 2 × OH), 8.28 (1 H, s, CH=N), 8.23 (1 H, s, CH=N), 7.26 (4 H, m, arom-H), 6.86 (4 H, m, arom-H), 4.80 (1 H, s, C*H*H=), 4.74 (1 H, s, CH*H*=), 3.91 (1 H, m, CHN), 3.65 (1 H, m, CH_2N), 2.44 (2 H, m, CH_2), 1.73 (3 H, s, CH_3).

2,2′-{[1-(*E*)-But-2-enylethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol 5c. δ_H (200 MHz; $CDCl_3$) 13.17 (2 H, br s, 2 × OH), 8.22 (1 H, s, CH=N), 8.20 (1 H, s, CH=N), 7.20 (4 H, m, arom-H), 6.81 (4 H, m, arom-H), 5.43 (2 H, m, CH=CH), 3.87 (1 H, m, C*H*HN), 3.52 (2 H, m, NCH*H*C*H*N), 2.34 (2 H, m, CH_2), 1.58 (3 H, d, CH_3).

2,2′-[(1-But-3-enylethane-1,2-diyl)bis(nitrilomethylidyne)]-diphenol 5d. δ_H (200 MHz; $CDCl_3$) 13.20 (2 H, br s, 2 × OH), 8.30 (2 H, s, 2 × CH=N), 7.20 (4 H, m, arom-H), 6.90 (4 H, m, arom-H), 5.80 (1 H, m, CH=), 5.00 (2 H, m, $=CH_2$), 3.90 (1 H, m, C*H*HN), 3.70 (1 H, m, CHN), 3.55 (1 H, m, CH*H*N), 2.10 (2 H, m, CH_2), 1.85 (2 H, m, CH_2).

2,2′-{[1-(3-Methylbut-3-enyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol 5e. δ_H (200 MHz; $CDCl_3$) 13.21 (2 H, br s, 2 × OH), 8.28 (2 H, s, 2 × CH=N), 7.25 (4 H, m, arom-H), 6.87 (4 H, m, arom-H), 4.73 (1 H, s, C*H*H=), 4.63 (1 H, s, CH*H*=), 3.93 (1 H, m, C*H*HN), 3.69 (1 H, m, CH*H*N), 3.52 (1 H, m, CHN), 2.06 (2 H, m, CH_2), 1.88 (2 H, m, CH_2), 1.69 (3 H, s, CH_3).

General procedure for the synthesis of cobalt(II) complexes 6a–e

A solution of H_2salen ligand **5** (1 mmol) in anhydrous THF (15 cm^3) was degassed by three freeze–pump–thaw cycles. $Co(OAc)_2$ (1 mmol) was added and the resulting mixture was stirred at 60 °C for 2 h. A red solution had formed, which was evaporated to dryness. The residue was washed thoroughly with deaerated H_2O and Et_2O. Drying *in vacuo* gave the Co^{II}(salen) derivatives **6a**–**e** as bright red microcrystalline solids (75–85% yield), which were characterised by ^1H NMR spectroscopy as their corresponding iodocobalt(III) derivatives.

{[2,2′-[(1-Prop-2-enylethane-1,2-diyl)bis(nitrilomethylidyne)]-diphenolato](2−)-κ²*N*,*N*′;κ²*O*,*O*′}cobalt 6a. (Found: C, 61.2; H, 5.1; N, 7.6; Co, 15.2. Calc for $C_{19}H_{18}N_2O_2Co\cdot 0.5\ H_2O$: C, 61.0; H, 5.1; N, 7.5; Co, 15.7%); δ_H (200 MHz; C_5D_5N, I_2) 8.72 (1 H, s, CH=N), 8.67 (1 H, s, CH=N), 7.4 (6 H, m, arom-H), 6.57 (2 H, m, arom-H), 5.8 (1 H, m, CH=), 5.1 (2 H, m, $=CH_2$), 5.0 (2 H, m, NC*H*HC*H*N), 3.75 (1 H, m, NCH*H*), 2.90 (1 H, m, C*H*H), 2.50 (1 H, m, CH*H*); δ_C (50.29 MHz, DMSO-d_6) 168.3, 168.0 (C-7/C-10), 165.1, 164.8 (C-1/C-16), 134.8, 134.7 (C-3/C-14), 134.4 (C-18), 134.2 (C-5/C-12), 122.6, 122.2 (C-2/C-15), 119.2, 118.8 (C-6/C-11), 117.9 (C-19), 115.1, 114.9 (C-4/C-13), 67.3 (C-9), 62.6 (C-8), 37.9 (C-17) [C-atom numbering is analogous to **7a** (Scheme 2)].

{[2,2′-{[1-(2-Methylprop-2-enyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](2−)-κ²*N*,*N*′;κ²*O*,*O*′}cobalt 6b. (Found: C, 59.9; H, 5.4; N, 6.8. Calc for $C_{20}H_{20}N_2O_2Co\cdot 1\ H_2O$: C, 60.4; H, 5.6; N, 7.1%); δ_H (200 MHz; DMSO-d_6, I_2) 8.22 (1 H, s, CH=N), 8.09 (1 H, s, CH=N), 7.5 (6 H, m, arom-H), 6.68 (2 H, m, arom-H), 4.95 (1 H, br s, C*H*H=), 4.68 (1 H, br s, CH*H*=), 4.2–3.9 (3 H, m, NCH_2CHN), 2.41 (2 H, m, CH_2), 1.73 (3 H, s, CH_3).

{[2,2′-{[1-(*E*)-But-2-enylethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](2−)-κ²*N*,*N*′;κ²*O*,*O*′}cobalt 6c. (Found: C, 62.6; H, 5.7; N, 7.2. Calc for $C_{20}H_{20}N_2O_2Co\cdot 0.5\ H_2O$: C, 61.9; H, 5.5; N, 7.2%); δ_H (200 MHz; DMSO-d_6, I_2) 8.27 (1 H, s, CH=N), 8.08 (1 H, s, CH=N), 7.44 (6 H, m, arom-H), 6.66 (2 H, m, arom-H), 5.47 (2 H, m, CH=CH), 4.4–3.9 (3 H, m, NCH_2CHN), 2.37 (2 H, m, CH_2), 1.64 (3 H, d, CH_3).

{[2,2′-[(1-But-3-enylethane-1,2-diyl)bis(nitrilomethylidyne)]-diphenolato](2−)-κ²*N*,*N*′;κ²*O*,*O*′}cobalt 6d. (Found: C, 60.2; H, 5.6; N, 6.8. Calc for $C_{20}H_{20}N_2O_2Co\cdot 1\ H_2O$: C, 60.4; H, 5.6; N, 7.1%); δ_H (200 MHz; C_5D_5N, I_2) 8.67 (1 H, s, CH=N), 8.62 (1 H, s, CH=N), 7.4 (6 H, m, arom-H), 6.59 (2 H, m, arom-H), 5.8 (1 H, m, CH=), 5.1 (2 H, m, $=CH_2$), 5.0 (2 H, m, NC*H*HC*H*N), 3.82 (1 H, m, NCH*H*), 2.2 (3 H, m, C*H*$_2$C*H*H), 1.55 (1 H, m, CH*H*).

{[2,2′-{[1-(3-Methylbut-3-enyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 6e. (Found: C, 60.8; H, 5.7; N, 6.5. Calc for $C_{21}H_{22}N_2O_2Co\cdot 1\ H_2O$: C, 61.3; H, 5.9; N, 6.8%); δ_H (200 MHz; DMSO-*d*$_6$, I_2) 8.33 (1 H, s, CH=N), 8.24 (1 H, s, CH=N), 6.97 (6 H, m, arom-H), 6.40 (2 H, m, arom-H), 4.75 (1 H, br s, C*H*H=), 4.68 (1 H, br s, CH*H*=), 4.4–4.0 (3 H, m, NCH_2CHN), 2.3–1.7 (4 H, m, CH_2CH_2), 1.70 (3 H, s, CH_3).

(*SPY*-5-54)-{2,2′-[{[1-(2-Methoxytrimethylene-κ*C*^{3})ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-κ^2*N*,*N*′;κ^2*O*,*O*′}-cobalt 7a

A solution of **6a** (0.50 g, 1.4 mmol) in MeOH (100 cm^3) was stirred in the dark for 3 h while being exposed to air. The resulting dark red solution was concentrated *in vacuo* at 30 °C and furnished **7a** as a green, microcrystalline solid. Traces of Co(II) material were removed by flash chromatography over Al_2O_3 using 10% MeOH in CH_2Cl_2 as eluent (0.48 g, 87%) (Found: C, 60.3; H, 5.4; N, 6.8; O, 12.2. Calc for $C_{20}H_{21}N_2O_3Co$: C, 60.6; H, 5.3; N, 7.1; O, 12.1%) (Found: M$^+$, 396.0880. $C_{20}H_{21}N_2O_3Co$ requires *M*, 396.0884); δ_H (200 MHz; $CDCl_3$) 8.17 (1 H, s, CH=N), 8.02 (1 H, s, CH=N), 7.30 (4 H, m, arom-H), 7.19 (2 H, dd, arom-H), 6.64 (2 H, m, arom-H), 4.66 (1 H, m, CoC*H*H), 4.25 (1 H, m, C*H*HN), 4.07 (1 H, m, CHN), 3.57 (1 H, m, NCH*H*), 3.42 (1 H, m, CoCH*H*), 3.33 (3 H, s, OCH_3), 3.25 (1 H, m, CHO), 2.25 (1 H, m, C*H*H), 1.51 (1 H, m, CH*H*); δ_C (100.63 MHz; $CDCl_3$) 166.1, 165.9 (s, s, C-1/C-16), 165.6 (d, J_{CH} 159, C-7), 163.1 (d, J_{CH} 158, C-10), 133.6, 133.5 (d, d, J_{CH} 158, C-3/C-14), 132.6 (d, J_{CH} 155, C-5/C-12), 124.0, 123.9 (d, d, J_{CH} 161, C-2/C-15), 119.7, 119.6 (s, s, C-6/C-11), 115.5, 115.4 (d, d, J_{CH} 162, C-4/C-13), 78.0 (d, C-18), 67.9 (d, J_{CH} 139, C-9), 62.9 (t, J_{CH} 138, C-8), 56.3 (q, J_{CH} 141, C-20), 44.5 (t, J_{CH} 127, C-17), 12.7 (br t, J_{CH} 143, C-19).

(*SPY*-5-54)-{2,2′-[{[1-(2-Methoxy-2-methyltrimethylene-κ*C*^{3})-ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 7b (I and II)

A solution of **6b** (236 mg, 0.6 mmol) in MeOH (8 cm^3) was stirred in the dark during 14 days while being exposed to air. After work-up as described for **6a**, the two diastereomers **7b(I)** (52 mg, 21%) and **7b(II)** (108 mg, 44%) were isolated by preparative TLC (SiO_2; 10% MeOH in CH_2Cl_2).

7b(I) (Found: M$^+$, 410.104121. $C_{21}H_{23}N_2O_3Co$ requires *M*, 410.104057); δ_H (200 MHz; $CDCl_3$) 8.19 (1 H, s, H-10), 7.95 (1 H, s, H-7), 7.37 (2 H, d, H-2/H-15), 7.27 (2 H, m, H-3/H-14), 7.20 (1 H, d, H-12), 7.14 (1 H, d, H-5), 6.61 (2 H, m, H-4/H-13), 4.86 (1 H, dd, H-19a), 4.13 (1 H, dd, H-8a), 3.89 (1 H, m, H-9), 3.76 (1 H, s, H-8a), 3.73 (1 H, d, H-19b), 2.67 (3 H, s, OCH_3), 2.11 (1 H, ddd, H-17a), 1.59 (1 H, dd, H-17b), 1.14 (3 H, s, Me); δ_C (50.29 MHz; $CDCl_3$) 166.0, 164.9 (C-1/C-16), 165.6 (C-7), 162.2 (C-10), 133.0, 132.7 (C-3/C-14), 132.4, 132.1 (C-5/C-12), 124.1, 123.2 (C-2/C-15), 120.3, 119.9 (C-6/C-11), 115.1, 115.0 (C-4/C-13), 77.1 (C-18), 67.3 (C-9), 62.2 (C-8), 50.9 (C-17), 49.0 (C-21), 22.0 (C-20), 16.5 (C-19).

7b(II) (Found: C, 61.4; H, 5.6; N, 6.4; Co, 13.6. Calc for $C_{21}H_{23}N_2O_3Co$: C, 61.5; H, 5.65; N, 6.8; Co, 14.4%); δ_H (200 MHz; $CDCl_3$) 8.13 (1 H, s, CH=N), 7.89 (1 H, s, CH=N), 7.3–7.0 (6 H, m, arom-H), 6.55 (2 H, m, arom-H), 4.91 (1 H, dd, CoC*H*H), 4.14 (1 H, dd), 3.85 (1 H, m, CHN), 3.26 (1 H, d, CH*H*N), 3.17 (1 H, d, CoCH*H*), 2.68 (3 H, s, OCH_3), 2.32 (1 H, m, C*H*H), 1.51 (1 H, dd, CH*H*), 1.06 (3 H, s, CH_3); δ_C (50.29 MHz; $CDCl_3$) 166.0, 165.9 (C-1/C-16), 165.3 (C-7), 164.0 (C-10), 133.4, 133.0 (C-3/C-14), 132.7 (C-5/C-12), 123.9, 123.4 (C-2/C-15), 119.8, 119.3 (C-6/C-11), 115.3, 115.0 (C-4/C-13), 78.6 (C-18), 68.1 (C-8), 64.7 (C-9), 49.0 (C-17), 48.9 (C-21), 23.0 (C-20), 17.9 (C-19).

(*SPY*-5-54)-{2,2′-[{[1-(2-Methoxy-3-methyltrimethylene-κ*C*^{3})-ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 7c

A solution of **6c** (173 mg, 0.43 mmol) in MeOH (6 cm^3) was processed as described for **6b** to yield **7c** (93 mg, 53%) (Found: C, 61.1; H, 5.7; N, 6.9; Co, 13.9. Calc for $C_{21}H_{23}N_2O_3Co$: C, 61.5; H, 5.65; N, 6.8; Co, 14.4%); δ_H (200 MHz; $CDCl_3$) 7.82 (2 H, s, CH=N), 7.2 (4 H, m, arom-H), 7.0 (2 H, m, arom-H), 6.51 (2 H, m, arom-H), 4.13 (1 H, m, C*H*HN), 4.03 (1 H, dd, CoCH), 3.85 (1 H, br s, CHN), 3.38 (1 H, m, CH*H*N), 3.17 (3 H, s, OCH_3), 2.82 (1 H, m, CHO), 2.11 (1 H, m, C*H*H), 1.23 (1 H, m, CH*H*), 0.24 (3 H, d, CH_3); δ_C (50.29 MHz; $CDCl_3$) 166.1, 165.7 (C-1/C-16), 165.0 (C-7), 162.8 (C-10), 133.2, 133.1 (C-3/C-14), 132.7, 132.5 (C-5/C-12), 123.5, 123.0 (C-2/C-15), 119.9, 119.6 (C-6/C-11), 115.2, 114.8 (C-4/C-13), 83.2 (C-18), 67.4 (C-9), 62.5 (C-8), 57.2 (C-21), 42.0 (C-17), 30.8 (C-19), 23.7 (C-20).

(*SPY*-5-54)-{2,2′-[{[1-(3-Methoxytetramethylene-κ*C*^{4})ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 8 and (*SPY*-5-54)-{2,2′-[{[1-(3-methoxymethyl-trimethylene-κ*C*^{3})ethane-1,2-diyl]bis(nitrilomethylidyne)}-diphenolato](3−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 9

A solution of **6d** (0.78 g, 2.1 mmol) in MeOH (150 cm^3) was oxidised during 8 h as described for **6a**, yielding a mixture of isomers **8** and **9** (ratio 2 : 1) (0.76 g, 90%). Purification of 150 mg of this mixture was achieved by preparative TLC (SiO_2, 5% MeOH in CH_2Cl_2).

8 (69 mg, 46%) (Found: C, 60.1; H, 5.7; N, 6.8; O, 12.7. Calc for $C_{21}H_{23}N_2O_3Co\cdot 0.5\ H_2O$: C, 60.1; H, 5.8; N, 6.7; O, 13.35%); δ_H (200 MHz; $CDCl_3$) 8.07 (1 H, s, CH=N), 7.91 (1 H, s, CH=N), 7.26 (4 H, m, arom-H), 7.08 (2 H, dd, arom-H), 6.60 (2 H, m, arom-H), 4.89 (1 H, m, CoC*H*H), 4.48 (1 H, m, NC*H*H), 4.10 (1 H, m, CHN), 3.60 (1 H, m, NCH*H*), 3.23 (3 H, s, OCH_3), 2.70 (2 H, m, CoCH*H*/C*H*O), 1.85 (3 H, m, C*H*$_2$C*H*H), 1.25 (1 H, m, CH*H*); δ_C (50.29 MHz, DMSO-*d*$_6$) 165.8, 165.3 (C-1/C-16), 164.1 (C-7), 162.6 (C-10), 133.4, 133.0 (C-3/C-14), 132.3, 132.1 (C-5/C-12), 121.9, 121.1 (C-2/C-15), 120.6, 119.9 (C-6/C-11), 112.6, 111.9 (C-4/C-13), 84.5 (C-19), 65.3 (C-9), 62.4 (C-8), 54.5 (C-21), 35.8 (C-17), 31.4 (C-18), 22 (C-20). The X-ray structure of **8** is described in ref. 10.

9 (36 mg, 24%): δ_H (200 MHz; $CDCl_3$) 8.15 (1 H, s, CH=N), 7.97 (1 H, s, CH=N), 7.30 (4 H, m, arom-H), 7.15 (2 H, dd, arom-H), 6.64 (2 H, m, arom-H), 4.25 (1 H, m, NC*H*H), 3.93 (1 H, m, CHN), 3.77 (1 H, m, CoCH), 3.53 (1 H, m, NCH*H*), 3.23 (2 H, d, CH_2O), 3.18 (3 H, s, OCH_3), 1.85 (2 H, m, CH_2), 1.20 (1 H, m, CH*H*), −0.46 (1 H, m, CoCRHC*H*H).

(*SPY*-5-54)-{2,2′-[{[1-(3-Methylidenetetramethylene-κ*C*^{4})-ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-κ^2*N*,*N*′; κ^2*O*,*O*′}cobalt 10

A solution of **6e** (393 mg, 1 mmol) in MeOH (10 cm^3) was stirred in the dark for 2.5 h while being exposed to air. A brown precipitate formed, which was isolated, washed with Et_2O and dried *in vacuo* to yield **10** as a dark green microcrystalline solid (255 mg, 60%) (Found: M$^+$, 391.0857. $[C_{21}H_{20}N_2O_2Co - H]^+$ requires *M*, 391.0857); δ_H (200 MHz, DMSO-*d*$_6$) 8.01 (2 H, s, CH=N), 7.2–7.0 (4 H, m, arom-H), 6.80 (2 H, dd, arom-H), 5.78 (2 H, d, $=CH_2$), 4.44 (1 H, d, CoC*H*H), 4.08 (2 H, m, NC*H*HC*H*N), 3.85 (1 H, d, CoCH*H*), 3.62 (1 H, m, NCH*H*), 2.28 (1 H, m, C*H*H), 1.93 (1 H, m, CH*H*), 1.83–1.53 (2 H, m, CH_2); δ_C (50.29 MHz, DMSO-*d*$_6$) 165.4, 160.4 (C-1/C-16), 163.5, 162.8 (C-7/C-10), 133.3, 133.1 (C-3/C-14), 132.0 (C-5/C-12), 122.0, 121.2 (C-2/C-15), 120.7, 119.8 (C-6/C-11), 112.6, 111.9

(C-4/C-13), 104.4 (C-21), 66.2 (C-9), 64.7 (C-19), 62.8 (C-8), 30.7 (C-18); C-17 and C-20 were not observed.

(*SPY*-5-54)-{2,2′-[{[1-(2-Methylidenetrimethylene-κ*C*^{3})ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 11

Oxygen was bubbled through a solution of **6b** (11 mg, 29 μmol) in CD_3OD (0.45 cm^3) containing 0.5 μL of a DCl solution in D_2O (11 mM, 5.5 × 10^{-3} μmol) for 12 min. After 7 days, a precipitate was isolated, washed with cold MeOH and dry Et_2O, dried *in vacuo* (5.3 mg, 48%) and identified as **11** (Found: C, 63.9; H, 5.3; N, 7.9; Co, 14.9. Calc for $C_{20}H_{19}N_2O_2Co$: C, 63.5; H, 5.1; N, 7.4; Co, 15.6%); δ_H (200 MHz; DMSO-*d*$_6$) 8.17 (1 H, s, CH=N), 7.83 (1 H, s, CH=N), 7.21–7.05 (4 H, m, arom-H), 6.82 (2 H, dd, arom-H), 6.44–6.32 (2H, m, arom-H), 4.84 (1 H, s, =C*H*H), 4.77 (1 H, s, =CH*H*), 4.12 (2 H, s, $CoCH_2$), 4.01 (1 H, m, NCH), 3.78 (1 H, dd, NC*H*H), 3.43 (1 H, d, NCH*H*), 2.45 (1 H, m, C*H*H), 2.25 (1 H, m, CH*H*).

Methoxo{[2,2′-{[ethane-1,2-diylbis(nitrilomethylidyne)}-diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt

In an NMR tube, Co^{II}(salen) (16 mg, 49 μmol) was dissolved in a mixture of CD_3OD (0.10 cm^3) and CH_3OH (0.40 cm^3). Oxygen was bubbled through the red suspension for 15 min. A brown solution had formed. ^{1}H and ^{13}C NMR spectra were recorded at 25 and −80 °C. Spectra at both temperatures were similar and showed that (MeO)Co^{III}(salen) had been formed; a resonance for the methoxy ligand was not observed; δ_H (200 MHz) 8.10 (2 H, s, CH=N), 7.5–7.25 (6 H, m, arom-H), 6.60 (2 H, m, arom-H), 4.41 (4 H, s, NCH_2CH_2N); δ_C (100.63 MHz) 168.5 (CH=N), 167.7 (qC-O), 135.5, 135.4, 123.8, 115.6 (arom-CH), 120.2 (qC), 59.6 (NCH_2). The following data for (MeO)Co(salen) were not previously reported: δ_H (200 MHz; DMSO-*d*$_6$) 8.05 (2 H, s, CH=N), 7.35–7.10 (6 H, m, arom-H), 6.47 (2 H, m, arom-H), 3.87 (4 H, m, NCH_2CH_2N), 1.21 (3 H, s, $CoOCH_3$); δ_C (50.29 MHz; DMSO-*d*$_6$) 166.7 (CH=N), 164.5 (qC-O), 133.8, 132.9, 121.9, 112.5 (arom-CH), 119.2 (qC), 57.8 (NCH_2), 51.9 ($CoOCH_3$).

Oxidation of 6a in alkaline methanol: formation of methoxo-{[2,2′-{(1-prop-2-enylethane-1,2-diyl)bis(nitrilomethylidyne)}-diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt(III) 12a

In an NMR tube, Co(salen) complex **6a** (18 mg, 49 μmol) was dissolved in a mixture of CD_3OD (0.10 cm^3) and CH_3OH (0.40 cm^3) containing 2 μL of a solution of NaOD (40%, 30 μmol) in D_2O. Oxygen was bubbled through the red solution for 1 min by which time the colour had changed to brown. ^{1}H and ^{13}C NMR indicated that (MeO)Co^{III}(salen) complex **12a** had been formed. Neither at 25 °C nor at −75 °C was a resonance for the expected cobalt-bound methoxy ligand observed; δ_H (200 MHz; CD_3OD–CH_3OH, 298 K) 8.02 (1 H, s, CH=N), 7.99 (1 H, s, CH=N), 7.45–7.28 (6 H, m, arom-H), 6.56 (2 H, m, arom-H), 6.05 (1 H, m, CH=), 5.28 (2 H, m, $=CH_2$), 4.3–3.8 (3 H, m, NCH_2CHN), 3.1–2.65 (2 H, m, CH_2); δ_C (100.63 MHz, 298 K) 168.3, 167.4 (C-7/C-10), 167.5 (C-1/C-16), 135.9 (C-18), 135.4 (C-5/C-12), 135.3, 135.0 (C-3/C-14), 123.8, 123.7 (C-2/C-15), 120.5, 120.2 (C-6/C-11), 119.2 (C-19), 115.4, 115.2 (C-4, C-13), 67.9 (C-9), 64.4 (C-8), 37.9 (C-17).

Methoxo{[2,2′-{[1-(2-methylprop-2-enyl)ethane-1,2-diyl]bis-(nitrilomethylidyne)}diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 12b

A solution of **6b** (98 mg, 0.259 mmol) in MeOH (25 cm^3) was stirred under air for 1 h at room temperature. The resulting brown solution was evaporated to dryness *in vacuo* at 30 °C. Crude product **12b** was obtained in almost quantitative yield (106 mg, 100%) as a mixture of two diastereomers (ratio *ca.* 2 : 1). Attempts at purification by chromatography or crystallization failed due to instability; δ_H (200 MHz; DMSO-*d*$_6$) 8.07 (s, CH=N, *maj*), 8.02 (s, CH=N, *min*), 7.91 (s, CH=N, *min*), 7.80 (s, CH=N, *maj*), 7.5–7.1 (6 H, m, arom-H), 6.45 (2 H, m, arom-H), 4.88 (1 H, br s, C*H*H=, *min*/*maj*), 4.74 (br s, CH*H*=, *min*), 4.65 (br s, CH*H*=, *min*), 4.29–3.63 (3 H, m, NCH_2CHN), 2.6–2.4 (2 H, m, CH_2), 1.87 (3 H, s, CH_3), 1.25 (s, OCH_3, *maj*), 1.14 (s, OCH_3, *min*).

Methoxo{[2,2′-{[1-(3-methylprop-2-enyl)ethane-1,2-diyl]bis-(nitrilomethylidyne)}diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 12c

A solution of **6c** (100 mg, 0.264 mmol) in MeOH (25 cm^3) was processed as for **6b** to give crude product **12c** in almost quantitative yield (105 mg, 97%) as a mixture of two diastereomers (ratio *ca.* 1 : 1). Attempts at purification by chromatography or crystallization failed due to instability; δ_H (200 MHz; DMSO-*d*$_6$) 8.10, 8.02, 8.01, 7.91 (4 H, s, 4 × CH=N), 7.5–7.0 (6 H, m, arom-H), 6.48 (2 H, m, arom-H), 5.44 (2 H, br s, CH=CH), 4.3–3.4 (3 H, m, NCH_2CHN), 2.6–2.4 (2 H, m, CH_2), 1.68 (3 H, s, CH_3), 1.32 (s, OCH_3), 1.27 (s, OCH_3).

{[2,2′-[(1-Prop-2-enylethane-1,2-diyl)bis(nitrilomethylidyne)]-diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}(2,2,2-trichloroethoxo)cobalt 13

A solution of **6a** (0.17 g, 0.47 mmol) and CCl_3CH_2OH (0.90 cm^3, 9.4 mmol, 20 equiv.) in CH_2Cl_2 was stirred for 8 h while being exposed to air. The dark brown solution was concentrated and Et_2O was added. A brown solid precipitated, which was filtered, washed with dry Et_2O and dried *in vacuo* (0.16 g, 66%). The ^{1}H NMR spectrum showed the presence of two diastereomers of **13** in a ratio of 1 : 1 (Found: C, 49.6; H, 4.1; N, 5.6; Cl, 20.5. Calc for $C_{21}H_{20}Cl_3N_2O_3Co$: C, 49.1; H, 3.9; N, 5.45; Cl, 20.7%); δ_H (200 MHz; DMSO-*d*$_6$) 8.11, 8.09, 7.96, 7.91 (2 H, 4 × s, CH=N), 7.4–7.15 (6 H, m, arom-H), 6.50 (2 H, m, arom-H), 5.85 (1 H, m, CH=), 5.10 (2 H, m, $=CH_2$), 4.2–3.7 (3 H, m, NCH_2CHN), 2.71 (2 H, s, $CoOCH_2$), 2.50 (2 H, m, CH_2); δ_C (50.29 MHz; C_5D_5N) 167.3, 167.2 (C-1/C-16), 166.0, 165.3 (C-7/C-10), 133.9 (C-3/C-14), 133.8 (C-5/C12), 133.8 (C-18), 122.1, 122.0 (C-2/C-15), 119.4 (C-19), 118.0, 117.8 (C-6/C-11), 113.3, 113.1 (C-4/C-13), 81.1 (C-21), 75.6 (C-20), 66.4 (C-9), 63.1 (C-8), 38.8 (C-17).

Iodo{[2,2′-[(1-prop-2-enylethane-1,2-diyl)bis(nitrilomethylidyne)]diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt 18

Cobalt(II) complex **6a** (528 mg, 1.44 mmol) and I_2 (183 mg, 0.72 mmol) were dissolved in THF (20 cm^3) and the resulting brown-black solution was stirred at room temperature for 1.5 h. After removal of the solvent *in vacuo*, the black residue was washed thoroughly with dry Et_2O and dried *in vacuo* to give **18** as a black solid (639 mg, 90%). All NMR data were identical to those of *in situ* oxidised **6a** (*vide supra*) (Found: M$^+$, 365.0704. $[C_{19}H_{18}IN_2O_2Co - I]^+$ requires *M*, 365.0700).

{[2,2′-[(1-Prop-2-enyl)ethane-1,2-diyl)bis(nitrilomethylidyne)]-diphenolato](2−)-κ^2*N*,*N*′;κ^2*O*,*O*′}cobalt tetraphenylborate 19

Compound **18** (383 mg, 0.777 mmol) was dissolved in acetonitrile (15 cm^3). A solution of $AgBPh_4$ (1 equiv.) in acetonitrile (15 cm^3) was added, upon which the dark brown solution of the cobalt(III) complex turned light green-brown and a light yellow precipitate formed. After stirring for 30 min in the dark, the mixture was filtered and the filtrate was evaporated to dryness *in vacuo* to give **19** (431 mg, 81%) as a green-brown solid. Attempts at crystallization in various solvents failed; δ_H (200 MHz; DMSO-*d*$_6$) 8.35 (1 H, s, CH=N), 8.25 (1 H, s, CH=N), 7.9–7.0 (26 H, m, arom-H), 6.75 (2 H, m, arom-H), 5.9 (1 H, m, CH=), 5.25 (2 H, m, $=CH_2$), 4.5–3.9 (3 H, m, NCH_2CHN), 2.50 (2 H, m, CH_2).

(*SPY*-5-54)-{2,2′-[{[1-(2-(2-Hydroxyethoxy)trimethylene-κC^3)-ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenolato](3−)-$\kappa^2 N,N'$;$\kappa^2 O,O'$}cobalt 20

Complex **6d** (0.21 g, 0.55 mmol) was dissolved in a 1 : 1 mixture of THF and ethylene glycol (10 cm^3). The red-brown solution was stirred for 5 days while being exposed to air. THF was removed *in vacuo* and water was added to give a brown precipitate, which was filtered and dried *in vacuo*. The crude product was purified by column chromatography (Al_2O_3; 2% MeOH in CH_2Cl_2) to give a green solid (0.14 g, 58%). This was shown by NMR spectroscopy to consist of a mixture of isomers **20** and **21** in a ratio of *ca.* 3 : 1. Pure **20** was obtained by selective crystallization from CH_2Cl_2; δ_H (400 MHz; DMSO-d_6) 8.07 (1 H, s, CH=N), 7.95 (1 H, s, CH=N), 7.14 (2 H, dd, H-3/H-14), 7.08 (2 H, dd, H-5/H-12), 6.79 (2 H, dd, H-2/H-15), 6.40 (1 H, dd, H-4), 6.36 (1 H, dd, H-13), 4.35 (1 H, t, OH), 4.18 (1 H, br s, CoC*H*H), 3.93 (2 H, m, NC*H*HC*H*N), 3.48 (1 H, m, NCH*H*), 3.37–3.11 (3 H, m, HOC*H*$_2$C*H*H), 2.85 (1 H, m, CHO), 2.47 (1 H, m, CoCH*H*), 1.85 (1 H, m, C*H*H), 1.69 (2 H, m, CH*H*-C*H*H), 1.23 (1 H, m, CH*H*CHO); δ_C (100.63 MHz; DMSO-d_6) 166.0, 165.6 (C-1/C-16), 164.2, 162.7 (C-7/C-10), 133.5, 133.2 (C-3/C-14), 132.4, 132.3 (C-5/C-12), 122.1, 121.3 (C-2/C-15), 120.9, 120.1 (C-6/C-11), 112.7, 112.1 (C-4/C-13), 83.5 (C-19), 69.1 (C-21), 65.5 (C-9), 62.7 (C-8), 60.6 (C-22), 36.4 (C-17), 31.9 (C-18), 22.7 (C-20).

Crystal structure determination of bridged [β-(2-hydroxyethoxy)-butyl]Co(salen) complex 20 ||

Single crystals of **20** were grown selectively from a saturated solution of **20** and **21** in dichloromethane. X-ray data were collected on an Enraf-Nonius CAD4T diffractometer (Mo-Kα, Rotating Anode, 150 K) for a needle shaped red crystal.

$C_{22}H_{25}N_2O_4Co\cdot CH_2Cl_2$, $M = 525.32$, monoclinic, $P2_1/c$, $a = 12.4467(14)$, $b = 11.4978(7)$, $c = 19.0943(18)$ Å, $\beta = 125.340(7)°$, $Z = 4$, μ(Mo-Kα) = 1.04 mm^{-1}, 4578 reflections scanned ($\theta_{max} = 25°$). 3932 Unique reflections (R(int) = 0.07) of which 2223 greater than $2\sigma(i)$.

The structure was solved by direct methods[38] using SHELXS86 and refined[39] on F^2 with SHELXL96. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. The CH_2Cl_2 molecule of crystallization was refined with a disorder model. Convergence was reached at $R = 0.0655$ ($wR_2 = 0.133$, $S = 1.02$).

|| CCDC reference number 207/403. See http://www.rsc.org/suppdata/p1/b0/b000196l/ for crystallographic files in .cif format.

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