Pergamon

Tetrahedron Vol. 51, No. 14, pp. 4161-4172, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00132-8

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

Bert van Arkel, Juul L. van der Baan,* Sijbe Balt, Friedrich Bickelhaupt, Martinus W.G. de Bolster, and Gerhard W. Klumpp

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract: The synthesis of Costa-type B_{12} models **1** with a carbon bridge between the equatorial ligand and cobalt has been accomplished by condensation of butanedione monoxime and 2-(ω-functionalized)alkyl-1,3-diaminopropanes **8** followed by complexation with Co(II), introduction of a leaving group and intramolecular alkylation *via* Co(I) intermediates. The solution structure of intramolecularly alkylated Costa complexes with a bridge of two (**1a**) or of three (**1b**) methylene groups was investigated by NMR spectroscopy and compared with that of propyl(iodo) Costa complex **13**.

Small organocobalt complexes such as the cobaloximes, salen and Costa complexes (Fig. 1) have been investigated extensively as mimics of coenzyme B_{12} (5'-deoxyadenosylcobalamin).[1]

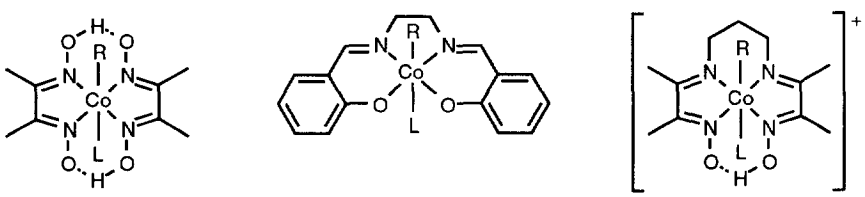


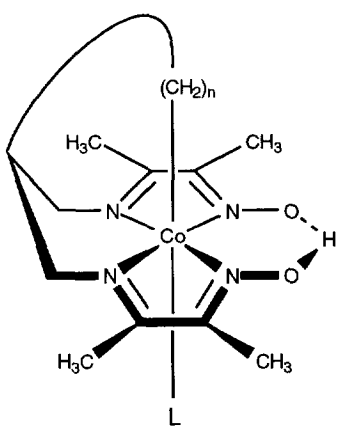
Figure 1 Model complexes for coenzyme B_{12}

Most of these model compounds have been designed to assess the factors that affect the strength of the Co–C bond in the coenzyme. Much interest has focused on steric interactions between the equatorial and axial ligands that might enhance Co–C bond homolysis since it is generally believed that conformational changes, both in the coenzyme and in the protein, are greatly responsible for the enzyme-accelerated Co–C bond cleavage. However, although these models have provided a wealth of information on relationships between the Co–C bond energy on the one hand and structural parameters on the other hand, it is obvious that none can resemble coenzyme B_{12} closely in *all* its essential chemical and physical properties. The cobaloximes are widely employed as coenzyme B_{12} models and have provided valuable structural information, but their Co(III)/Co(II) reduction potentials and

rates of axial ligand exchange differ strikingly from those of the cobalamines.[2,3] The Schiff base complexes derived from salen and saloph have, like the cobaloximes, quite deviating redox properties, but their axial ligand exchange rates suggest that, in this respect, these complexes are much better models than the cobaloximes.[4] The Costa complex, *i.e.* a hybrid Schiff base/dioxime model with an uni-negative N_4 equatorial ligand system, is an excellent electrochemical mimic of the cobalamines but its axial ligand exchange properties are comparable to those of the cobaloximes.[5] The H_2mdo model, in which the propylene bridge of the Costa ligand has been replaced by a methylenedioxy bridge (which causes increased rigidity and stronger steric repulsion) is expected to be a better mimic than the Costa complex with respect to axial ligand exchange rates, but this has not yet been fully investigated.[6]

Intramolecularly alkylated coenzyme B_{12} model compounds, *i.e.* organocobalt complexes in which the cobalt-bound carbon atom is linked to the equatorial ligand by a polymethylene bridge permit, on the one hand, a study of the reactivity of the cobalt–carbon bond and its dependence on the distortions imposed by the carbon bridge (of various lengths) and, on the other hand, an investigation of the properties of carbon-centred radicals forced to stay in proximity of a Co(II) complex (as a mimic of the situation in the holoenzyme).

Within this context, Retéy has synthesized $(CH_2)_n$-bridged cobaloxime-derived model compounds.[7] Recently, we have published results with intramolecularly alkylated cobalt complexes derived from the salen model.[8] Here, we report on the synthesis and NMR spectroscopic characterization of Costa complexes **1** with an intramolecular carbon bridge between the equatorial ligand and cobalt.



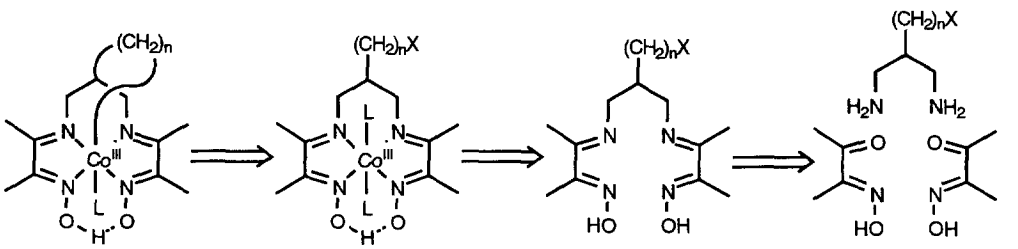
1

RESULTS AND DISCUSSION

Synthesis

Alkylated cobalt(III) Costa complexes are generally synthesized by condensation[9] of two equivalents of butanedione monoxime with one equivalent of 1,3-diaminopropane followed by complexation[10] with a cobalt(II) dihalogenide salt and oxidation by O_2 to give a dihalogenidocobalt(III) Costa complex which then is alkylated, either directly with a Grignard reagent or *via* reduction to the corresponding Co(I) complex and reaction with an alkyl halide.[5,10,11] Along the same lines, the synthesis of intramolecularly alkylated Costa complexes **1** is realized starting with the reaction between butanedione monoxime and a 2-(ω-X-alkyl)propane-

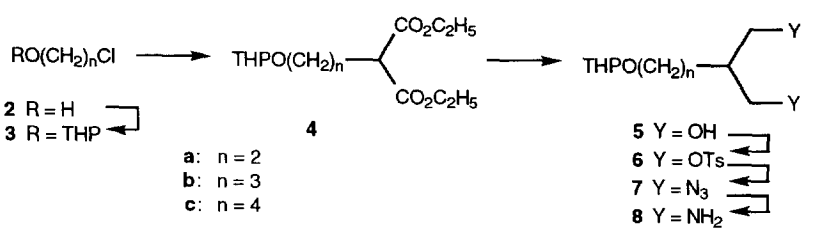
1,3-diamine which carries a functional group X that can be converted into a leaving group for intramolecular Co–C bond formation (Scheme 1). Inspection of molecular models showed that Costa complexes **1** with a bridge consisting of two, three, or four methylene groups (n = 2,3,4) seemed to have the best chance of a successful preparation.



Scheme 1

A practical procedure for the synthesis of the required 2-(ω-X-alkyl)propane-1,3-diamines involves reduction of the corresponding 1,3-diazidopropanes which, in turn, can be obtained from malonic acid derivatives in a three-step procedure. Thus, the commercially available ω-chloroalkanols **2** (n = 2,3,4) were selected as convenient starting materials (Scheme 2).

Treatment of **2** with dihydropyran in the presence of a catalytic amount of pyridinium toluene-*p*-sulfonate[12] gave the 1-chloro-ω-(tetrahydropyran-2-yloxy)alkanes **3**. These were used to alkylate diethyl malonate in DMF. The resulting products **4** were purified by distillation and then reduced[13] by $LiAlH_4$ in refluxing diethyl ether to give 2-substituted propane-1,3-diols **5** which, without purification, were treated with *p*-toluenesulfonyl chloride in pyridine[14] to give 1,3-ditosylates **6** in *ca.* 45 % overall-yield from **2**.

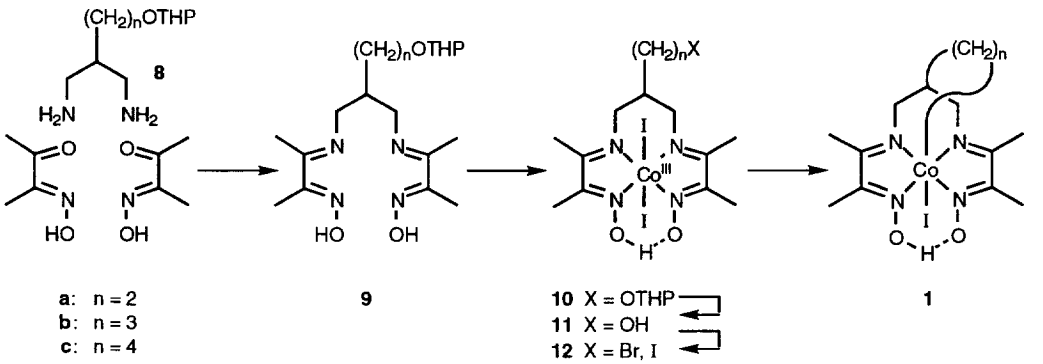


Scheme 2

The tosyloxy groups were replaced by azido groups through reaction with sodium azide in a boiling mixture of benzene and DMF using tetrabutylammonium bromide as phase transfer catalyst.[15] After column chromatographic purification, the 2-substituted-1,3-diazidopropanes **7** were reduced to the corresponding 1,3-diamines **8**, either by $LiAlH_4$ in refluxing THF or by treatment with triphenylphosphine and water in THF at room temperature.[16] As the isolation of the diamines was hampered considerably by their tendency to form complexes with aluminum, we preferred the latter reduction method because it afforded the products in high yield (*ca.* 90 %) by a simple work-up procedure.

Condensation of diamines **8** with 2 equivalents of butanedione monoxime was effected by heating in di-*n*-propyl ether and azeotropic removal of water (Scheme 3).[9] The crude Costa ligands **9**, highly viscous liquids, could not be purified by chromatography because of decomposition and were used as such. Costa complexes **10** were obtained according to the standard procedure[10] by reaction of **9** with $CoCl_2$ and O_2. A large excess of

potassium iodide was used in the work-up procedure to convert the chloro- into the iodo-complexes. The crude products were purified by column chromatography and subsequent crystallization from a mixture of chloroform and diethyl ether and gave **10** in an over-all yield (based on **8**) of *ca.* 35 %.



Scheme 3

Because direct replacement of the THPO-group by bromide through reaction with triphenylphosphine dibromide[17] gave a mixture of non-separable products, the protective group was removed by treatment with an acidic cation exchange resin in methanol.[18] The alcohols **11** were then converted into the iodides **12** (contaminated with minor amounts of the corresponding bromides) by reaction with tetrabromomethane and triphenylphosphine in dichloromethane,[19] followed by exchange of axially coordinated triphenylphosphine and bromide ions by dissolving the crude products in chloroform and washing repeatedly with a saturated aqueous potassium iodide solution (60% over-all yield based on **10**).

Intramolecular alkylation was effected in a one-pot reaction by the modified procedure of Marzilli.[5] Under a nitrogen atmosphere, Costa complexes **12** were suspended in methanol (to prevent intermoleculair alkylation the concentration of **12** was reduced by a factor of 10 as compared to the original procedure), dissolved by adding 0.15 N aqueous sodium hydroxide (5 molar equivalents) and treated with a large excess of sodium borohydride. The colour of the mixture changed immediately from orange to very dark blue (characteristic for a Co(I) Costa complex) and then, more slowly, to dark green. Acetone (to destroy sodium borohydride) and potassium iodide (to introduce iodide as an axial ligand) were added and, after further work-up, the crude complexes were purified by crystallization at –20 ^{0}C from a mixture of chloroform and diethyl ether. Starting from **12a** and **12b**, brown-red microcrystalline solids were obtained in 49% and 68% yield, respectively. Both products displayed ^{1}H-NMR spectra with well-resolved sharp signals as is expected for diamagnetic alkylcobalt(III) complexes (see next section). The UV-VIS spectra of the complexes showed an absorption band at 473 nm (ε = 2.28×10^{3} M^{-1} cm^{-1}) and 476 nm (ε = 2.35×10^{3} $M^{-1}cm^{-1}$), respectively, which is characteristic of alkylCosta complexes.[20] Mass spectrometric analysis (FAB) convincingly demonstrated these complexes to be monomers. The most abundant fragment in the spectra had also the highest value for m/z (325 respectively 339) and is most probably due to cleavage of the cobalt-iodide bond in the complexes **1a** and **1b**.

A similar treatment of **12c** with sodium borohydride, however, gave a completely different result. The ^{1}H-NMR spectrum of the light-brown product obtained displayed several very broad resonances indicative of a paramagnetic Co(II) complex. In the UV-VIS spectrum no absorption band between 470 and 480 nm was present and so it was clear that the alkylCo(III) complex **1c** had not been formed. Apparently, a bridge of 4 methylene groups can not be accommodated in a Costa complex, probably due to excessive strain in the eight-membered -Co-N-$CH_2CHCH_2CH_2CH_2CH_2$-ring.

NMR-spectroscopy of 1a and 1b

Although the preparation of a large number of alkylated Costa complexes has been described in the literature, only scarce and incomplete information is available on the ^{1}H-NMR (and ^{13}C-NMR) spectroscopy of alkyl(halogenido) Costa complexes[21] to compare with and permit full interpretation of the corresponding data of **1a** and **1b**. NMR data of several alkyl Costa-type perchlorate complexes have also been reported but the chemical shifts of the cobalt-bound alkyl groups were not or not completely listed.[22] We therefore prepared *n*-propyl(iodo) Costa complex **13**, assigned all resonances of its 250 MHz ^{1}H-NMR spectrum (supported by 1D decoupling and 2D-COSY experiments) and its 50 MHz ^{13}C-NMR spectrum and thus were able to obtain relevant structural data for the intramolecularly alkylated complexes **1a** and **1b** in solution.

In general, two main effects act upon the atoms of the axial and equatorial ligands of alkylmetal complexes determining the chemical shift differences of the respective NMR signals of free and coordinated ligands: the deshielding inductive effect of the metal atom, and the ring-current effect resulting from the delocalized electron system of the coordinated equatorial ligand which shields the nuclei on top and deshields those at the sides of the ring.[23] Thus, the changes in chemical shifts of the ^{1}H and ^{13}C NMR signals observed in going from the free ligands to the alkyl(iodo) Costa complexes **1a**, **1b** and **13** are mainly determined by the position of the atoms in question relative to the equatorial ligand whence inductive and ring-current effects can cooperate or counteract.

In solution, **13** has a dynamic structure[5] due to the fast interconversion of two conformations in which the central carbon (C-*4*) of the propylene bridge of the equatorial ligand occupies alternately a position above and below the equatorial plane. If the interconversion of conformations is fast on the NMR-time scale, the chemical shift of each proton of the propylenediimine group will be the time-average of its shift in either conformation and a total of four groups of resonances is expected for H-*3a*, H-*3b*, H-*4a* and H-*4b*. Indeed, at room temperature, four multiplets originating from the propylenediimine group are found centred at 2.06 and 2.69 ppm (H-*4a,b*) and at 3.62 and 4.11 ppm (H-*3a,b*) (Table 1). At *ca.* 200K, the number of these signals has doubled, indicating that the interconversion of conformers is very slow on the NMR time scale at this temperature. NOE experiments could not discriminate between the protons *a* and *b* (above or below the equatorial plane), but comparison with the relevant protons of the H_2mdo model[6] seems to indicate that the low-field protons are the *a*-protons which are more proximate to the alkyl substituent on Co than the *b*-protons.

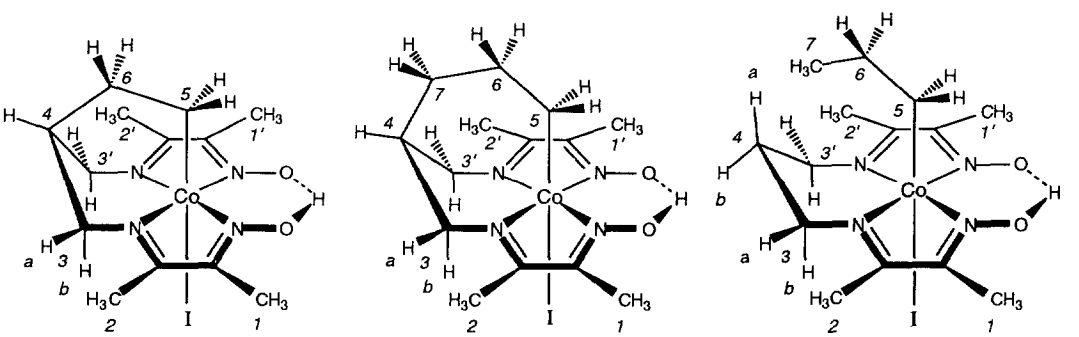


Figure 2 Structures and numbering system of **1a**, **1b**, and **13**

In **1a** and **1b**, the carbon bridge between cobalt and the equatorial ligand fixes the propylenediimine group in a single position. Inspection of molecular models showed that the conformation of this group in complex **1a** is not the same as the conformation in **1b**. Notably, the N–C-*3*–C-*4* and C-*3*–C-*4*–C-*7* angles in **1b** are

larger than the corresponding angles in **1a** on account of the difference in length of the carbon bridge (Fig.2). Furthermore, neither of these conformations is equivalent to the average conformation of the propylenediimine moiety in propyl(iodo) Costa complex **13**. Consequently, the corresponding protons of the propylenediimine group have a different chemical environment in each of the alkylated complexes and, accordingly, a different chemical shift. The chemical shifts of the equatorial methyl groups are, on the other hand, independent of these conformations and, therefore, are virtually identical (*ca.*δ 2.3 ppm) in the spectra of the three alkylated Costa complexes. For all protons of the equatorial ligand in **1a**, **1b** and **13**, the inductive and ring-current effects cooperate so that these protons appear downfield from those of the free ligand (*ca.* 0.5 ppm).

Table 1 ^{1}H NMR spectral data of **1a**, **1b**, and **13** in $CDCl_3$ at 25 °C (chemical shifts δ in ppm; coupling constants *J* in Hz; mult. = multiplicity; for numbering, see Fig. 2)

	1a				**1b**				**13**				
proton	δ	mult.	*J*		δ	mult.	*J*		proton	δ	mult.	*J*	
H-*1*	2.30	s			2.30	s			H-*1*	2.29	s		
H-*2*	2.24	d	$J_{2,3b}$	1.5	2.25	d	$J_{2,3b}$	1.5	H-*2*	2.25	s		
H-*3a*	3.65	dd	$J_{3a,3b}$	14.0	3.91	dd	$J_{3a,3b}$	15.0	H-*3a*	3.62	m	$J_{3a,3b}$	14.8
			$J_{3a,4}$	4.6			$J_{3a,4}$	3.6				$J_{3a,4b}$	6.7
												$J_{3a,4a}$	2.9
H-*3b*	3.88	bd	$J_{3b,3a}$	14.0	4.23	bd	$J_{3b,3a}$	15.0	H-*3b*	4.11	m	$J_{3b,3a}$	14.8
			$J_{3b,2}$	1.5			$J_{3b,2}$	1.5				$J_{3b,4a}$	9.2
												$J_{3b,4b}$	2.0
H-*4*	2.74	m	$J_{4,3a}$	4.6	2.60	m	$J_{4,3a}$	3.6	H-*4a*	2.06	m	$J_{4a,3b}$	9.2
			$J_{4,6}$	3.2			$J_{4,7}$	6.0				$J_{4a,3a}$	2.9
									H-*4b*	2.69	m	$J_{4b,3a}$	6.7
												$J_{4b,3b}$	2.0
H-*5*	1.60	t	$J_{5,6}$	8.2	1.45	t	$J_{5,6}$	6.2	H-*5*	1.39	dd	$J_{5,6a}$	9.5
												$J_{5,6b}$	7.4
H-*6*	1.14	dt	$J_{6,4}$	3.2	0.86	m	$J_{6,5}$	6.2	H-*6*	0.63	m	$J_{6a,5}$	9.5
			$J_{6,5}$	8.2			$J_{6,7}$	6.3				$J_{6b,5}$	7.4
												$J_{6,7}$	6.8
H-*7*	-				1.60	m	$J_{7,4}$	6.0	H-*7*	0.75	t	$J_{7,6}$	6.8
							$J_{7,6}$	6.3					

In comparison with that of the methylene protons of butane (δ = 1.30 ppm) the resonance of the protons of the cobalt-bound methylene group CH_2-*5* in **1a**, **1b** and **13** occurs at lower field, whereas CH_2-*6* is shifted to higher field. The chemical shift of CH_2-*5* is subject to both the deshielding inductive effect of cobalt and the shielding anisotropic effect of the equatorial part of the complex. Apparently, these counteracting influences result in a net deshielding as compared with the methylene group in butane. Because of its greater distance from cobalt, CH_2-*6* is much less influenced by the inductive effect so that in this case the ring-current shielding predominates and the protons are shifted upfield from δ = 1.30 ppm. The protons of CH_2-*7* in **1b** are probably outside the shielding cone and thus are shifted downfield.

The chemical shift of CH_2-*5* and notably of CH_2-*6* decreases in the order **1a** > **1b** > **13** (Table 1). Because the chemical shifts of both types of methylene protons are affected whereas cobalt can exert only a weak inductive effect on the shift of CH_2-*6*, this phenomenon must be caused by the ring-current whose effect in this case (where the axial and equatorial ligands of the three complexes are of equal nature) depends only on the

position of the protons in question relative to the equatorial part of the complex. According to molecular models, complex **1a** has a quite rigid structure in which CH_2-*5* and CH_2-*6* are not positioned directly above the ring-current in the two five-membered rings, but occupy a fixed position more or less between these two rings. In **1b**, the carbon bridge is more flexible so that the protons of CH_2-*5* and CH_2-*6* will experience a stronger shielding anisotropic effect from the ring-current than the corresponding protons in **1a**. In **13**, the propyl group is free to rotate about the cobalt-carbon bond and, consequently, some period of time occupies positions directly above the ring-current. As a result, the protons of C-*5*, C-*6* and C-*7* in **13** will experience a stronger shielding effect than those in **1a** and **1b**.

The distances between the methylene groups CH_2-*5* or CH_2-*6* and the equatorial part of the complexes will also increase with the lengths of the cobalt-carbon bonds. It is likely that this bond is longer in **1a** than in **1b** because of the greater ring strain. Accordingly, lengthening of the Co-C bond could also account for the decrease in chemical shift of CH_2-*5* and CH_2-*6* in the order **1a>1b.** This point awaits clarification by X-ray analysis. Suitable crystals of **1a** and **1b** were, however, not yet obtained.

The ^{13}C NMR spectral data of **1a** and **1b** generally resemble those observed for propyl(iodo) Costa complex **13** (see Experimental section) and most resonances could be assigned by comparison. The resonance of the carbon atom attached to cobalt (C-*5*) is easily identified by its considerable broadening due to the large quadrupole moment and large spin-quantum number (I = 7/2) of cobalt. All other assignments were affirmed by CH-COSY.

CONCLUSION

Intramolecularly alkylated Costa complexes with a bridge of two (**1a**) or of three (**1b**) methylene groups between cobalt and the central carbon atom of the propylenediimine moiety have been obtained in a synthesis starting with condensation of butanedione monoxime with suitable 2-(ω-X-alkyl)-1,3-diaminopropanes.

^1H NMR and ^{13}C NMR spectroscopic analysis reveals that **1a** and **1b** in general resemble simple alkylated Costa complexes, *e.g.* propyl(iodo) Costa complex **13**. Small differences, most evident in **1a,** are ascribed to conformational restrictions and strain imposed by the carbon bridge.

EXPERIMENTAL

General information

^1H NMR spectra were recorded on either a Brucker WH 90 or a Brucker WM 250 spectrometer. ^{13}C NMR spectra were recorded on a Brucker WM 250 spectrometer at a frequency of 62.89 MHz. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane using the solvent signal as internal reference. Coupling constants (*J*) are given in Hz. $CDCl_3$ was used as solvent unless specified otherwise.

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 in $CHCl_3$ on a Beckman DU-70 spectrophotometer. Wavelengths (λ) and extinction coefficients (ε) are given in nm and M^{-1} 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 F_{254} 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.

1-Chloro-ω-(tetrahydropyran-2-yloxy)alkanes (3a-c)

To a stirred solution of ω-chloroalkanol **2** (200 mmol) in dry CH_2Cl_2 (250 ml) were added freshly distilled dihydropyran (25.2 g, 300 mmol) and pyridinium *p*-toluenesulfonate (5.0 g, 20 mmol). After 20 h at room temperature, the colourless solution was washed with ice-cold saturated aqueous $NaHSO_3$, saturated aqueous $NaHCO_3$ and brine, respectively, dried over Na_2SO_4, concentrated and distilled under reduced pressure to give **3** as a colourless liquid.

1-Chloro-2-(tetrahydropyran-2-yloxy)ethane (**3a**): Yield 94 %. B.p. 86-87 °C/ 1 mbar. ^{1}H-NMR: 1.3-2.1 (m, 6H), 3.4-4.2 (m, 6H), 4.68 (bs, 1H).

1-Chloro-3-(tetrahydropyran-2-yloxy)propane (**3b**): Yield 95 %. B.p. 99-100 °C/ 1 mbar. ^{1}H-NMR: 1.3-1.9 (m, 8H), 2.04 (m, 2H, *J*= 6.2), 3.3-4.1 (m, 6H), 4.59 (bs, 1H).

1-Chloro-4-(tetrahydropyran-2-yloxy)butane (**3c**): Yield 96 %. B.p. 60-61 °C/ 10^{-1} mbar. ^{1}H-NMR: 1.3-2.2 (m, 10H), 3.3-4.1 (m, 6H), 4.58 (bs, 1H).

Diethyl ω-(tetrahydropyran-2-yloxy)alkane-1,1-dicarboxylates (4a-c)

A solution of diethyl malonate (32.0 g, 0.2 mol) in dry DMF (200 ml) was added at 5 °C in *ca.* 45 min to a stirred suspension of NaH (4.8 g, 0.2 mol) in dry DMF (200 ml). After an additional 45 min stirring at room temp, alkyl chloride **3** (0.19 mol) and NaI (3.0 g, 20 mmol) were added. The mixture was then stirred at 70 °C until TLC analysis (light petroleum [b.p. 40-60 °C]/EtOAc 4/1) showed that **3** had disappeared (*ca.* 20 h). After cooling to room temp the mixture was poured into water (3 l) and extracted with Et_2O (3x). After washing with saturated aqueous $NaHCO_3$ and with brine, drying over Na_2SO_4 and evaporation of the solvent, the residue was purified by short-path distillation to yield **4** as a colourless liquid.

Diethyl 3-(tetrahydropyran-2-yloxy)propane-1,1-dicarboxylate (**4a**): Yield 74 %. B.p. 108-111 °C/10^{-3} mbar. ^{1}H-NMR: 1.27 (t, 6H, *J*= 7.1), 1,4-1.9 (m, 6H), 2.20 (dt, 2H, *J*= 7.2/6.3), 3.37 (t, 1H, *J*= 6.3), 3.4-4.0 (m, 4H), 4.20 (q, 4H, *J*= 7.1), 4.57 (m, 1H). Mass-spectrum: Calculated for $C_{14}H_{24}O_6$: 288.157; found: 288.156.

Diethyl 4-(tetrahydropyran-2-yloxy)butane-1,1-dicarboxylate (**4b**): Yield 76 %. B.p. 117-119 °C/10^{-3} mbar. ^{1}H-NMR: 1.26 (t, 6H, *J*= 7.2), 1.4-1.8 (m, 8H), 1.96 (m, 2H), 3.2-4.0 (m, 5H), 4.21 (q, 6H, *J*= 7.2), 4.57 (bs, 1H). Mass-spectrum: Calculated for $C_{15}H_{26}O_6$: 302.173; found: 302.171.

Diethyl 5-(tetrahydropyran-2-yloxy)pentane-1,1-dicarboxylate (**4c**): Yield 79 %. B.p. 124-126 °C/10^{-3} mbar. ^{1}H-NMR: 1.27 (t, *J*= 7.2), 1.4-1.8 (m, 10H), 1.94 (m, 2H, *J*= 8.1/7.6), 3.34 (t, 1H, *J*= 7.6), 3.4-4.0 (m, 4H), 4.20 (q, 4H, *J*= 7.2), 4.57 (bs, 1H). Mass-spectrum: Calculated for $C_{16}H_{28}O_6$: 316.189; found: 316.190.

2-[ω-(Tetrahydropyran-2-yloxy)alkyl]propane-1,3-diols (5a-c)

To a vigorously stirred suspension of $LiAlH_4$ (5.7 g, 150 mmol) in Et_2O (150 ml) was added **4** (120 mmol) in dry Et_2O (150 ml) at such a rate that reflux was maintained. Then the reaction mixture was refluxed for about 6 h, cooled to 0 °C and cautiously treated with, successively, EtOAc, EtOH and H_2O. Finally, 15 ml of 2N aqueous NaOH was added. The mixture was filtrated through Celite and the organic layer was separated. The aqueous layer was saturated with NaCl and extracted with EtOAc (3x). The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave **5** as a colourless liquid, which was homogeneous on TLC (light petroleum [b.p. 40-60 °C] /EtOAc 1/1).

2-[2-(Tetrahydropyran-2-yloxy)ethyl]propane-1,3-diol (**5a**): Yield 99 %. ^{1}H-NMR: 1.4-2.0 (m, 9H), 2.51 (bs, 2H), 3.52 (m, 2H), 3.76 (m, 4H), 3.89 (m, 2H), 4.61 (bs, 1H). Mass-spectrum: Calculated for $C_{10}H_{20}O_4$: 204.136; found: 204.134.

2-[3-(Tetrahydropyran-2-yloxy)propyl]propane-1,3-diol (**5b**): Yield 95 %. ^{1}H-NMR: 1.1-2.0 (m, 11H), 2.56 (bs, 2H), 3.3-4.1 (m, 8H), 4.54 (bs,1H). Mass-spectrum: Calculated for $C_{11}H_{22}O_4$: 218.152; found: 218.153.

2-[4-(Tetrahydropyran-2-yloxy)butyl]propane-1,3-diol (**5c**)): Yield 99 %. ^{1}H-NMR: 1.0-2.0 (m, 14H), 2.22 (bs, 2H), 3.2-4.0 (m, 8H), 4.57 (bs, 1H). Mass-spectrum: Calculated for $C_{12}H_{24}O_4$: 232.168; found: 232.168.

2-[ω-(Tetrahydropyran-2-yloxy)alkyl]propane-1,3-diol di-*p*-toluenesulfonates (6a-c)

To a stirred solution of *p*-toluenesulfonyl chloride (55.3 g, 290 mmol) in dry pyridine (100 ml) was slowly added at 5 °C diol **5** (115 mmol) in dry pyridine (80 ml). After stirring for 18 h at 5 °C, TLC analysis (light petroleum [b.p. 40-60 °C] /EtOAc 3/2) showed complete conversion. The mixture was diluted with H_2O (500 ml) and after, stirring at 5 °C for 1 h, extracted with EtOAc (3x). The organic extracts were cooled to 0 °C and washed, successively, with ice-cold 1N H_2SO_4 (until acid reaction), with saturated aqueous $NaHCO_3$ and with brine. After drying over Na_2SO_4, concentrating and purifying by means of liquid

chromatography (MPLC; (light petroleum [b.p. 40-60 °C] /EtOAc 3/2), ditosylate **6** was obtained as a colourless viscous liquid, which was homogeneous on TLC.

2-[2-(Tetrahydropyran-2-yloxy)ethyl]propane-1,3-diol di-*p*-toluenesulfonate (**6a**): Yield 63 %. ^{1}H-NMR: 1.3-1.9 (m, 8H), 2.26 (m, 1H), 2.46 (s, 6H), 3.1-3.9 (m, 4H), 3.95 (m, 2H, *J*=10.4/6.4), 4.11 (m, 2H, *J*= 10.4/5.5), 4.44 (bs, 1H), 7.36 (d, 4H, *J*= 8.4), 7.77 (d, 4H, *J*= 8.4). Mass-spectrum: Calculated for $C_{24}H_{33}O_8S_2$: 513.161; found: 513.160

2-[3-(Tetrahydropyran-2-yloxy)propyl]propane-1,3-diol di-*p*-toluenesulfonate (**6b**): Yield 68 %. ^{1}H-NMR: 1.1-1.9 (m, 10H), (m, 1H), 2.00 (m, 1H), 2.46 (s, 6H), 3.1-3.8 (m, 4H), 3.96 (m, 4H), 4.5 (bs, 1H), 7.35 (d, 4H, *J*= 8.5), 7.75 (d, 4H, *J*= 8.5). Mass-spectrum: Calculated for $C_{25}H_{35}O_8S_2$: 527.177; found: 527.175

2-[4-(Tetrahydropyran-2-yloxy)butyl]propane-1,3-diol di-*p*-toluenesulfonate (**6c**): Yield 63 %. ^{1}H-NMR: 1.1-1.9 (m, 12H), 1.98 (m, 1H), 2.47 (s, 6H), 3.2-3.9 (m, 4H), 3.91 (m, 2H, *J*= 9.8/4.6), 3.98 (m, 2H, *J*= 9.8/6.2), 4.53 (m, 1H), 7.35 (d, 4H, *J*= 8.3), 7.74 (d, 4H, *J*= 8.3). Mass-spectrum: Calculated for $C_{26}H_{37}O_8S_2$: 541.193; found: 541.196

1,3-Diazido-2-[ω-(tetrahydropyran-2-yloxy)alkyl]propanes (7a-c)

A mixture of **6** (70 mmol), NaN_3 (18.2 g, 280 mmol) and Bu_4NBr (2.3 g, 7 mmol) in dry benzene (40 ml) and dry DMF (40 ml) was vigorously stirred at 80 °C. After 20 h the reaction mixture was cooled to room temperature and poured into H_2O (500 ml). The organic layer was separated and the aqueous layer extracted with benzene (3x). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure at 30 °C and the residue purified by liquid chromatography (MPLC). Elution with light petroleum [b.p. 40-60 °C] /EtOAc 4 /1 afforded **7** as a colourless liquid, which was homogeneous on TLC.

1,3-Diazido-2-[2-(tetrahydropyran-2-yloxy)ethyl]propane (**7a**): Yield 71 %. ^{1}H-NMR: 1.4-1.9 (m, 8H), 1.99 (m, 1H), 3.3-4.0 (m, 8H), 4.57 (bs, 1H).

1,3-Diazido-2-[3-(tetrahydropyran-2-yloxy)propyl]propane (**7b**): Yield 69 %. ^{1}H-NMR: 1.3-2.1 (m, 11H), 3.2-4.0 (m, 8H), 4.56 (bs, 1H).

1,3-Diazido-2-[4-(tetrahydropyran-2-yloxy)butyl]propane (**7c**): Yield 65 %. ^{1}H-NMR: 1.3-2.0 (m, 13H), 3.2-4.0 (m, 8H), 4.57 (bs, 1H).

2-[ω-(Tetrahydropyran-2-yloxy)alkyl]propane-1,3-diamines (8a-c)

A solution of **7** (45 mmol) in THF (50 ml) and H_2O (2.5 ml, 140 mmol) was treated portionwise with Ph_3P (23.6 g, 90 mmol), keeping the temperature below 40 °C by cooling in ice-water. After stirring at room temperature for 18 h the reaction mixture was cooled to 0 °C and light petroleum [b.p. 40-60 °C] was added to precipitate Ph_3PO. After filtration and exhaustive extraction with light petroleum (b.p. 40-60 °C), the filtrate was evaporated to dryness and the residue was extracted again with boiling light petroleum (b.p. 40-60 °C). The extract was cooled to 0 °C which caused more Ph_3PO to precipitate. This was removed again and the procedure was repeated a number of times until only trace amounts of Ph_3PO could be detected by ^{1}H-NMR. Distillation of the remaining product afforded **8** as a colourless liquid.

2-[2-(Tetrahydropyran-2-yloxy)ethyl]propane-1,3-diamine (**8a**): Yield 87 %. B.p. 101-104 °C/ 10^{-3} mbar. ^{1}H-NMR: 1.16 (bs, 4H), 1.4-1.9 (m, 9H), 2.76 (d, 4H, *J*= 5.9), 3.2-4.0 (m, 8H), 4.60 (bs, 1H). Mass-spectrum: Calculated for $C_{10}H_{22}N_2O_2$: 202.168; found: 202.170.

2-[3-(Tetrahydropyran-2-yloxy)propyl]propane-1,3-diamine (**8b**): Yield 89 %. B.p. 119-122 °C/ 10^{-3} mbar. ^{1}H-NMR: 1.06 (bs, 4H), 1.2-2.0 (m, 11H), 2.73 (d, 4H, *J*= 6.2), 3.2-4.0 (m, 4H), 4.56 (bs, 1H). Mass-spectrum: Calculated for $C_{11}H_{24}N_2O_2$: 216.184; found: 216.184.

2-[4-(Tetrahydropyran-2-yloxy)butyl]propane-1,3-diamine (**8c**): Yield 98 %. B.p. 124-127 °C/ 10^{-3} mbar. ^{1}H-NMR: 1.23 (bs, 4H), 1.3-2.0 (m, 13H), 2.74 (d, 4H, *J*= 5.6), 3.2-4.1 (m, 4H), 4.57 (bs, 1H). Mass-spectrum: Calculated for $C_{12}H_{26}N_2O_2$: 230.199; found: 230.200.

3,3'-{2-[ω-(Tetrahydropyran-2-yloxy)alkyl]trimethylenedinitrilo}bis(butan-2-one) dioximes (9a-c)

A solution of **8** (40 mmol) and 2,3-butadione monoxime (8.1 g, 80 mmol) in dry di-*n*-propyl ether (100 ml) was refluxed for approximately 5 h. H_2O formed during the reaction was collected in a Dean-Stark-trap filled with 4 Å molecular sieves. Evaporation of the solvent under reduced pressure yielded a light brown very viscous liquid, which according to its ^{1}H-NMR spectrum contained *ca.* 70 % dioxime **9**. This crude product was used without further purification in the complexation with $CoCl_2$.

3,3'-{2-[2-(Tetrahydropyran-2-yloxy)ethyl]trimethylenedinitrilo}bis(butan-2-one) dioxime (**9a**): Yield 80 %. ^{1}H-NMR: 1.3-1.9 (m,

8H), 2.01 (s, 6H), 2.08 (s, 6H), 2.41 (m, 1H), 3.3-4.1 (m, 8H), 4.60 (bs, 1H).
3,3'-{2-[3-(Tetrahydropyran-2-yloxy)propyl]trimethylenedinitrilo}bis(butan-2-one) dioxime (**9b**): Yield 75 %. ^{1}H-NMR: 1.3-1.9 (m, 10H), 2.00 (s, 6H), 2.06 (s, 6H), 2.14 (m, 1H), 3.2-4.0 (m, 8H), 4.59 (bs, 1H).
3,3'-{2-[4-(Tetrahydropyran-2-yloxy)butyl]trimethylenedinitrilo}bis(butan-2-one) dioxime (**9c**): Yield 75 %. ^{1}H-NMR: 1.2-1.9 (m, 12H), 2.01 (s, 6H), 2.07 (s, 6H), 2.14 (m, 1H), 3.2-4.1 (m, 8H), 4.58 (bs, 1H).

4-[2-(ω-(Tetrahydropyran-2-yloxy)alkyl]Costa complexes (10a-c)

To a solution of crude **9** (20 mmol) in acetone (100 ml) were added $CoCl_2.6H_2O$ (4.8 g, 20 mmol) in H_2O (35 ml) and KI (33.2 g, 200 mmol) in H_2O (65 ml). The mixture was stirred at room temperature while air was bubbled through. After 4 h the solvent was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$, washed with H_2O (3x) and dried over Na_2SO_4. Evaporation of the solvent afforded a dark brown very viscous liquid, which was applied to a column of silica 60H (MPLC). Elution with EtOAc gave diiodo-complex **10** as a dark brown solid, which was further purified by recrystallization at 5 °C from a mixture of $CHCl_3$ and Et_2O.
(*OC*-6-13)-Diiodo[[3,3'-{2-[2-(tetrahydropyran-2-yloxy)ethyl]trimethylenedinitrilo}bis(butan-2-one)dioximato](1-)-κ^4N,N',N'',N''']cobalt (**10a**): Yield 50 %. ^{1}H-NMR (250 MHz): 1.5-1.9 (m, 6H), 1.93 (m,2H), 2.54 (d, 6H, *J*= 1.7), 2.57 (s, 6H), 3.22 (m, 1H), 3.53 (m, 1H), 3.64 (m, 1H), 3.70 (m, 2H, *J*= 14.9/11.9/1.7), 3.90 (m, 1H), 4.04 (m, 1H, *J*= 10.0/7.2/5.5), 4.40 (dd, 1H, *J*= 14.9/2.5), 4.44 (dd, 1H, *J*= 14.9/2.5), 4.66 (m, 1H, *J*= 3.8/2.9).
(*OC*-6-13)-Diiodo[[3,3'-{3-[2-(tetrahydropyran-2-yloxy)propyl]trimethylenedinitrilo}bis(butan-2-one)dioximato](1-)-κ^4N,N',N'',N''']cobalt (**10b**): Yield 51 %. ^{1}H-NMR (250 MHz): 1.5-1.9 (m, 10H), 2.54 (d, 6H, *J*= 1.4), 2.57 (s, 6H), 3.03 (m, 1H), 3.51 (m, 2H), 3.65 (m, 2H, *J*= 14.9/12.6/1.4), 3.88 (m, 2H), 4.32 (m, 2H, *J*= 14.9/2.6), 4.60 (m, 1H, *J*= 4.4/2.5).
(*OC*-6-13)-Diiodo[[3,3'-{4-[2-(tetrahydropyran-2-yloxy)butyl]trimethylenedinitrilo}bis(butan-2-one)dioximato](1-)-κ^4N,N',N'',N''']cobalt (**10c**): Yield 30 %. ^{1}H-NMR (250 MHz): 1.4-1.9 (m, 12H), 2.54 (d, 6H, *J*= 1.1), 2.57 (s, 6H), 3.02 (m, 1H), 3.50 (m, 2H), 3.64 (m, 2H, *J*= 15.0/11.9/1.1), 3.87 (m, 2H), 4.30 (m, 2H, *J*= 15.0/2.5), 4.59 (dd, 1H, *J*= 4.2/2.5).

4-(ω-Hydroxyalkyl)Costa complexes (11a-c)

Costa complex **10** (3 mmol) was dissolved in a mixture of MeOH (100 ml) and CH_2Cl_2 (50 ml) and Dowex 50W-x8 acidic cation exchange resin (200-400 mesh) (1.5 g) was added. After 9 h stirring at room temperature TLC analysis (EtOAc/$CHCl_3$ 1/1) showed complete conversion of the starting material. The resin was removed by filtration and washed thoroughly with MeOH. The filtrate was concentrated until precipitation of the product was observed and then kept overnight at -20 °C. The precipitate was collected by filtration, washed with ice-cold MeOH and dried *in vacuo* over P_2O_5, yielding **11** as a dark brown solid.
(*OC*-6-13)-Diiodo[{3,3'-[2-(2-hydroxyethyl)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4N,N',N'',N''']cobalt (**11a**): Yield 89 %. ^{1}H-NMR (250 MHz): 1.74 (bs, 1H), 1.90 (q, 2H, *J*= 6.2), 2.55 (d, 6H, *J*= 1.5), 2.58 (s, 6H), 3.17 (m, 1H), 3.71 (m, 2H, *J*= 15.2/11.7/1.5), 3.95 (t, 2H, *J*= 6.2), 4.41 (dd, 2H, *J*= 15.2/2.8). ^{13}C-NMR: 14.0 (q, *J*= 130), 18.0 (q, *J*= 130), 34.6 (t, *J*= 125), 37.6 (d, *J*= 129), 56.0 (t, *J*= 143), 60.6 (t, *J*= 143), 157.4 (s), 174.0 (s). Anal. calcd. for $C_{13}H_{23}N_4O_3I_2Co$: C 26.19, H 3.89, N 9.40, I 42.58, Co 9.89 %; found: C 26.33, H 4.04, N 9.19, I 44.93, Co 9.6 %.
(*OC*-6-13)-Diiodo[{3,3'-[2-(3-hydroxypropyl)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4N,N',N'',N''']cobalt (**11b**): Yield 89 %. ^{1}H-NMR (250 MHz): 1.47 (t, 1H, *J*= 4.9), 1.76 (m, 2H), 1.85 (m, 2H), 2.55 (d, 6H, *J*= 1.6), 2.58 (s, 6H), 3.07 (m, 1H), 3.67 (m, 2H, *J*= 15.1/11.8/1.6), 3.78 (m, 2H, *J*= 5.8/4.9), 4.33 (dd, 2H, *J*= 15.1/2.8). ^{13}C-NMR:= 14.0 (q, *J*= 130), 17.9 (q, *J*= 130), 28.5 (t, *J*= 129), 29.8 (t, *J*= 133), 39.3 (d, *J*= 133), 56.0 (t, *J*= 135), 62.5 (t, *J*= 143), 157.4 (s), 174.0 (s).
Anal. calcd. for $C_{14}H_{25}N_4O_3I_2Co$: C 27.56, H 4.13, N 9.19, I 41.60, Co 9.66 %; found: C 26.85, H 4.26, N 8.71, I 44.83, Co 9.4 %.
(*OC*-6-13)-Diiodo[{3,3'-[2-(4-hydroxybutyl)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4N,N',N'',N''']cobalt (**11c**): Yield 85 %. ^{1}H-NMR (250 MHz): 1.65 (bs, 1H), 2.55 (d, 6H, *J*= 1.3), 2.57 (s, 6H), 3.03 (m, 1H), 3.65 (m, 2H, *J*= 15.0/11.7/1.3), 3.74 (m, 2H), 4.31 (dd, 2H, *J*= 15.0/2.6). ^{13}C-NMR: 14.0 (q, *J*= 130), 18.0 (q, *J*= 130), 23.3 (t, *J*= 123), 32.0 (t, *J*= 129), 32.8 (t, *J*= 127), 39.5 (d, *J*= 133), 56.0 (t, *J*= 136), 62.4 (t, *J*= 141), 157.4 (s), 173.9 (s). Anal. calcd. for $C_{15}H_{27}N_4O_3I_2Co$: C 28.86, H 4.36, N 8.98, I 40.66, Co 9.44 %; found: C 29.12, H 4.59, N 8.75, I 39.97, Co 9.7 %.

4-(ω-Bromoalkyl)Costa complexes and 6-(ω-iodoalkyl)Costa complexes (12a-c)

To a solution of Costa complex **11** (2.0 mmol) and CBr_4 (0.66 g, 2.0 mmol) in dry CH_2Cl_2 (50 ml) was added

portionwise and under continuous stirring at 0 °C Ph_3P (0.52 g, 2.0 mmol). The resulting mixture was stirred at room temperature, until TLC analysis (EtOAc/$CHCl_3$ 1/1) showed complete conversion (after 0.5-1 h). Then the solvent was evaporated under reduced pressure at room temperature and the dark brown solid residue was extracted with hot light petroleum [b.p. 40-60 °C] to remove any unreacted CBr_4 and Ph_3P. The remaining solid was dissolved in $CHCl_3$ and washed with saturated aqueous KI. The $CHCl_3$ layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was applied to a column of silica 60H. Elution with EtOAc/$CHCl_3$ 1/1 gave a product which still contained some Ph_3PO. Recrystallization from a mixture of $CHCl_3$ and Et_2O to remove the remaining impurities yielded **12** as a dark brown solid. This product consisted of two different complexes, one with bromide at the end of the polymethylene side chain (*1*) and the other with iodide (*2*). The two components were not separated, but used together in the intramolecular alkylation reaction.

(*OC*-6-13)-Diiodo[{3,3'-[2-(2-bromo/iodoethyl)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4*N,N',N'',N'''*]cobalt (**12a**): Yield 72 % (**12a-*1*/12a-*2***: 5/2). ^{1}H-NMR (250 MHz): 2.23 (m, 2H, *J*= 6.9), 2.56 (d, 6H, *J*= 1.5), 2.59 (s, 6H), 3.27 (m, 1H), 3.40 (t, 0.6H, *J*= 7.6), 3.63 (t, 1.4H, *J*= 7.1), 3.72 (m, 2H, *J*= 14.9/11.8/1.5), 4.34 (dd, 2H, *J*= 14.9/2.7).

(*OC*-6-13)-Diiodo[{3,3'-[2-(3-bromo/iodopropyl)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4*N,N',N'',N'''*]cobalt (**12b**): Yield 65 % (**12b-*1*/12b-*2***: 4/1). ^{1}H-NMR (250 MHz): 1.79 (m, 2H), 2.12 (m, 2H), 2.56 (d, 6H, *J*= 1.5), 2.58 (s, 6H), 3.06 (m, 1H), 3.30 (t, 0.4H, *J*= 6.6), 3.52 (t, 1.6H, *J*= 6.3), 3.69 (m, 2H, *J*= 15.1/11.5/1.5), 4.31 (dd, 2H, *J*= 15.1/2.6).

(*OC*-6-13)-Diiodo[{3,3'-[2-(4-bromo/iodobutyl)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4*N,N',N'',N'''*]cobalt (**12c**): Yield 79 % (**12c-*1*/12c-*2***: 4/3). ^{1}H-NMR (250 MHz): 1.73 (m, 4H), 1.96 (m, 2H), 2.56 (d, 6H, *J*= 0.9), 2.58 (s, 6H), 3.06 (m, 1H), 3.29 (t, 0.9H, *J*= 6.6), 3.51 (t, 1.1H, *J*= 6.4), 3.67 (m, 2H, *J*= 15.1/11.5/0.9), 4.31 (dd, 2H, *J*= 15.1/2.7).

Intramolecularly alkylated (iodo)Costa complexes (1a,b)

To a suspension of **12** (1.0 mmol) in MeOH (350 ml) was added an aqueous 0.15 N NaOH solution (35 ml). N_2 was continuously bubbled through the reaction mixture. When all of the starting material had dissolved 15 ml of a 0.1 M solution of $NaBH_4$ in H_2O (flushed thoroughly with N_2) was added. The colour of the mixture changed at once from orange to dark blue and then slowly to dark green. After 30 min stirring at room temperature the N_2 purging was stopped and acetone (10 ml) was added to destroy the excess of $NaBH_4$. Then a solution of KI (1.7 g, 10 mmol) in H_2O (30 ml) was added and after an additional 10 min stirring the bright orange solution was concentrated under reduced pressure at room temperature. The residue was extracted with $CHCl_3$ and the combined extracts were washed with saturated aqueous KI (5x) and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure at room temperature, the crude product was recrystallized at -20 °C from a mixture of $CHCl_3$ and Et_2O yielding either a brown red (**1a**) or a dark red (**1b**) microcrystalline solid.

(*OC*-6-43)-Iodo[{3,3'-[2-(ethylene-κC^2)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4*N,N',N'',N'''*]cobalt (**1a**): Yield 49 %. ^{1}H-NMR (250 MHz): see Table 1. ^{13}C-NMR: 12.9 (q, *J*= 130), 16.9 (q, *J*= 129), 26.5 (t, *J*= 127), 34.6 (t, *J*= 132), 40.6 (d, *J*= 131), 54.3 (t, *J*= 138), 153.5 (s), 167.7 (s). UV-VIS: 248 (ε= 20.06x10^3), 374 (ε= 7.55x10^3), 473 (ε= 2.28x10^3).

Anal. calcd. for $C_{13}H_{22}N_4O_2ICo$: C 34.53, H 4.90, N 12.39, I 28.06, Co 13.03 %; found: C 35.30, H 4.99, N 11.89, I 29.43, Co 12.3 %.

(*OC*-6-43)-Iodo[{3,3'-[2-(trimethylene-κC^3)trimethylenedinitrilo]bis(butan-2-one)dioximato}(1-)-κ^4*N,N',N'',N'''*]cobalt (**1b**): Yield 68 %. ^{1}H-NMR (250 MHz): see Table 1. ^{13}C-NMR: 12.8 (q, *J*= 129), 16.9 (q, *J*= 129), 29.4 (t, *J*= 125), 30.1 (t, *J*= 124), 34.0 (d, *J*= 125), 39.8 (t, *J*= 137), 54.4 (t, *J*= 137), 152.3 (s), 168.3 (s). UV-VIS: 255 (ε= 18.84x10^3), 375 (ε= 8.10x10^3), 476 (ε= 2.35x10^3). Anal. calcd. for $C_{14}H_{24}N_4O_2ICo$: C 36.07, H 5.19, N 12.02, I 27.22, Co 12.64 %; found: C 35.26, H 5.23, N 11.65, I 28.17, Co 12.5 %.

(*OC*-6-43)-Iodo(propyl-κC^1)[{3,3'-(trimethylenedinitrilo)bis(butan-2-one)dioximato}(1-)-κ^4*N,N',N'',N'''*]cobalt (13)

To a suspension of diiodoCosta complex[10] (1.10 g, 2.0 mmol) in MeOH (50 ml) was added an aqueous 0.5 N NaOH solution (10 ml). N_2 was continuously bubbled through the reaction mixture. When all of the complex had dissolved propyl bromide (730 µl, 8.0 mmol) was added, followed by 5.0 ml of a 0.6 M $NaBH_4$ solution in H_2O (flushed thoroughly with N_2). The colour of the mixture changed immediately from orange to dark blue and then within a few minutes to dark red. After 15 min stirring at room temperature the N_2 purging was stopped and acetone (10 ml) was added. Subsequently, a solution of KI (2.5 g, 15 mmol) in H_2O (10 ml) was added and after an additional 10 min stirring the bright orange solution was concentrated under reduced pressure at room temperature. The residue was extracted with $CHCl_3$ and the combined extracts were washed with saturated aqueous KI (5x) and

dried over Na_2SO_4. After evaporation of the solvent, the crude product was recrystallized at -20 °C from a mixture of $CHCl_3$ and Et_2O yielding propyl(iodo)Costa complex **13** as a orange microcrystalline solid: Yield 63 %. ^{1}H-NMR (250 MHz): see Table 1. ^{13}C-NMR: 13.0 (q, *J*= 130), 14.3 (q, *J*= 127), 17.0 (q, *J*= 129), 23.0 (t, *J*= 129), 28.1 (t, *J*= 128), 40.7 (t, *J*= 133), 49.0 (t, *J*= 137), 151.8 (s), 169.0 (s). UV-VIS: 258 (ε= 17.81x10^3), 383 (ε= 8.45x10^3), 480 (ε= 2.58x10^3).

REFERENCES

1. Halpern, J. in *B_{12}*; Dolphin, D., Ed.; J. Wiley: New York; vol 1, **1982**; ch. 14, p. 501. Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.*, **1984**, *31*, 105-204; Randaccio, L.; Bresciani-Pahor, N.; Zangrando, E.; Marzilli, L. G. *Chem. Soc. Rev.*, **1989**, *18*, 225-250.
2. Summers, M. F.; Marzilli, L. G.; Bresciani-Pahor, N.; Randaccio, L. *J. Am. Chem. Soc.* **1984**, *106*, 4478-4485.
3. Elliot, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558-5566.
4. Marzilli, L. G.; Summers, M. F.; Bresciani-Pahor, N.; Zangrando, E.; Charland, J.-P.; Randaccio, L. *J. Am. Chem. Soc.* **1985**, *107*, 6880-6888.
5. Parker, W. O.; Bresciani-Pahor, N.; Zangrando, E.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1985**, *24*, 3908-3913.
6. Altink, R.; Van Arkel, B.; Van der Baan, J. L.; Balt, S.; De Bolster, M. W. G.; Van Delft, R. J.; Klumpp, G. W.; De Koning, H.; Van den Winkel, Y. *Rec. Trav. Chim. Pays Bas* **1994**, *113*, 329-333.
7. Robinson, J. A.; Flohr, H.; Kempe, U. M.; Pannhorst, W.; Rétey, J. *Liebigs Ann. Chem.* **1983**, 181-203.
8. Van Arkel, B.; Van der Baan, J. L.; Balt, S.; Bickelhaupt, F.; De Bolster, M. W. G.; Kingma, I. E.;. Klumpp, G. W.; Moos, J. W. E.;.Spek, A. L. *J. Chem. Soc. Perkin Trans 1*, **1993**, 3023-3032.
9. Uhlig, E.; Friedrich, M.; Z. *Anorg. Allg. Chem.* **1966**, *343*, 299-307.
10. Costa, G.; Mestroni, G.; De Savorgnani, E.; *Inorg. Chim. Acta* **1969**, *3*, 323-328.
11. Langer, E. in *Houben-Weyl, Methoden der organischen Chemie*; Georg Thieme Verlag, Stuttgart; vol. 13/9b, **1984**, p. 1-284.
12. Miyashita, N.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772-3776.
13. Irwin, A. J.; Lok, K. P.; Huang, K. W-C.; Bryan Jones, J. *J. Chem. Soc. Perkin Trans 1*, **1978**, 1636-1642.
14. Stuart Tipson, R. *J. Org. Chem.* **1944**, *9*, 235-241.
15. Koziara, A.; Osowska-Pacewicka, K.; Zawadzki, S.; Zwierzak, A. *Synthesis*, **1985**, 202-204.
16. Knouzi, N.; Vaultier, M.; Carrié, R. *Bull. Soc. Chim. France*, **1985**, 815-219.
17. Sonnet, P. E. *Synth. Commun.* **1976**, *6*, 21-26.
18. Beier, R.; Mundy, B. P. *Synth. Commun.* **1979**, *9*, 271-273.
19. Kocienski, P. J.; Cernigliaro, G.; Feldstein, G. *J. Org. Chem.* **1977**, *42*, 353-355.
20. Finke, R. G.; Schiraldi, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 7605-7617.
21. Pellizer, G.; Tauszik, G. R.; Costa, G. *J. Chem. Soc. Dalton Trans.* **1973**, 317-322; Finke, R. G.; Smith, B. L.; McKenna, W. A.; Christian, P. A. *Inorg. Chem.* **1981**, *20*, 687-693; Daikh, B. E.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 4160-4172.
22. Magnuson, V. E.; Weber, J. H. *J. Organomet. Chem.* **1975**, *92*, 233-243; Parker, W. O.; Zangrando, E.; Bresciani-Pahor, N.; Marzilli, P. A.; Randaccio, L.; Marzilli, L. G. *Inorg. Chem.* **1988**, *27*, 2170-2180.
23. López, C.; Alvarez, S.; Solans, X.; Font-Altaba, M. *Inorg. Chim. Acta* **1986**, *111*, L19-L21.

(*Received in UK* 12 *January* 1995; *accepted* 9 *February* 1995)