Intramolecularly Alkylated Salen Complexes: New Models for Coenzyme B_{12} with a Cobalt-to-Ligand Carbon Bridge

Bert van Arkel,†,[a] Juul L. van der Baan,*,[a] Sijbe Balt,[a] Friedrich Bickelhaupt,[a] Martinus W. G. de Bolster,[a] Irene E. Kingma,‡,[a] Gerhard W. Klumpp,[a] Jan W. E. Moos[a] and Anthony L. Spek[a]
[a] Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
[b] Vakgroep Kristal- en Structuurchemie, Universiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

The synthesis of H_2salen {2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenol} derived models **1** for coenzyme B_{12} with a carbon bridge between the ligand and cobalt has been accomplished by condensation of salicylaldehyde and ω-substituted 1,2-diamines **8** followed by complexation with Co^{II}, reduction to Co^{I} complexes, and intramolecular alkylation. The structures of intramolecularly alkylated Co(salen) complexes with a bridge of three, **1b**, and of four methylene groups, **1c**, have been investigated by NMR spectroscopy and determined by X-ray crystallography.

Since Schrauzer reported the successful alkylation of cobaloximes[1] and showed that the chemistry of alkylcobaloximes and coenzyme B_{12} are closely similar,[2] numerous other small organocobalt complexes have been developed as models for coenzyme B_{12}. Many of these models allow a systematic change of the cobalt atom environment so that information regarding relationships between structural factors on the one hand, and physical and chemical properties on the other hand can be obtained. The three most common coenzyme B_{12} model complexes are depicted in Fig. 1.

The study of these and other model complexes[3] has provided the basis of our current understanding of the characteristics of the cobalt–carbon σ-bond and the chemistry of coenzyme B_{12}.

It is widely accepted now that the essential first step in coenzyme B_{12}-catalysed rearrangements is the homolytic dissociation of the Co–C σ-bond of B_{12} to generate cob(II)alamin and a 5′-deoxyadenosyl radical. This radical then abstracts a hydrogen atom from the substrate and a 1,2-rearrangement ensues.[4] The coenzyme B_{12} Co–C bond cleavage in the holoenzyme has been shown to be *ca.* 10^{13} times faster as compared to the cleavage of this bond in the absence of the enzyme.[5] It has been postulated that this enzyme-accelerated homolysis is triggered by conformational changes in both the enzyme and the enzyme–bound coenzyme upon accommodation of the substrate, *e.g.* upward conformational distortion of the corrin ring of B_{12}, distortion of angles, tilting and/or lengthening of the Co–C bond, or changes in the position of the axial 5,6-dimethylbenzimidazole ligand.[6] Very recently, it has been demonstrated for the B_{12}-dependent methylmalonyl-CoA-mutase reaction that homolysis of the Co–C bond only occurs *after* addition of the substrate.[7] However, the precise nature of the factors that promote the dissociation process are far from fully understood. A second important aspect of the mechanism of B_{12}-dependent enzymatic rearrangements concerns the question whether a substrate radical, once formed by H-abstraction by the adenosyl radical, undergoes 1,2-rearrangement as free radical[8] or substrate-derived organocobalt intermediates are the rearranging species.[9] Currently, the notion of protein-bound radicals[10] (without any involvement of Co in the rearrangement step itself) seems to be favoured but is by no means undisputed.[9]

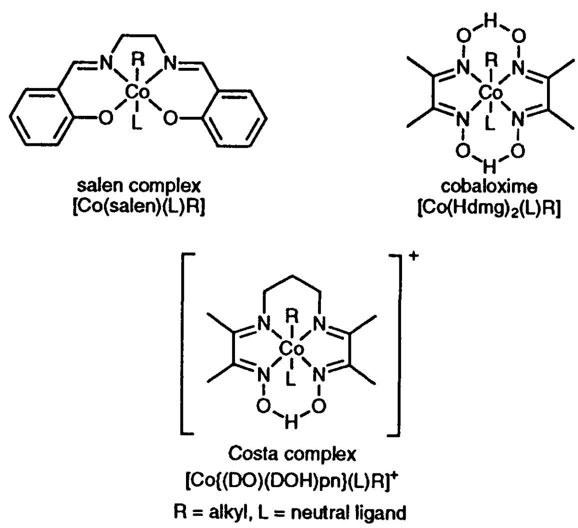

Fig. 1 Model complexes for coenzyme B_{12}

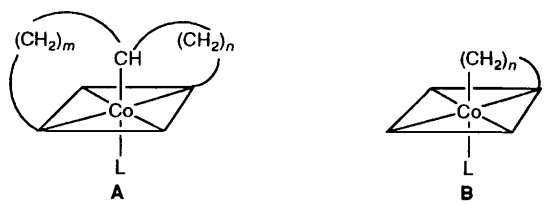

Fig. 2 Schematic structures of two types of intramolecularly alkylated coenzyme B_{12} model complexes

In order to gather further information on these issues and to contribute to the solution of the questions raised we decided to synthesize and study model organocobalt complexes in which the cobalt-bound carbon atom is linked to the equatorial ligand by a polymethylene bridge. In Fig 2, schematic structures of two basic types of intramolecularly alkylated coenzyme B_{12} model complexes are depicted. These model compounds can mimic possible conformational distortions of the coenzyme upon binding of a substrate, *e.g.* tilt of the cobalt–carbon bond with respect to the equatorial plane and bending of the corrin ring system towards the axial adenosyl group. Comparison of the dissociation energies of the Co–C bonds in a series of these

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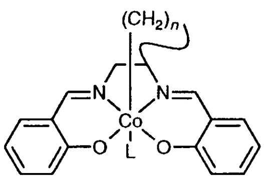


Fig. 3 Intramolecularly alkylated Co(salen) complexes **1**

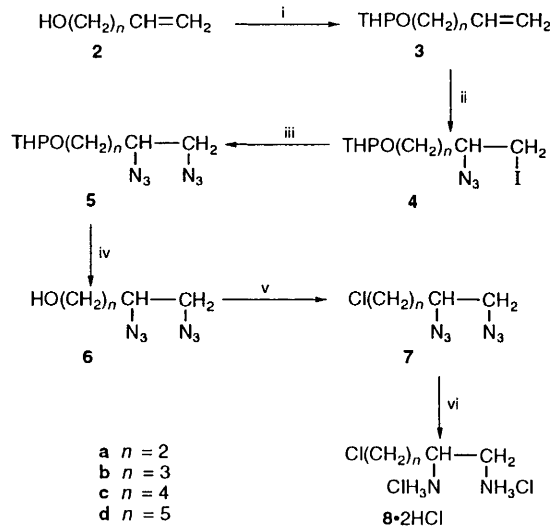
complexes differing by the number of methylene groups in the bridge, will provide insight into the relevance of these factors governing the strength of the Co–C bond. The same models might also give information on the mechanism of the 1,2-rearrangement of the substrate radical. In resemblance of biological systems in which the substrate radical is contained inside the active site of the enzyme together with cob(II)alamin, the carbon radical that results from homolysis of the Co–C bond in these model complexes is retained in the proximity of a Co^{II}-complex. Comparison of the properties of these species to those of free radicals might help to answer the question concerning the involvement of Co^{II} in B_{12}-catalysed 1,2-rearrangements. Cobaloxime-derived model compounds of general structure A (Fig. 2) have been synthesized by Retéy who has shown that in a methylmalonic acid ester derivative of such a complex an efficient 1,2-radical rearrangement to succinic acid ester can be induced.[11] In the present paper, we report[12] on the synthesis and structure of intramolecularly alkylated model complexes **1** (Fig. 3) based on the salen ligand (type B in Fig. 2) which are synthetically more readily accessible and, in some respect,[3] better models for cobalamins than cobaloximes.

Results and Discussion

Synthesis.—Alkylcobalt(III)(salen) complexes are generally prepared by condensation of salicylaldehyde (2 equiv.) with ethylenediamine (1 equiv.)[13] followed by complexation with a cobalt(II) salt under anaerobic conditions[14] and alkylation, either *via* the Co^{I}(salen) complex and a suitable alkyl halide[15] or *via* the Co^{III} complex and a Grignard reagent.[16] Accordingly, the synthesis of intramolecularly alkylated salen complexes **1** was accomplished by condensation of salicylaldehyde and an alkane-1,2-diamine ω-substituted with a suitable leaving group, followed by complexation with Co^{II} and intramolecular alkylation.

Several different procedures for the preparation of primary vicinal diamines have been reported in the literature,[17] none of which, however, seemed particularly suited for the synthesis of the desired ω-substituted alkane-1,2-diamines; therefore, we have developed a general method in which the required 1,2-diamines are synthesized by reduction of 1,2-diazides which, in turn, are prepared in a two-step procedure from the corresponding alkenes. From examination of molecular models, complexes **1** (Fig. 3) with a bridge containing, respectively, two, three, four and five methylene groups (*i.e.* n = 2–5) seemed most promising from a preparative point of view. Therefore, the easily available ω-alken-1-ols **2** (n = 2–5) were selected as convenient starting materials (Scheme 1).

Treatment of **2** with dihydropyran and a catalytic amount of pyridinium toluene-*p*-sulfonate gave the corresponding ω-(2-tetrahydropyranyloxy)alkenes **3**. Addition of iodine azide, prepared *in situ* from sodium azide and iodine monochloride, produced 2-azido-1-iodo-ω-(tetrahydropyran-2-yloxy)alkanes **4**,[18] contaminated with a small amount of the 1-azido-2-iodo isomers. Without purification, crude **4** was then converted into the diazides **5** through reaction with sodium azide in a boiling mixture of benzene and dimethylformamide.[19] After column chromatographic purification, **5** was treated with an acidic cation-exchange resin in methanol[20] to remove the protecting tetrahydropyranyl group and giving the 1,2-diazido-ω-hydroxyalkanes **6** in almost quantitative yield.



Scheme 1 *Reagents and conditions:* i, DHP, cat. toluene-*p*-sulfonate, CH_2Cl_2, 20 h, room temp.; ii, ICl, NaN_3, MeCN, 20 h, room temp.; iii, NaN_3, C_6H_6, DMF, 20 h, reflux; iv, Dowex 50X8, MeOH, 3 h, room temp.; v, $SOCl_2$, $CHCl_3$, DMF, 6 h, room temp.; vi, PPh_3, H_2O, HCl, THF, 6 h, room temp.

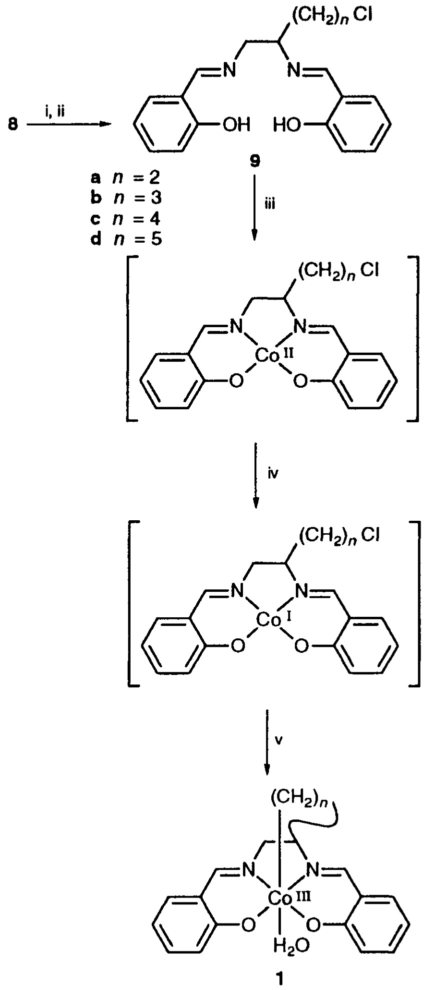
The latter were treated with thionyl chloride in a mixture of chloroform and dimethylformamide[21] to yield the ω-chloro-1,2-diazidoalkanes **7** which were purified by column chromatography. The desired ω-chloroalkane-1,2-diamines **8** were then obtained by treatment of **7** with triphenylphosphine and water[22] in the presence of an amount of hydrochloric acid sufficient for formation of dihydrochloride salts **8**•2HCl, thus protecting the diamines **8** from intramolecular alkylation to give cyclic secondary amines.

Condensation of the diamines **8** with salicylaldehyde (2 equiv.) to afford the substituted H_2salen ligands **9** was effected by rapidly mixing an ice-cold solution of **8**•2HCl in aqueous ethanol with aqueous sodium acetate at 0 °C and adding the resulting mixture *immediately* to a rapidly stirred hot solution of salicylaldehyde in ethanol[23] (Scheme 2). Under these conditions, the undesired ring-closure of the free diamines **8** is largely prevented so that H_2salen ligands **9** were obtained as highly viscous liquids in reasonable yield and purity, the only contamination being salicylaldehyde. Since purification by chromatography invariably led to partial decomposition, the crude ligands were used in the next step.

Complexation with Co^{II} and, subsequently, reduction to the Co^{I} complexes followed by immediate intramolecular alkylation was carried out in a one-pot reaction using a modified procedure of Schrauzer.[15] Treatment of **9** with cobalt dichloride in de-aerated alkaline methanol gave Co^{II}(salen) complexes which, without isolation, were reduced to the corresponding Co^{I} complexes by sodium borohydride in the presence of a small amount of palladium chloride (Scheme 2). The obtained crude complexes were purified by precipitation from methanol by water and recrystallization from wet acetone.

Substantially higher yields in the reduction/alkylation step were achieved by increasing the molecular ratio of sodium hydroxide relative to cobalt chloride from approximately 6 : 1 to 45 : 1 and by reducing the concentration of the cobalt complex in the reaction mixture by a factor of 15 as compared to the conditions originally reported by Schrauzer.

The brown–red microcrystalline solids obtained from the



Scheme 2 *Reagents and conditions:* i, NaOAc, H_2O, EtOH, 0 °C; ii, salicylaldehyde, EtOH, 15 min, 60 °C; iii, NaOH, $CoCl_2 \cdot 6H_2O$, MeOH, 5 min, room temp.; iv, $NaBH_4$, $PdCl_2$; v, 1 h, room temp.

ligands **9b** and **9c** displayed complex ^{1}H NMR spectra with relatively sharp, well-resolved signals. These spectra were too complicated, however, for straightforward interpretation (see next section) but clearly demonstrated the products to be diamagnetic alkylcobalt(III) complexes.[24] In non-coordinating solvents such as chloroform or toluene these complexes dissolve to give an intense green colour and display UV–VIS absorption at *ca.* 650 nm ($\varepsilon \approx 1.3 \times 10^3$) which is characteristic for five-coordinate species of [Co^{III}(salen)alkyl] complexes.[12] The brown–red complexes, therefore, probably contain water as the sixth ligand which is lost on dissolution in non-coordinating solvents. Likewise, on drying *in vacuo*, green five-coordinate complexes are formed. Mass spectrometric analysis (FAB as well as EI) of the dried compounds clearly showed the molecular ions of five-coordinated **1b** and **1c** at the calculated values *m*/*z* 366, respectively *m*/*z* 380, thus proving the monomeric structure of these complexes. Fragment ions originating from dimeric or oligomeric complexes were not observed.

On the basis of this evidence, it was concluded that intramolecularly alkylated complexes **1b** and **1c** had indeed been synthesized from the ligands **9b** and **9c**, respectively. Decisive proof was obtained by extensive ^{1}H and ^{13}C NMR investigations and, after suitable crystals had been obtained, X-ray structural analysis (see following sections).

Attempts to prepare intramolecularly alkylated salen complexes starting from the ligands **9a** and **9d** were not successful. The UV–VIS spectrum of the crude product obtained from **9a**, a brown solid, displayed absorption characteristic of an alkylated five-coordinate Co^{III}(salen) complex. However, the ^{1}H NMR spectrum showed two types of signals: a number of small sharp signals, which were reminiscent of the signals observed in the spectra of **1b** and **1c**, and several broad signals indicative of the presence of a paramagnetic cobalt(II) complex. Recrystallization of the crude product in order to remove these paramagnetic impurities resulted in the disappearance of both the absorption band at *ca.* 650 nm and the sharp resonances in the ^{1}H NMR spectrum. It was concluded that the crude product probably did contain a certain amount of an alkylcobalt(III) complex which is, however, too unstable to be isolated at room temperature. Supposedly due to excessive strain in the five-membered ring containing cobalt, it decomposes into a paramagnetic cobalt(II) complex by homolytic cleavage of the cobalt–carbon bond.

The product obtained from the ligand **9d**, a dark-brown solid, proved to be a paramagnetic cobalt(II) complex. The UV–VIS spectrum showed no absorption band near 650 nm and the ^{1}H NMR spectrum displayed only the characteristic broad resonances of a paramagnetic complex. Probably, the strain in the cobalt-containing eight-membered ring is too high to permit an intramolecularly alkylated salen complex with a bridge of five methylene groups to be stable at room temperature.

Attempts to prepare the complexes **1a** and **1d** at lower temperature have not yet given significantly better results.

^{1}H *and* ^{13}C *NMR Spectroscopic Investigations*.—The ^{1}H NMR spectral data of the new intramolecularly bridged complexes **1b** and **1c** in deuteriochloroform are tabulated in Table 1. For comparison, data for [Co(salen)butyl] **10** are also given.*

The reasonably sharp NMR peaks indicate that **1b** and **1c**, like **10** are diamagnetic organocobalt low-spin d^6 systems. The asymmetric structures of **1b** and **1c** are evidenced by the non-equivalency of all geminal protons, resulting in ^{1}H NMR spectra much more complicated than those of **10** although many similarities exist. Use of the NOESY technique facilitated the interpretation of these spectra considerably (see Fig. 4).

For both **1b** and **1c** the following applies (the carbon and hydrogen atoms are identified by the computer numbering system in the X-ray structure analysis, see Fig. 4 and next section). The singlet signals in the lowfield region are assigned to the imine protons 7-H and 10-H which are differentiated by the significant NOE found with the ethanediyl bridge protons 8-H$_a$ and 9-H, respectively. The aromatic protons are found between δ 6.56 and 7.28. Of these hydrogen atoms, 4-H and 13-H appear at the highfield boundary and 5-H and 12-H are found as doublets around δ 7. The signals of the methine (9-H) and methylene (8-H$_{a,b}$) protons of the ethanediyl units are located in the same region as the protons of the cobalt-bonded methylene group. The chemical shifts of the latter are δ 3.96 (19-H$_b$) and 4.91 (19-H$_a$) for **1b**, respectively 3.16 (20-H$_a$) and 5.06 (20-H$_b$) for **1c**. In butylCo(salen) **10**, the corresponding chemical shift is δ 3.55.

The low chemical shift of the α-protons which is exhibited by all alkylCo(salen) complexes is not only due to the inductive effect of the cobalt atom—in most other alkyl cobalt complexes, *e.g.* alkylcobaloximes and alkyl Costa complexes, the α-protons resonate at much higher field—but mainly to the *cis* effect of the equatorial ligand. The large difference between the chemical shifts of the two geminal α-protons of **1b** and **1c** can be explained by the different positions of these protons with respect to the equatorial system. The geminal coupling between these protons is relatively small (*ca.* 5 Hz), a phenomenon that has also been reported for α-protons of other organometallic compounds and

* ^{1}H NMR data of a six-coordinated Co(salen)butyl derivative have been published for samples measured in a coordinating solvent (dimethyl sulfoxide).[25] Our data are for a five-coordinate complex in a non-coordinating solvent (chloroform).

Table 1 1H NMR spectral data of **1b**, **1c** and **10** in $CDCl_3$ (chemical shifts δ in ppm; coupling constants *J* in Hz; mult. = multiplicity; for numbering, see Fig. 4)

	1b				1c					10			
Proton	δ	mult.	*J*		δ	mult.	*J*		Proton	δ	mult.	*J*	
2-H/15-H	7.28	m			7.24	m			2,2'-H	7.28	m		
3-H/14-H	7.28	m			7.24	m			3,3'-H	7.28	m		
4-H/13H	6.62	m			6.56	m			4,4'-H	6.57	m		
5-H	7.10	dd	$J_{5,4}$	7.8	6.97	dd	$J_{5,4}$	7.4	5,5'-H	7.06	dd		
			$J_{5,3}$	1.6			$J_{5,3}$	1.4					
7-H	7.95	s			7.88	s			7,7'-H	7.94	s		
8-H$_a$	3.47	d	$J_{8a,8b}$	13.2	3.58	d	$J_{8a,8b}$	12.5	8,8'-H	3.67	br m		
8-H$_b$	4.23	m	$J_{8b,8a}$	13.2	4.55	m	$J_{8b,8a}$	12.5					
			$J_{8b,9}$	5.6			$J_{8b,9}$	4.9					
9-H	3.98	m	$J_{9,8b}$	5.6	4.15	br s			8.8'-H	4.01	br m		
			$J_{9,17a}$	3.2									
			$J_{9,17b}$	3.6									
10-H	8.19	s			7.96	s							
12-H	7.21	dd	$J_{12,13}$	7.3	7.08	dd	$J_{12,13}$	7.7					
			$J_{12,14}$	1.2			$J_{12,14}$	1.4					
17-H$_a$	2.08	m	$J_{17a,17b}$	13.3	1.87	m			12-H	0.74	t	$J_{12,11}$	7.3
			$J_{17a,9}$	3.2									
			$J_{17a,18a}$	5.6									
17-H$_b$	1.51	m	$J_{17b,17a}$	13.3	1.63	m							
			$J_{17b,9}$	3.6									
			$J_{17b,18b}$	5.7									
			$J_{17b,18a}$	13.3									
18-H$_a$	1.20	m	$J_{18a,18b}$	15.7	1.07	m	$J_{18a,18b}$	12.3	11-H	1.32	m	$J_{11,10}$	7.3
			$J_{18a,17b}$	13.3			$J_{18a,17b}$	12.3				$J_{11,12}$	7.3
			$J_{18a,17a}$	5.6			$J_{18a,19b}$	12.3					
			$J_{18a,19b}$	13.2									
			$J_{18a,19a}$	4.9									
18-H$_b$	−0.49	m	$J_{18b,18a}$	15.7	1.75	m							
			$J_{18b,17b}$	5.7									
			$J_{18b,19b}$	4.9									
19-H$_a$	4.91	m	$J_{19a,19b}$	4.9	−0.63	m	$J_{19a,19b}$	16.3	10-H	0.65	m	$J_{10,9}$	8.4
			$J_{19a,18a}$	4.9			$J_{19a,18b}$	8.4				$J_{10,11}$	7.3
							$J_{19a,20a}$	3.4					
							$J_{19a,20b}$	3.0					
19-H$_b$	3.96	m	$J_{19b,19a}$	4.9	0.81	m	$J_{19b,19a}$	16.3					
			$J_{19b,18b}$	4.9			$J_{19b,18a}$	12.3					
			$J_{19b,18a}$	13.2			$J_{19b,20a}$	13.0					
							$J_{19b,20b}$	4.0					
20-H$_a$	—				3.16	m	$J_{20a,20b}$	5.7	9-H	3.55	t	$J_{9,10}$	8.4
							$J_{20a,19a}$	3.4					
							$J_{20a,19b}$	13.0					
20-H$_b$	—				5.06	m	$J_{20b,20a}$	5.7					
							$J_{20b,19a}$	3.0					
							$J_{20b,19b}$	4.0					

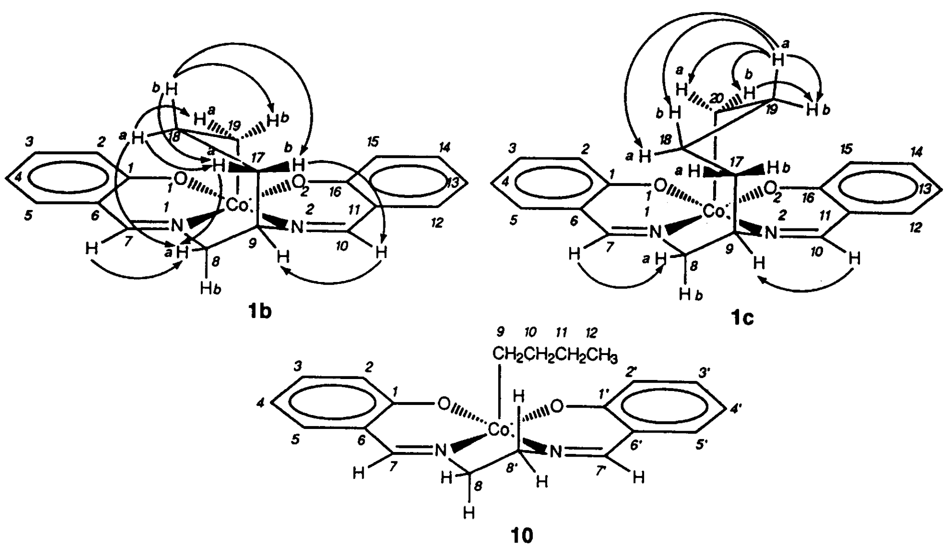


Fig. 4 Numbering system and selected NOE connectivities for **1b**, **1c** and **10**

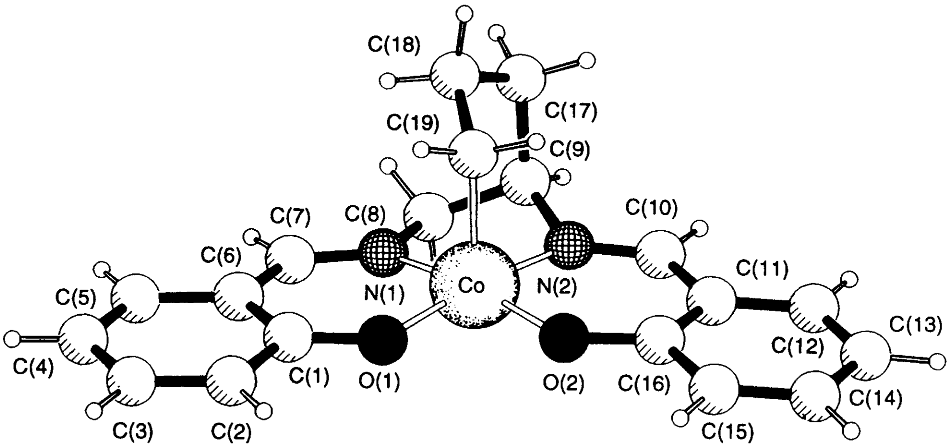


Fig. 5 X-Ray structure of **1b**

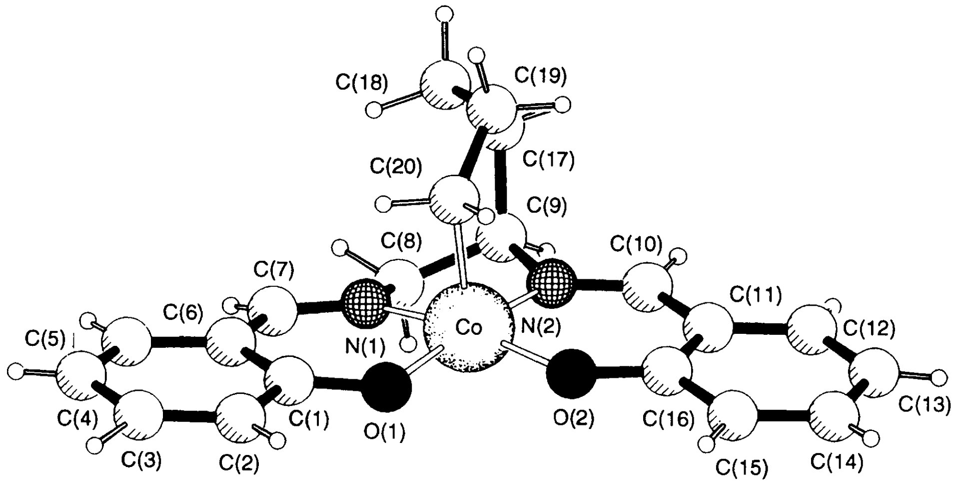


Fig. 6 X-Ray structure of **1c**

has been ascribed to the low electronegativity of the metal ion.[23]

Interestingly, in both **1b** and **1c**, *one* of the β-protons exhibits a large highfield shift (δ −0.49 and −0.63, respectively) as compared to the β-protons in Co(salen)butyl **10** which are found as a single multiplet at δ 0.65. The other β-proton of **1b** and **1c** has a positive δ value (δ 1.20 and 0.81, respectively). Unexpectedly, but unambiguously proven by the NOE-experiments, the protons resonating at highest field are 18-H_b in **1b** and 19-H_a in **1c**, *i.e.* protons which are located most distal from the equatorial plane, anti-periplanar with respect to cobalt. An anisotropic effect of the ring current in the equatorial ligand is, therefore, probably insufficient explanation. As the Co–C bond and the C_β–18-H_b bond, respectively the C_β–19-H_a bond, are almost parallel (see X-ray analysis in the next section) hyperconjugation might be invoked to account for these striking highfield shifts.[26]

The coupling constants found for the protons contained in the oligomethylene bridge of **1b** and **1c** (Table 1) clearly show that the methylene groups are not eclipsed. Between −50 and +50 °C no significant change in chemical shift or coupling constants of the bridge protons is observed. Thus, a rigid zig-zag structure of the carbon bridge seems to be the most likely conformation. However, from the NMR data the position of the β-CH_2 group in the zig-zag, *i.e.* on the side of N(1)–O(1) or on the side of N(2)–O(2) of the equatorial ligand, could not be inferred.

The ^{13}C NMR spectral data of the five-coordinated complexes **1b** and **1c** in deuteriochloroform generally resemble those observed for Co(salen)butyl **10** (see Experimental section) and most resonances could be assigned by comparison. All assignments, especially those of the carbon bridge, were affirmed by CH-COSY. The most interesting feature in these spectra is the broad resonance at highfield, which can easily be assigned to the carbon atom attached to cobalt. This peak is broadened by the large spin quantum number (I = 7/2) and quadrupole moment of cobalt. The large ^{13}C–^{1}H coupling constant for the cobalt-bound methylene group (J_{CH} 158 Hz) indicates non-sp^3-hybridization of this carbon atom.

X-Ray Crystal Structure Analysis.—Crystals of **1b** and **1c** suitable for X-ray structure analysis were obtained by slow evaporation of deuteriochloroform solutions. The crystal structures are shown in Fig. 5 and Fig 6 together with the atom numbering system. Bond lengths and selected angle data are given in Table 2.

The cobalt atom in both **1b** and **1c** is five-coordinated which is quite rare for alkylcobalt Schiff base complexes in the solid state[26] and, as far as we know, unique for cobalt(salen)alkyl complexes. The few examples of the latter which are structurally characterized are six-coordinate species, either by coordination with water, methanol or pyridine[27] or by dimerization *via* a long bond from the oxygen atom of one salen unit to the cobalt atom in a second one, as is the case in [{Co(salen)ethyl}$_2$].[28] The cobalt atom is shifted by 0.136(3) and 0.142(10) Å for **1b** and **1c**, respectively, out of the coordination plane defined by the two nitrogen and two oxygen atoms of the equatorial ligand towards the axial carbon donor atom. Such displacement is usually found in analogous cobalt complexes when the sixth coordination site is vacant.[26,27] In the six-coordinated dimer

Table 2 Selected bond lengths (Å), angles (°) and torsion angles (°) in **1b** and **1c** with e.s.d.s in parentheses

Bond	1b	1c
Co–O(1)	1.862(5)	1.879(2)
Co–O(2)	1.858(4)	1.873(3)
Co–N(1)	1.867(5)	1.861(2)
Co–N(2)	1.843(6)	1.857(3)
Co–C(19)/C(20)	1.975(6)	1.975(3)
O(1)–C(1)	1.298(7)	1.319(4)
O(2)–C(16)	1.318(7)	1.313(4)
N(1)–C(7)	1.288(8)	1.286(4)
N(1)–C(8)	1.482(10)	1.476(4)
N(2)–C(9)	1.494(8)	1.488(4)
N(2)–C(10)	1.263(8)	1.291(4)
C(1)–C(2)	1.406(9)	1.410(4)
C(1)–C(6)	1.433(9)	1.419(4)
C(2)–C(3)	1.378(9)	1.377(4)
C(3)–C(4)	1.402(10)	1.404(4)
C(4)–C(5)	1.352(10)	1.371(4)
C(5)–C(6)	1.420(9)	1.413(4)
C(6)–C(7)	1.423(10)	1.434(4)
C(8)–C(9)	1.464(10)	1.526(4)
C(9)–C(17)	1.605(9)	1.537(4)
C(10)–C(11)	1.436(8)	1.433(4)
C(11)–C(12)	1.403(9)	1.408(4)
C(11)–C(16)	1.405(9)	1.427(4)
C(12)–C(13)	1.381(9)	1.367(4)
C(13)–C(14)	1.394(11)	1.400(5)
C(14)–C(15)	1.378(9)	1.381(4)
C(15)–C(16)	1.430(8)	1.411(4)
C(17)–C(18)	1.503(11)	1.524(4)
C(18)–C(19)	1.540(9)	1.526(4)
C(19)–C(20)	—	1.512(5)
O(1)–Co–O(2)	84.1(2)	84.3(1)
O(1)–Co–N(1)	93.8(2)	93.6(1)
O(2)–Co–N(2)	93.7(2)	94.8(1)
N(1)–Co–(N(2)	87.2(2)	85.9(1)
O(1)–Co–C(19)/C(20)	98.9(2)	91.2(1)
O(2)–Co–C(19)/C(20)	98.0(2)	96.6(1)
N(1)–Co–C(19)/C(20)	92.0(2)	93.3(1)
N(2)–Co–C(19)/C(20)	88.1(2)	95.9(1)
C(9)–C(17)–C(18)	113.1(6)	117.3(3)
C(17)–C(18)–C(19)	115.8(5)	115.1(3)
C(18)–C(19)–C(20)	—	117.0(3)
C(18)–C(19)/C(20)–Co	114.2(4)	119.3(2)
N(1)–C(8)–C(9)–N(2)	37.5(7)	34.8(3)

[{Co(salen)ethyl}$_2$], the cobalt atom is almost coplanar with the atoms of the coordination plane. Consequently, the interatomic distances of the coordinating atoms in **1b, c**, particularly between O(1) and O(2), can be much shorter than in [{Co(salen)ethyl}$_2$] (2.491(6) Å in **1b** and 2.516(3) in **1c** *vs.* 2.69 Å in [{Co(salen)ethyl}$_2$].

The equatorial ligand systems of **1b** and **1c** are strikingly planar. The angle between the planes formed by [O(1),N(1),C(7),C(6),C(1)] and [O(2),N(2),C(10),C(11),C(16)] is only 5.0(3) and 3.47(7)° for **1b** and **1c**, respectively. In contrast, [{Co(salen)ethyl}$_2$] has a stepped conformation in which this angle is 17.5°. Neither in **1b** nor in **1c** is the angle between the Co–bond and the plane through the equatorial coordinating atoms 90°, the acute angles being 84.0(2)° and 87.0(1)° for **1b** and **1c**, respectively.

The Co–C bond lengths, *i.e.* 1.975(6) for **1b** and 1.975(3) Å for **1c**, are barely affected by the five-coordinate nature of these complexes and are quite comparable with the values found in related six-coordinate organocobalt Schiff base complexes.[27] In contrast, the Co–N and, especially, the Co–O bond lengths (see Table 2) are significantly shorter, which probably gives compensation for the absence of a sixth ligand.

The carbon bridges in **1b** and **1c** lie zig-zag over the equatorial system as was already inferred from the ^{1}H NMR data. The Co–C–C angles are 114.2(4)° for **1b**, respectively 119.3(2)° for **1c**. These values, which deviate strongly from an ideal tetrahedral geometry, can be rationalized by the non-sp^3-hybridization of the C_α atom. Because of bonding to the metal, C_α has considerable sp^2-character as is also evident from its values of $^2J(^{13}C\text{-}^1H)$ (see above). In [{Co(salen)ethyl}$_2$] the Co–C–C angle is 119.5(7)°. Steric constraints probably require the C–C–C angles in the carbon bridges to be quite large as is recorded in Table 2.

Crystallization of **1b** and **1c** from chloroform yields crystals in which one molecule of chloroform is weakly hydrogen bonded to both oxygen atoms of every salen unit (not depicted in Fig. 5 and 6). Similar solvent hydrogen bonding is also found in related five-cordinate Co^{III}-complexes.[26]

Suitable crystals from solutions of **1b** and **1c** in coordinating solvents could not be obtained yet. Therefore, we are still uncertain whether the monomeric nature and nearly planar conformation of the equatorial ligand of **1b** and **1c** is due to steric factors imposed by the oligomethylene bridges or to specific effects originating from co-crystallization of chloroform.*

Conclusion

Intramolecularly alkylated Co(salen) complexes with a bridge of three, **1b**, and of four, **1c**, methylene groups between cobalt and one of the carbon atoms of the ethylene group in the equatorial ligand, have been synthesized by a modified procedure of Schrauzer starting with condensation of salicylaldehyde with suitable ω-substituted 1,2-diamines. Similar complexes with a bridge of two and of five methylene groups are not stable at room temperature. ^{1}H NMR and ^{13}C NMR spectroscopic analysis shows that many similarities exist between **1b**, **1c** and simple alkylated five-coordinate Co(salen) complexes, *e.g.* [Co(salen)butyl] **10**. Owing to the asymmetric zig-zag conformation of the oligomethylene bridges, all geminal protons are non-equivalent which, however, can be completely assigned by application of NOESY techniques. The most characteristic feature of these spectra is the presence of a relatively highfield resonance assigned to that one of the β-protons which is positioned most distal from the equatorial plane, *i.e.* anti-periplanar with respect to cobalt.

In non-coordinating solvents as well as in the solid state, both **1b** and **1c** are five-coordinate. Probably therefore, the crystal structure data differ somewhat from what is usually found in structurally characterized [Co(salen)alkyl] complexes which are six-coordinate species in the solid state. Especially the monomeric and nearly planar conformation of **1b** and **1c** is a characteristic feature which is also found in related five-coordinate alkylcobalt Schiff base complexes.[26]

Both **1b** and **1c** are relatively stable compounds which undergo thermal decomposition, *via* Co–C bond homolysis, at much higher temperatures than, *e.g.* [Co(salen)butyl] **10**. Kinetic data and mechanistic implications will be reported in due course.

Experimental

^{1}H NMR spectra were recorded on either a Brucker WH-90 or a WM-250 spectrometer. ^{13}C NMR spectra were recorded on a Brucker WM-250 spectrometer at a frequency of 62.89 MHz.

* Recently, we have prepared a related intramolecularly alkylated Co(salen) complex which in the unit cell of its crystals obtained from chloroform solutions contain one dimer, two monomers and four chloroform molecules. The monomeric parts closely resemble five-coordinate **1b**, **c**; the dimeric part is similar to six-coordinate [{Co(salen)ethyl}$_2$].[29]

Chemical shifts (δ) are reported in ppm relative to tetramethylsilane using the solvent signal as internal reference. Coupling constants *J* are given 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 direct inlet, probe temperature 160 °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. Wavelengths (λ) and extinction coefficients (ε) are given in nm and $mol^{-1}\ dm^3\ cm^{-1}$, respectively.

Melting points were measured on a Kofler hot stage apparatus equipped with a Reichert microscope and are uncorrected. Merck DC Alufolien Kieselgel 60 F254 were used for TLC analysis. Preparative medium pressure liquid chromatography (MPLC) on Merck silica 60H was performed on a Jobin-Yvon Miniprep LC.

All reactions were performed under a nitrogen atmosphere, unless stated otherwise. In order to prevent cleavage of the cobalt–carbon bond, all alkylcobalt complexes were handled with minimal exposure to light and were not subjected to temperatures above 30 °C.

Alk-ω-en-1-ols **2**.—But-3-en-1-ol **2a**,[30] pent-4-en-1-ol **2b**,[31] hex-5-en-1-ol **2c**,[32] and hept-6-en-1-ol **2d**[33] were prepared according to literature procedures.

ω-(Tetrahydropyran-2-yloxy)alk-1-enes **3a–d**.—To a solution of ω-hydroxyalk-1-ene **2** (200 mmol) in dry dichloromethane (250 cm^3) were added freshly distilled dihydropyran (25.2 g, 300 mmol) and pyridinium toluene-*p*-sulfonate (5.0 g, 20 mmol). After being stirred at room temperature for 20 h, the colourless solution was successively washed with ice-cold saturated aqueous sodium bisulfite, saturated aqueous sodium hydrogen carbonate and brine. The organic layer was dried (Na_2SO_4) and the solvent evaporated under reduced pressure. Distillation of the crude product yielded **3** as a colourless liquid.

4-(Tetrahydropyran-2-yloxy)but-1-ene **3a** (83%), b.p. 42–44 °C/0.1 mmHg; δ_H(90 MHz; $CDCl_3$) 1.3–2.0 (m, 6 H), 2.34 (m, 2 H, *J* 6.5/1.3), 3.49 (m, 2 H), 3.85 (m, 2 H), 4.58 (br s, 1 H), 5.06 (m, 2 H) and 5.83 (m, 1 H, *J* 17.0/9.8/6.5).

5-(Tetrahydropyran-2-yloxy)pent-1-ene **3b** (85%), b.p. 54–56 °C/0.1 mmHg; δ_H(90 MHz; $CDCl_3$) 1.4–2.0 (m, 8 H), 2.16 (m, 2 H, *J* 6.7), 3.47 (m, 2 H), 3.84 (m, 2 H), 4.58 (br s, 1 H), 4.99 (m, 2 H) and 5.86 (m, 1 H, *J* 17.0/10.0/6.3).

6-(Tetrahydropyran-2-yloxy)hex-1-ene **3c** (90%), b.p. 62–64 °C/0.1 mmHg; δ_H(90 MHz; $CDCl_3$) 1.2–1.9 (m, 10 H), 2.08 (q, 2 H, *J* 6.5), 3.45 (m, 2 H), 3.83 (m, 2 H), 4.56 (br s, 1 H), 4.99 (m, 2 H) and 5.82 (m, 1 H, *J* 17.4/10.0/6.5).

7-(Tetrahydropyran-2-yloxy)hept-1-ene **3d** (80%), b.p. 67–69 °C/0.1 mmHg; δ_H(90 MHz; $CDCl_3$) 1.2–1.9 (m, 12 H), 2.09 (m, 2 H, *J* 6.5), 3.46 (m, 2 H), 3.84 (m, 2 H), 4.57 (br s, 1 H), 4.98 (m, 2 H) and 5.82 (m, 1 H, *J* 17.2/10.0/6.5).

1-*Iodo-ω-(tetrahydropyran-2-yloxy)alkane* **4a–d**.—At 0 °C, iodine chloride (9.5 cm^3, 180 mmol) was added over 10 min to a stirred suspension of sodium azide (26.0 g, 400 mmol) in dry acetonitrile (160 cm^3). After the mixture had been stirred for a further 5 min at 0 °C, the olefin **3** was added to it. The reaction mixture was then stirred at room temperature for *ca.* 20 h after which it was poured into water (400 cm^3) and extracted with diethyl ether (× 3). The combined extracts were successively washed with aqueous 5% sodium thiosulfate (250 cm^3) and with water (4 × 350 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure at 30 °C to yield **4** as a pale brown viscous liquid which was used without further purification.

2-Azido-1-iodo-4-(tetrahydropyran-2-yloxy)butane **4a** (97%); δ_H(90 MHz; $CDCl_3$) 1.4–2.2 (m, 8 H), 3.27 (m, 2 H), 3.4–4.0 (m, 5 H) and 4.59 (br s, 1 H).

2-Azido-1-iodo-5-(tetrahydropyran-2-yloxy)pentane **4b** (89%); δ_H(90 MHz; $CDCl_3$) 1.4–2.1 (m, 10 H), 3.26 (m, 2 H), 3.4–4.2 (m, 5 H) and 4.58 (br s, 1 H).

2-Azido-1-iodo-6-(tetrahydropyran-2-yloxy)hexane **4c** (98%); δ_H(90 MHz; $CDCl_3$) 1.3–1.9 (m, 12 H), 3.26 (m, 2 H), 3.3–3.9 (m, 5 H) and 4.56 (br s, 1 H).

2-Azido-1-iodo-7-(tetrahydropyran-2-yloxy)heptane **4d** (94%); δ_H(90 MHz; $CDCl_3$) 1.3–2.0 (m, 14 H), 3.27 (m, 2 H), 3.3–4.1 (m, 5 H) and 4.57 (br s, 1 H).

1,2-*Diazido-ω-(Tetrahydropyran-2-yloxy)alkane* **5a–d**.—A mixture of **4** (140 mmol), sodium azide (18.2 g, 280 mmol and tetrabutylammonium bromide (4.5 g, 14 mmol) in dry benzene (60 cm^3) and dry dimethylformamide (60 cm^3) was stirred vigorously at reflux for *ca* 20 h. The reaction mixture was then cooled to room temperature and poured into water (500 cm^3). The organic layer was separated and the aqueous layer extracted with benzene (× 3). The combined organic extracts were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure at 30 °C. The residue was purified by column chromatography (MPLC), eluting with ethyl acetate–light petroleum (b.p. 40–60 °C) (1:9) to afford **5** as a colourless liquid, which was homogeneous on TLC.

1,2-Diazido-4-(tetrahydropyran-2-yloxy)butane **5a** (45%); δ_H(90 MHz; $CDCl_3$) 1.3–2.0 (m, 8 H), 3.2–4.1 (m, 7 H) and 4.59 (br s, 1 H).

1,2-Diazido-5-(tetrahydropyran-2-yloxy)pentane **5b** (65%); δ_H(90 MHz; $CDCl_3$) 1.4–2.0 (m, 10 H), 3.2–4.0 (m, 7 H) and 4.58 (br s, 1 H).

1,2-Diazido-6-(tetrahydropyran-2-yloxy)hexane **5c** (44%); δ_H(90 MHz; $CDCl_3$) 1.3–1.9 (m, 12 H), 3.2–4.0 (m, 7 H) and 4.54 (br s, 1 H).

1,2-Diazido-7-(tetrahydropyran-2-yloxy)heptane **5d** (46%); δ_H(90 MHz; $CDCl_3$) 1.3–1.9 (m, 14 H), 3.2–4.1 (m, 7 H) and 4.57 (br s, 1 H).

1,2-Diazidoalkan-ω-ols **6a–d**. The diazide **5** (60 mmol) was dissolved in methanol (100 cm^3) and stirred with Dowex 50W-× 8 acidic cation-exchange resin (200–400 mesh; 15 g) at room temperature. After *ca.* 3 h, TLC analysis [light petroleum (b.p. 40–60 °C)–ethyl acetate (4:1)] showed complete conversion of the starting material at which point the resin was filtered off and washed thoroughly with methanol. The filtrate was evaporated to dryness under reduced pressure at 30 °C to give **6** as a colourless liquid, which was used without purification.

3,4-Diazidobutan-1-ol **6a** (98%); δ_H(90 MHz; $CDCl_3$) 1.70 (m, 3 H), 3.40 (m, 2 H), 3.79 (m, 2 H, *J* 6.0) and 3.93 (m, 1 H).

4,5-Diazidopentan-1-ol **6b** (97%); δ_H(90 MHz; $CDCl_3$) 1.44 (br s, 1 H), 1.68 (m, 4 H), 3.44 (m, 2 H) and 3.70 (m, 3 H).

5,6-Diazidohexan-1-ol **6c** (99%); δ_H(90 MHz; $CDCl_3$) 1.3–1.9 (m, 7 H), 3.40 (m, 3 H) and 3.64 (m, 2 H).

6,7-Diazidoheptan-1-ol **6d** (99%); δ_H(90 MHz; $CDCl_3$) 1.3–2.0 (m, 9 H), 3.39 (m, 3 H) and 3.62 (m, 2 H).

ω-Chloro-1,2-diazidoalkanes **7a–d**.—To a solution of thionyl chloride (13.5 g, 113 mmol) in dry chloroform (60 cm^3) was added at −5 °C over 15 min a solution of **6** (55 mmol) in dry chloroform (10 cm^3). After being stirred for 1 h at room temperature, the mixture was cooled to 0 °C and dry DMF (70 cm^3) was added to it over *ca.* 30 min. It was subsequently stirred at room temperature for 6 h and then poured into ice–water (300 cm^3). The organic layer was separated and the aqueous layer extracted with chloroform (× 3). The combined extracts were washed with half-saturated aqueous sodium hydrogen carbonate, dried (Na_2SO_4) and evaporated under reduced pressure at 30 °C. The residue was purified by column chromatography (MPLC), eluting with light petroleum (b.p. 40–60 °C)–ethyl acetate (4:1) to afford **7** as a colourless liquid which was homogeneous on TLC.

4-Chloro-1,2-diazidobutane **7a** (73%); δ_H(90 MHz; $CDCl_3$) 1.92 (q, 2 H, *J* 6.3), 3.44 (m, 2 H), 3.67 (t, 2 H, *J* 6.3) and 3.80 (m, 1 H).

5-Chloro-1,2-diazidopentane (92%); δ_H(90 MHz; $CDCl_3$) 1.84 (m, 4 H), 3.43 (m, 3 H) and 3.58 (t, 2 H, *J* 6.1).

6-Chloro-1,2-diazidohexane **7c** (85%); δ_H(90 MHz; $CDCl_3$) 1.4–2.0 (m, 6 H), 3.40 (m, 3 H) and 3.57 (t, 2 H, *J* 6.2).

7-Chloro-1,2-diazidoheptane (79%); δ_H(90 MHz; $CDCl_3$) 1.3–2.0 (m, 8 H), 3.39 (m, 3 H) and 3.56 (t, 2 H, *J* 6.4).

ω-*Chloroalkane*-1,2-*diamine Dihydrochlorides* **8a–d**.—Triphenylphosphine (21.0 g, 80 mmol) was added portionwise to the diazide **7** (40 mmol) dissolved in a mixture of tetrahydrofuran (45 cm^3) and concentrated hydrochloric acid (13 cm^3) while the reaction mixture was kept < 40 °C (ice–water bath). After the mixture had been stirred for an additional 6 h at room temperature the solvent was evaporated and water was added to the residue. The insoluble material (mainly triphenylphosphine oxide) was filtered off and washed thoroughly with water. The filtrate was evaporated to dryness under reduced pressure and the residue dissolved in ethanol. Filtration and evaporation of the solvent gave the 1,2-diamine dihydrochloride **8** either as a hygroscopic colourless solid (**8a** and **8c**) or as a highly viscous colourless liquid (**8b** and **8d**). The two solid products were recrystallized from 96% ethanol, whereas the two non-crystalline 1,2-diamines dihydrochlorides were used without further purification. For analytical purposes, small portions of both **8b** and **8d** were converted into the corresponding dipicrates (**8b′** and **8d′**), which were purified by recrystallization from ethyl acetate–diethyl ether.

4-Chlorobutane-1,2-diamine dihydrochloride **8a** (68%) (Found: C, 23.5; H, 6.7; Cl, 51.4; N, 13.6. $C_4H_{13}Cl_3N_2 \cdot 0.5H_2O$ requires C, 23.49; H, 6.90; Cl, 52.00; N, 13.70%); δ_H(90 MHz; [$^2H_6$]-DMSO) 2.17 (m, 2 H, *J* 6.7), 3.17 (d, 2 H, *J* 5.6), 3.59 (m, 1 H), 3.81 (t, 2 H, *J* 6.7) and 8.7 (br s, 6 H).

5-Chloropentane-1,2-diamine dihydrochloride **8b** (77%); δ_H(90 MHz; [$^2H_6$]-DMSO) 1.83 (m, 4 H), 3.12 (d, 2 H, *J* 5.4), 3.46 (m, 1 H), 3.67 (t, 2 H, *J* 5.8) and 8.7 (br s, 6 H).

5-Chloropentane-1,2-diamine dipicrate **8b′** (Found: C, 33.5; H, 3.5; Cl, 5.8; N, 18.2. $C_{17}H_{19}ClN_8O_{14} \cdot 1H_2O$ requires C, 33.31; H, 3.45; Cl, 5.78; N, 18.29%); δ_H(90 MHz; [$^2H_6$]-DMSO) 1.83 (m, 4 H), 3.12 (d, 2 H, *J* 5.4), 3.46 (m, 1 H), 3.67 (t, 2 H, *J* 5.8) and 8.6 (br s, 6 H).

6-Chlorohexane-1,2-diamine dihydrochloride **8c** (75%) (Found: C, 32.3; H, 7.5; Cl, 47.6; N, 12.6. $C_6H_{17}Cl_3N_2$ requires C, 32.23; H, 7.66; Cl, 47.58; N, 12.53%); δ_H(90 MHz; [$^2H_6$]-DMSO) 1.3–1.9 (m, 6 H), 3.06 (d, 2 H, *J* 6.1), 3.41 (m, 1 H), 3.64 (t, 2 H, *J* 6.3) and 8.6 (br s, 6 H).

7-Chloroheptane-1,2-diamine dihydrochloride **8d** (73%); δ_H(90 MHz; [$^2H_6$]-DMSO) 1.1–1.9 (m, 8 H), 3.09 (d, 2 H, *J* 5.8), 3.42 (m, 1 H), 3.62 (t, 2 H, *J* 6.5) and 8.6 (br s, 6 H).

7-Chloroheptane-1,2-diamine dipicrate **8d′** (Found: C, 35.8; H, 4.0; Cl, 5.5; N, 17.4. $C_{19}H_{23}ClN_8O_{14} \cdot 1H_2O$ requires *C*, 35.60; H, 3.93; Cl, 5.53; N, 17.49%); δ_H(90 MHz; [$^2H_6$]-DMSO) 1.1–1.9 (m, 8 H), 3.09 (d, 2 H, *J* 5.8), 3.42 (m, 1 H), 3.62 (t, 2 H, *J* 6.5) and 8.6 (br s, 6 H).

2,2′-{[1-(ω-*Chloroalkyl*)*ethane*-1,2-*diyl*]*bis*(*nitrilomethylidyne*)}*diphenol* **9a–d**.—To a stirred solution of **8** (25 mmol) in a mixture of water (10 cm^3) and ethanol (15 cm^3) was added at 0 °C a solution of sodium acetate trihydrate (9.3 g, 68 mmol) in water (10 cm^3). The resulting mixture was added *immediately* to a stirred hot solution (60 °C) of freshly distilled salicylaldehyde (5.0 cm^3, 48 mmol) in ethanol (250 cm^3) which turned bright yellow at once. After the mixture had been stirred for 15 min at 60 °C, the solvent was evaporated under reduced pressure and the residue was dissolved in chloroform. The solution was washed with water (× 3), dried (Na_2SO_4) and evaporated to yield **9** as a highly viscous yellow liquid, which was used without further purification.

2,2′-{[1-(2-Chloroethyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol **9a** (70%); δ_H(250 MHz; $CDCl_3$) 2.34 (m, 2 H), 3.44 (m, 1 H, *J* 11.1/7.5), 3.67 (m, 1 H, *J* 11.1/5.0), 3.83 (m, 3 H), 6.85 (m, 2 H), 6.94 (m, 2 H), 7.26 (m, 4 H), 8.30 (s, 1 H) and 8.39 (s, 1 H); δ_C($CDCl_3$) 36.2 (t, *J* 129), 41.5 (t, *J* 151), 64.4 (m, *J* 137/9), 66.7 (d, *J* 134), 116.9 (dd, *J* 160/8), 117.0 (dd, *J* 160/8), 118.4 (m, *J* 5), 118.5 (m, *J* 5), 118.7 (m, *J* 162/5), 118.9 (m, *J* 162/9), 131.5 (m, *J* 156/12), 131.8 (m, *J* 157/12), 132.5 (m, *J* 157/10), 132.7 (m, *J* 158/11), 160.9 (m, *J* 6), 166.7 (m, *J* 160/7) and 166.8 (m, *J* 160/6).

2,2′-{[1-(3-Chloropropyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol **9b** (56%); δ_H(250 MHz; $CDCl_3$) 1.89 (m, 4 H), 3.57 (m, 3 H, *J* 6.1), 3.72 (m, 1 H, *J* 12.1/7.7), 3.95 (m, 1 H, *J* 12.1/4.1/1.2), 6.86 (m, 2 H), 6.94 (m, 2 H), 7.22 (m, 2 H), 7.31 (m, 2 H), 8.31 (s, 1 H) and 8.33 (s, 1 H); δ_C($CDCl_3$) 29.2 (t, *J* 130), 31.3 (t, *J* 130), 44.5 (t, *J* 149), 64.5 (m, *J* 137/10), 69.4 (d, *J* 135), 116.9 (dd, *J* 160/7), 118.3 (m, *J* 8), 118.5 (m, *J* 8), 118.6 (m, *J* 161/8), 118.8 (m, *J* 161/8), 131.4 (dd, *J* 157/9), 131.7 (dd, *J* 154/9), 132.3 (dd, *J* 157/6), 132.6 (dd, *J* 157/9), 160.9 (m, *J* 8), 166.6 (m, *J* 160/7) and 165.6 (m, *J* 160/7).

2,2′-{[1-(4-Chlorobutyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol **9c** (83%); δ_H(250 MHz; $CDCl_3$) 1.54 (m, 2 H), 1.81 (m, 4 H), 3.54 (m, 3 H, *J* 6.0/3.0), 3.71 (m, 1 H, *J* 12.2/7.7/0.7), 3.94 (m, 1 H, *J* 12.2/4.2/1.3), 6.86 (m, 2 H), 6.94 (m, 2 H), 7.23 (m, 2 H), 7.30 (m, 2 H), 8.31 (s, 1 H) and 8.33 (s, 1 H); δ_C($CDCl_3$) 23.3 (t, *J* 125), 32.2 (t, *J* 124), 33.1 (t, *J* 123), 44.5 (m, *J* 150/4), 64.3 (m, *J* 137/10), 69.8 (d, *J* 136), 116.7 (dd, *J* 160/8), 118.3 (m, *J* 8), 118.4 (m, *J* 8), 118.5 (m, *J* 161/7), 118.6 (m, *J* 161/6), 131.3 (m, *J* 157/8), 131.4 (m, *J* 156/9), 132.2 (dd, *J* 157/9), 160.8 (m, *J* 8), 165.1 (m, *J* 160/8) and 166.3 (m, *J* 160/8).

2,2′-{[1-(5-Chloropentyl)ethane-1,2-diyl]bis(nitrilomethylidyne)}diphenol **9d** (86%); δ_H(250 MHz; $CDCl_3$) 1.44 (m, 4 H), 1.77 (m, 4 H), 1.85 (m, 2 H), 3.53 (m, 3 H, *J* 6.6), 3.70 (m, 1 H, *J* 12.2/7.7/0.7), 3.92 (m, 1 H, *J* 12.2/4.2/1.2), 6.86 (m, 2 H), 6.94 (m, 2 H), 7.22 (m, 2 H), 7.30 (m, 2 H), 8.30 (s, 1 H) and 8.32 (s, 1 H); δ_C($CDCl_3$) 25.4 (t, *J* 125), 26.7 (t, *J* 128), 32.4 (t, *J* 124), 33.9 (t, *J* 125), 44.9 (t, *J* 149), 64.7 (m, *J* 135/7), 70.1 (d, *J* 138), 116.9 (dd, *J* 159/7), 118.5 (m, *J* 7), 118.6 (dd, *J* 161/8), 118.7 (dd, *J* 161/8), 131.4 (d, *J* 156), 131.5 (d, *J* 156), 132.4 (dd, *J* 157/9), 161.0 (m, *J* 7), 165.2 (m, *J* 159/7) and 166.5 (m, *J* 159/8).

Intramolecularly Alkylated Salen Complexes **1b**, **c**.—To a solution of the crude ligand **9** (3 mmol) in de-aerated methanol (350 cm^3) was first added 50% aqueous sodium hydroxide (7.3 cm^3, 140 mmol) and then, after the mixture had been stirred for 10 min, a solution of cobalt dichloride hexahydrate (0.71 g, 3.0 mmol) in de-aerated methanol (20 cm^3). Nitrogen was bubbled continuously through the vigorously stirred orange coloured reaction mixture. After 5 min, palladium chloride (10 mg) and sodium borohydride (0.19 g, 5.0 mmol) were added to the reaction mixture which immediately turned brown–red. It was then stirred vigorously for 1 h at room temperature before the nitrogen purging was stopped and the solvent was evaporated under reduced pressure at room temperature. The dark brown residue was extracted with chloroform and the dark green extract washed with water (× 3), dried (Na_2SO_4) and evaporated to dryness at room temperature under reduced pressure. Finally, the crude product was recrystallized from aqueous methanol at 5 °C to yield **1** as a brown–red microcrystalline solid.

(SPY-5-54)-{2,2′-{{[1-(Trimethylene-κC^3)ethane-1,2-diyl]-bis(nitrilomethylidyne)}diphenolato}(3 −)-κ^2*N*,*N*′;κ^2*O*,*O*′} cobalt **1b** (49%) (Found: C, 61.3; H, 5.4; Co, 15.7; N, 7.6.

$C_{19}H_{19}CoN_2O_2·0.5H_2O$ requires C, 60.80; H, 5.37; Co, 15.70; N, 7.47%. Found: M, 366.078. Calc. for $C_{19}H_{19}CoN_2O_2$: 366.0779); $\lambda_{max}(CHCl_3)$/nm 345 (ε 10.68 × 10^3), 406sh (4.89 × 10^3) 460 sh (2.44 × 10^3) and 646 (1.31 × 10^3); δ_H(250 MHz; $CDCl_3$): see Table 1; $\delta_C(CDCl_3)$ 166.1 (s, C-1 or C-16), 165.7 (s, C-16 or C-1), 164.2 (d, *J* 162, C-7), 161.9 (d, *J* 162, C-10), 133.1 (d, *J* 156, C-3 or C-14), 132.9 (d, *J* 156, C-14 or C-3), 132.5 (d, *J* 156, C-12), 132.4 (d, *J* 156, C-5), 124.1 (d, *J* 161, C-2 or C-15), 123.8 (d, *J* 161, C-15 or C-2), 120.3 (s, C-11 or C-6), 120.1 (s, C-6 or C-11), 115.1 (d, *J* 162, C-4 and C-13), 67.0 (d, *J* 137, C-9), 62.6 (t, *J* 133, C-8), 38.5 (t, *J* 127, C-17), 26.9 (t, *J* 125, C-18) and 17.7 (t, *J*, 146, C-19).

(SPY-5-54)-{2,2'-{[(1-*Tetramethylene*-κC^4)*ethane*-1,2-*diyl*]-*bis*(*nitrilomethylidyne*)}*diphenolato*(3−)-κ^{2}N,N';κ^{2}O,O'}-*cobalt* **1c** (68%) (Found: C, 62.3; H, 5.9; Co, 15.0; N, 7.2. $C_{20}H_{21}CoN_2O_2·0.5H_2O$ requires C, 61.70; H, 5.70; N, 7.20, Co 15.14%. Found: M, 380.092. Calc. for $C_{20}H_{21}CoN_2O_2$: 380.0935); $\lambda_{max}(CHCl_3)$/nm 343 (ε 9.34 × 10^3), 406sh (4.89 × 10^3), 463sh (2.13 × 10^3) and 648 (1.24 × 10^3); δ_H(250 MHz; $CDCl_3$): see Table 1; $\delta_C(CDCl_3)$ 165.9 (s, C-1 or C-16), 165.5 (s, C-16 or C-1), 163.9 (d, *J* 163, C-10), 163.7 (d, *J* 163, C-7), 133.0 (d, *J* 157, C-3 or C-14), 132.8 (d, *J* 157, C-14 or C-3), 132.7 (d, *J* 157, C-12), 132.5 (d, *J* 157, C-5), 123.9 (d, *J* 161, C-2 or C-15), 123.5 (d, *J* 161, C-15 or C-2), 120.4 (s, C-6 or C-11), 119.8 (s, C-11 or C-6), 115.1 (d, *J* 161, C-4 or C-13), 114.7 (d, *J* 161, C-13 or C-4), 68.5 (d, *J* 141, C-9), 64.0 (t, *J* 134, C-8), 38.7 (t, *J* 129, C-17), 35.1 (t, *J* 125, C-19), 23.6 (t, *J* 128, C-18) and 22.1 (t, *J* 149, C-20).

(SPY-5-32)-(*Butyl*-κC'){2,2'-{[(*ethane*-1,2-*diyl*)*bis*(*nitrilomethylidyne*)]*diphenolato*}(2−)-κ^{2}N,N',κ^{2}O,O'}*cobalt* **10**.—{2,2'-[Ethane-1,2-diylbis(nitrilomethylidyne)]diphenol[13] (0.80 g, 3 mmol) in de-aerated methanol (120 cm^3) was converted into the Co^I(salen) complex as described for **1**. Subsequently, butyl bromide (1.0 cm^3, 9 mmol) was added to the mixture, which immediately turned brown–red and was then stirred vigorously for 1 h at room temperature. The solvent was then evaporated at room temperature under reduced pressure and the dark brown residue was extracted with chloroform. The dark green extracts were washed with water (×3), dried (Na_2SO_4) and evaporated to dryness at room temperature under reduced pressure. The resulting crude product was recrystallized from aqueous methanol (at 5 °C) to yield **10** as a dark red microcrystalline solid (46%); $\lambda_{max}(CHCl_3)$/nm 342 (ε 9.21 × 10^3), 406sh (3.98 × 10^3), 460sh (1.76 × 10^3) and 658 (0.96 × 10^3); δ_H(250 MHz; $CDCl_3$): see Table 1; $\delta_C(CDCl_3)$ 165.8 (s, C-1, C-1'), 163.9 (d, *J* 163, C-7, C-7'), 132.9 (d, *J* 157, C-3, C-3'), 132.5 (d, *J* 155, C-5, C-5'), 123.8 (d, *J* 161, C-2, C-2'), 119.7 (s, C-6, C-6'), 114.9 (d, *J* 162, C-4, C-4'), 59.0 (t, *J* 140, C-8, C-8'), 18.9 (br t, *J* 158, C-9), 35.5 (t, *J* 127, C-10), 20.3 (t, *J* 126, C-11) and 13.4 (q, *J* 125, C-(12).

X-Ray Crystal Structure Determination of **1b**.—*Crystal data*. $C_{19}H_{19}CoN_2O_2·CDCl_3$, $M = 486.69$, Monoclinic, $a = 10.121(5)$, $b = 22.218(15)$, $c = 9.387(7)$ Å, $\beta = 110.83(5)°$, $V = 1973(2)$ (by least squares from the SET_4 setting angles of 21 reflections in the range $12 < \theta < 18°$, $\lambda = 0.710\,73$ Å), space group $P2_1/c$ (no. 14), $Z = 4$, $D_x = 1.638$ g cm^{-3}. Black crystals with approximate dimensions 0.20 × 0.25 × 0.30 mm, μ(Mo-Kα) = 13 cm^{-1}, $T = 100$ K.

Data collection and processing.[34] CAD4 diffractometer, $\omega/2\theta$ scan mode with $\Delta\omega = 1.0 + 0.35 \tan\theta°$, Zr filtered Mo-Kα radiation, 100 K; 4901 reflections measured ($0.92 < \theta < 27.5°$, $\pm h$, $-k$, $\pm l$), 4511 unique reflections [merging index $R = 0.049$ after DIFABS (correction range 0.74:1.17)], giving 3036 reflections with $I > 2.5\,\sigma(I)$. No decay.

Structure analysis and refinement. Direct methods (SHELXS86). Full matrix least-squares refinement on *F* (SHELX76) with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions with two, common, refined U_{iso}. The weighting scheme $w = 1/\sigma^2(F)$, with $\sigma(F)$ from counting statistics. Final R and R_w values are 0.066 and 0.069. Programs and computers used and sources of scattering factor data are given in ref. 34.

X-Ray Crystal Structure Determination of **1c**.—See ref. 12.

Structural co-ordinates and thermal parameters together with full listings of the bond lengths and bond angles have been deposited with the Cambridge Crystallographic Centre for compound **1b**.* Those for compound **1c** were similarly deposited earlier.[12]

* For details of the X-ray crystallographic deposition scheme with the CCDC, see Instructions for Authors (1993), *J. Chem. Soc., Perkin Trans. 1*, 1993, issue 1.

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