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Template synthesis of organocobalt chelates with tridentate Schiff bases. Crystal structure of [MeCo(7-Me-salen-*N*-Me)(*N*-Me-en)]I *

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Abstract

Series of alkylcobalt(III) chelates with tridentate Schiff bases composed of a ketoenol and a diamine in a 1/1 ratio have been prepared via template synthesis. Stereochemical features of resulting structures have been studied by X-ray and NMR techniques. Scope of the template reaction as well as its route is considered.

Introduction

Several years ago we reported the first preparation of alkylcobalt(III) chelates with tridentate ligands [1,2]. Further studies [3–9] revealed some features of the structure and reactivity of these complexes. Especially noteworthy was their ready homolytic decomposition under the action of acids, which involves intermediate formation of alkyl free radicals, as proved by the spin-trapping technique [5]. Because of this reaction, organocobalt chelates with tridentate ligands can be used to initiate radical polymerization at or even below room temperature [3].

The route to the complexes in question is in itself of some interest, since this is the only case in organocobalt chemistry in which the template technique leads to products that could not be obtained by stepwise procedures, and so it seems appropriate to describe the template synthesis of organocobalt chelates with tridentate Schiff bases in detail. We also consider here the scope and mechanistic aspects of the process, as well as the structures of resulting complexes.

In the formulae, established abbreviations for Schiff base ligands are modified to indicate the number of carbonyl components (-ydenate residues).

* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

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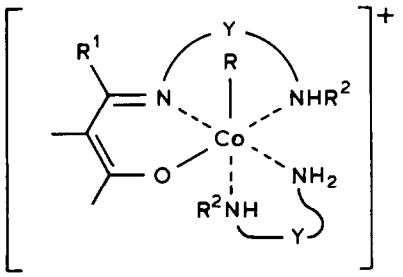
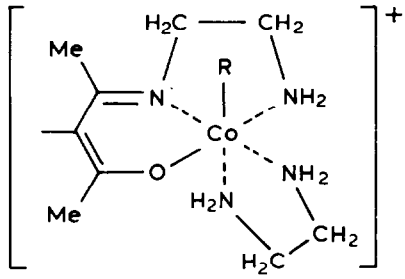
Results and discussion

1. General

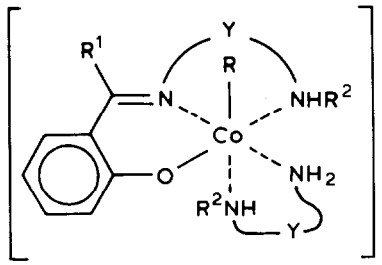
Alkylcobalt(III) chelates with a tridentate ligand (I, II) were prepared by template syntheses. The starting materials were a cobalt(II) salt, two chelating agents, viz. a ketoenol and a diamine containing at least one primary amino group, the reducing system $NaBH_4$/Pd, and a primary or secondary alkyl bromide or iodide. The preparations, like known template syntheses of alkylcobalt chelates with tetradentate Schiff bases [10,11], were carried out in strongly alkaline methanolic media at ambient temperature. The resulting tridentate anion ligand is derived from the Schiff base composed of ketoenol and diamine in a 1/1 ratio. The complexes obtained in this way (they are listed in the Experimental section) also contain a bidentate ligand, viz. diamine (in I) or ketoenolate (in II), so that the central atom is six-coordinate, as in most cobalt(III) compounds.



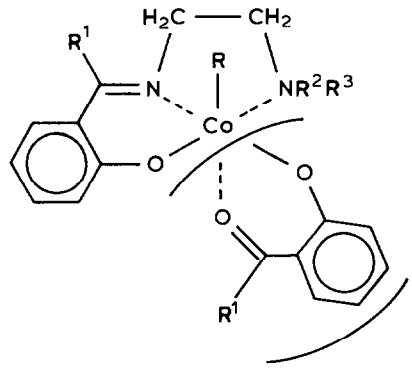
(I)



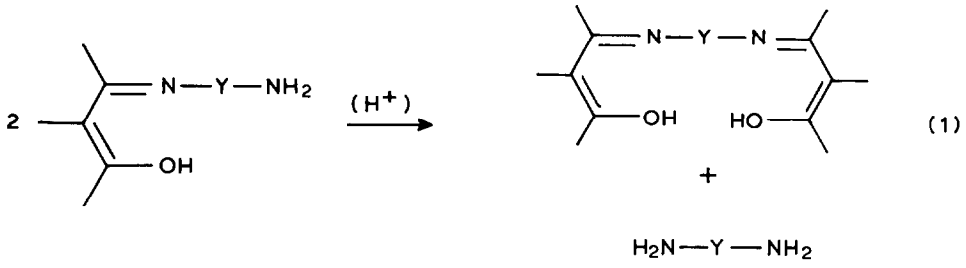
(Ia, R = Et)



(Ib, R = prim-or s-alkyl;
R^1 = Me, Et;
R^2 = H, Me;
Y = $(CH_2)_2$, $(CH_2)_3$, $CHMeCH_2$)

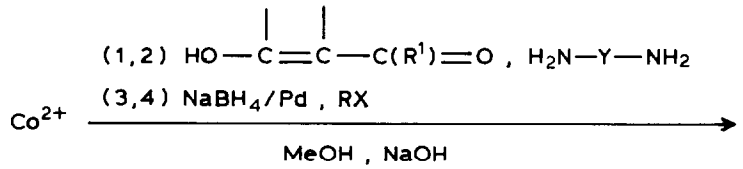


(II, R = Me, Et;
R^1 = Me, Et;
R^2, R^3 = Me)

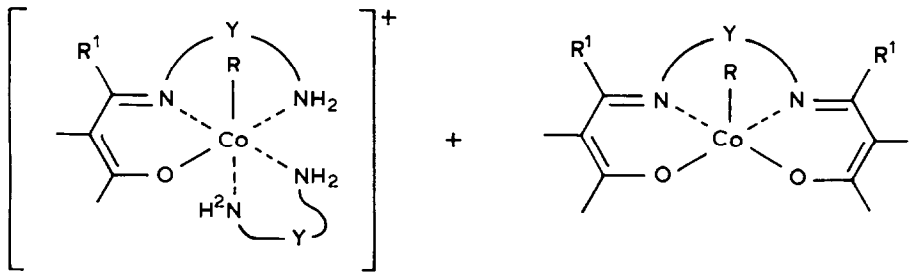


(1)

Is is noteworthy that the tridentate ligands in complexes I with $R^2 = H$, i.e. those derived from diamines with both primary amino groups, correspond to the Schiff bases which are quite unstable towards disproportionation (eq. 1), particularly in protolytic media [12,13]. Concurrent formation of two organometallic products was observed in these cases *; in addition to the above-mentioned cationic complexes, we isolated compounds of the well-known type III, i.e. alkylcobalt chelates with tetradentate Schiff bases **:



(2)



(I , R^2 = H) (III)

Despite the complexity of the template reactions, organocobalt chelates with tridentate ligands were usually obtained in satisfactory yields. In the most thoroughly studied series [RCo(7-Me-salen)(en)]$^+$ we succeeded in raising them even to 80–90%. As was shown for the case of R = Et, the outcome of the syntheses depends heavily on the ratio of the chelating agents. The maximum yield of the complex with tridentate ligand was reached with a ratio of ketone to diamine of ca. 1/1. In the

* When R was Me, a third alkylcobalt complex, with *N*-methylated chelating diamine, (e.g. [MeCo(7-salen)(*N*-Me-en)]$^+$ – see [8]) was obtained.

** Some of them, namely complexes of the series RCo(acac$_2$en) (IIIa) and RCo{(7-Me-sal)$_2$en} (IIIb, R^1 = Me and Y = $(CH_2)_2$) were synthesized by Costa and by Schrauzer et al. [10,14–16] by various routes.

Table 1

Diagnostic criteria for distinguishing structural types of organocobalt chelates with Schiff base ligands obtained in template syntheses

Types of complex	Characteristic reactions (and products and/or symptoms)					LC behaviour on SiO_2	N–H stretches in IR spectra
	Photolysis by visible radiation	Action of acids	Ligand substitution		Ag^+-Test for halide ion		
			Direct, by py	H^+-Assisted, by phen			
I [a]	+(RH, R_{-H}, R_2; colour change)	Decomposition (RH, R_{-H}, R_2, initial diamine and ketoenol, and Co^{2+})	–	+(initial diamine and a new organocobalt complex)	+	Immobile unless eluent contains electrolyte	Strong broad bands at 3100–3260 cm^{-1}, and weaker sharp bands at 3280–3350 cm^{-1}
II	+(RH, R_{-H}, R_2; colour change)	Decomposition (RH, R_{-H}, R_2 initial diamine and ketoenol, and Co^{2+})	–	Decomposes under conditions used	–	Decomposes under conditions used	–
III	+(RH, R_{-H}, R_2; colour change)	Reversible protonation [b] (colour change)	+ [c] (colour change)	–	–	Mobile whether eluent contains electrolyte or does not	–

[a] Isolated as salts with halide anions. [b] Cf. [20]. [c] Strictly, the addition of pyridine, i.e. the formation of hexacoordinate complex (see [16]).

case of acetylacetone and ethylenediamine, their ratio affects the course of synthesis so strongly that either of the organometallic complexes Ia or IIIa where Y = $(CH_2)_2$ (i.e. $[RCo(acacen)(en)]^+$ or $RCo(acac_2en)$), can be the main product *.

To obtain the high yields, it proved necessary to maintain the reducing agent in the reaction mixture for a long time. Since the syntheses were accompanied by the catalytic solvolysis of $NaBH_4$, it had to be added continuously during several hours.

An additional factor evidently operates in the synthesis of organometallic complexes II derived from diamine with a tertiary amino group; their preparations were badly affected if the reaction medium contained more than a certain amount of water. Thus, when its content was reduced from 8 to 1.5% (by volume), the yield of the compound II with R = Et and R^1, R^2, R^3 = Me increased by a factor of 4–5, and there was less of the by-product, the known [17] inorganic complex $[Co(o\text{-}OC_6H_4COMe)_2]$. The latter is probably formed as a result of hydrolysis of tridentate ligands in more highly-coordinate complexes that would be overcrowded by bulky groups.

Our attempts to extend the scope of the template synthesis revealed certain limitations. Thus, we failed to obtain t-butyl-, benzyl-, or phenyl-cobalt complexes by procedures similar to those used for preparation of alkylcobalt chelates of the series $[RCo(7\text{-Me-salen})(en)]^+$. These results are not surprising. First, Co^{III}–C (tertiary) bonds are generally labile because of steric hindrances [18]. Second, the lack of success in the case of benzyl halides may be due to an easy dissociation of the transient metal–carbon bond; this feature is typical of benzylcobalt complexes [19]. Third, under the conditions of the template synthesis, PhBr proved essentially unreactive, while PhI underwent hydrogenolysis.

We also failed to obtain alkylcobalt chelates with tridentate Schiff bases starting from diamines which contain one or two aromatic amino groups, viz. *N*-Ph-en and $o\text{-}C_6H_4(NH_2)_2$. (Other 'ligand sources' were MeI or EtBr, and $o\text{-}HOC_6H_4COMe$). This failure may be the result of the low donor ability of 'aniline' nitrogen or of ready solvolysis of the related Schiff base ligands.

We also failed to prepare alkylcobalt complexes with tridentate ligands starting from an aromatic *o*-hydroxyaldehyde (namely $o\text{-}HOC_6H_4CHO$) rather than the ketone. Both ethylenediamine and its *N*-methyl derivative were tried as the other chelating agent; the failure in the latter case is noteworthy since it rules out competitive formation of the compound with tetradentate ligand. The cause of this failure is not clear.

2. Characterization and structure

For convenience, the criteria used to distinguish the structural types of organocobalt chelates with Schiff base ligands obtained in template reactions are summarized in Table 1.

All the complexes under consideration ** readily decompose in strongly acidic

* An earlier finding by Schrauzer et al. [10] is relevant. Using the template technique at the single reagent ratio of $CoCl_2/en/CH_2(COMe)_2$ of 1/1/2, they obtained only one series of organocobalt complexes, viz. that with the tetradentate Schiff base.

** A few of them, viz. [RCo(7-Me-salen)(en)]X (where R is Me or Et) and [MeCo(7-Me-salen)(*N*-Me-en)]X (with X = Br or I), [MeCo(7-Me-salen-*N*-Me)(*N*-Me-en)]I and [EtCo(7-Me-saltn)(tn)]I were characterized previously [1,2,4,8].

Table 2

Signals from the alkyl ligands in the ^1H NMR spectra of complexes of the series $[RCo(7\text{-Me-salen})(en)]^+$ [a]

R	Solvent	Assigned signal [b]: δ (ppm vs. TMS), multiplicity			
		α-H	β-H	γ-H	δ-H
Me	D_2O	CH_3: 2.22, s			
Et		CH_2: 3.3–3.5 [c,d]	CH_3: 0.54, t		
i-Pr	[e]	CH: 3.97, m [c]	CH_3: 0.60, d; 0.66, d		
c-Hex	[e]	CH: 3.88, m [c]	CH_2: 1.50, br; 1.63, br		
4-Br-c-Hex [f]	$CDCl_3$	CH: 3.80, m	CH_2: 1.68, br; 2.08, br		CH: ≈ 4.8

[a] The remaining signals in the spectra are very similar throughout the series. Assignments of the spectra for the 1st and 2nd members of the series have been made previously [8]. [b] The intensities of these and other signals in the spectra are consistent with the assignments. [c] The assignment is based on double resonance experiments. [d] A system of diastereotypic protons (type ABX_3). [e] Made alkaline with NaOH. [f] The complex evidently consists of both of the geometrical isomers.

solutions to give hydrocarbons arising from disproportionation and coupling of the alkyl groups R. The analysis of the other products of the 'acidolysis' is useful in elucidating the composition of the remaining ligands, as described previously [8].

The properties of the complexes derived from diamines containing only primary and secondary amino groups are indicative of cationic species. Thus, they were characterized by (a) a positive test (with Ag^+) for halide (counter-) ion, (b) strong and broad bands in IR spectra (at 3100–3260 cm^{-1}) due to stretching vibrations of coordinated N–H groups participating in inter-ion hydrogen bonds (cf. [1,2,8]), and (c) LC mobility developing only under ion exchange conditions (on SiO_2 with a NaOAc solution as eluent). These characteristics of the complexes in question, as well as their reactivity toward acids, allow them to be easily distinguished from alkylcobalt chelates with tetradentate Schiff bases (Table 1). In particular, the latter exhibit LC mobility regardless of the presence of electrolyte.

The suggested formulae (I) of the former complexes, with bis-primary or primary-secondary diamines as bidentate ligands, are also consistent with the NMR data (Tables 2, 3; see also [8]) and the elemental analyses. Finally, the nature of the bidentate ligands was directly confirmed by their proton-assisted replacement by a weaker Lewis base (Table 1) under conditions described elsewhere [8].

On the other hand, the organocobalt complexes derived from diamine with a tertiary amino group were shown to be neutral, with anionic hydroxyketone residue acting as a bidentate ligand. Structure II is confirmed by the elemental analyses (see Experimental section) and by the absence of N–H stretches in the IR spectra (Table 1).

It was established by Sacconi et al. [22] that the coordination geometry in complexes of potentially tridentate Schiff bases is governed mainly by the steric requirements of the ligands. In accord with this general conclusion, later studies [4,23] revealed that tridentate Schiff base ligands composed of ethylenediamine and aromatic *o*-hydroxyaldehyde or -ketone are located in a meridional coordination position (i.e. nearly in-plane with the central atom) in octahedral complexes of trivalent chromium and cobalt. Evidently, the alternative facial attachment of these

Table 3

Comparison of ^{1}H NMR data for [EtCo(acacen)(en)]$^+$ and some related complexes

Complex	Solvent	Signal [a]: δ (ppm vs TMS), multiplicity				Refs.
		CH_3CH_2	Tridentate ligand			
			CH_3		=CH	
			Me–C=N	Me–C=O		
[EtCo(acacen)(en)]Br	D_2O	0.60, t	1.70, s	1.94, s	4.98, s	
[EtCo(7-Me-salen)(en)]Br		0.54, t	2.50, s	–	–	
[EtCo(acac$_2$en)(py)]	$CDCl_3$	0.37, t	1.90, s	1.93, s	4.86, s	[21]
[Co(acacen)$_2$]Br		–	1.94, s	2.29, s	5.01, s	[13]

[a] Intensities of the signals are consistent with their assignments.

ligands would have necessitated considerable distortions of bond angles. Further, we found the Co–C bonds in the alkylcobalt complexes with tridentate Schiff bases to be approximately normal to the planes of chelate nodes of these ligands * [1,4,8]. Even though both of the above limitations were taken into account, there could be isomerism in certain of the cases under consideration **. In particular, there may be diastereomers if the molecule involves extra chiral center(s) (apart from the cobalt atom), and geometric isomers if the bidentate ligand lacks two-fold symmetry axis relative to its donor atoms. Some evidence for such isomerism has been reported [8,9], and we now encounter a further example, since according to ^{1}H NMR data, the complex [EtCo(7-Me-salpn)(pn)]$^+$, prepared by template synthesis starting from (racemic) propylenediamine, consists of no less than 4 isomers. (The theoretical limit is 16).

On the other hand, there are some cases where a single isomer is obtained. Thus, the ^{1}H NMR data strongly suggest that the cations [MeCo(7-Me-salen)(*N*-Me-en)]$^+$ and [MeCo(7-Me-salen-*N*-Me)(*N*-Me-en)]$^+$ are individual species [8], and an X-ray diffraction study of the iodide salt, (IV), of the latter has allowed us to elucidate steric factors affecting structures of organocobalt complexes with tridentate Schiff bases. (The role of polar effects, which are mainly due to a labilizing *trans*-influence of the carbanionic ligand R, has been considered in our previous papers [1,4,8]) ***.

The hydrogen-bonded ionic structure of IV is generally similar to that of [EtCo(7-Me-salen)(en)]Br (V) which was studied earlier [1,4]. In particular, this is true for the main features of the coordination octahedron in the organometallic cation (Fig. 1), namely the meridional mode of coordination of the tridentate ligand, the axial orientation of Co–C bond, the fact that its length is normal for a n-alkylcobalt(III) complex (cf. [24]), and the substantial difference between Co–N distances in the chelate ring formed by the diamine ligand. On the other hand, the structure of IV shows a much larger deviation of the six-membered chelate cycle from planarity; thus, the tetragon OC(2)C(1)C(7) can be regarded as planar to, within ± 0.01 Å for V but only ±0.06 Å for IV. Furthermore, another atom of the

* For brevity, we will call such a plane equatorial. *(Continued on p. 170)*

** Enantiomerism is set aside here and below.

*** The atomic coordinates for complex IV are listed in Table 4, and the bond distances and angles are given in Table 5.

Table 4

Atomic coordinates ($\times 10^5$ for Co and I, $\times 10^3$ for H, and $\times 10^4$ for the other atoms) for complex IV with e.s.d.'s in parentheses

Atom	x	y	z
I	24940(4)	−278(2)	13325(1)
Co	21304(8)	70134(5)	87016(2)
O	3000(4)	5842(2)	9241(1)
N(1)	502(5)	5946(3)	8315(2)
N(2)	1199(5)	8253(3)	8148(2)
N(3)	3664(5)	8110(3)	9179(2)
N(4)	117(5)	7486(3)	9337(2)
C(1)	1644(6)	4127(4)	8756(2)
C(2)	3049(6)	4706(4)	9106(2)
C(3)	4474(6)	3987(4)	9334(2)
C(4)	4519(7)	2780(4)	9236(2)
C(5)	3129(7)	2211(4)	8926(2)
C(6)	1706(7)	2871(4)	8690(2)
C(7)	257(7)	4815(4)	8426(2)
C(8)	−1413(6)	4175(4)	8199(2)
C(9)	−794(6)	6595(4)	7928(2)
C(10)	223(6)	7615(5)	7659(2)
C(11)	2435(7)	9183(4)	7908(2)
C(12)	2559(7)	8844(4)	9582(2)
C(13)	1130(7)	8049(3)	9837(2)
C(14)	−1074(7)	6515(4)	9548(2)
C(15)	4151(6)	6644(4)	8170(2)

Atom	x	y	z
HN(2)	39(6)	861(4)	834(2)
HN(3.1)	439(6)	758(4)	942(2)
HN(3.2)	437(7)	846(5)	897(2)
HN(4)	−55(7)	816(4)	919(2)
H(3)	549(5)	444(3)	955(2)
H(4)	552(8)	226(5)	936(3)
H(5)	319(6)	121(4)	886(2)
H(6)	81(6)	259(4)	847(2)
H(8.1)	−124(8)	397(5)	777(3)
H(8.2)	−147(8)	346(5)	838(3)
H(8.3)	−233(8)	456(6)	829(3)
H(9.1)	−123(8)	610(5)	761(2)
H(9.2)	−173(7)	694(5)	819(2)
H(10.1)	109(6)	731(4)	738(2)
H(10.2)	−53(6)	828(4)	748(2)
H(11.1)	293(8)	980(5)	823(2)
H(11.2)	148(11)	970(7)	763(3)
H(11.3)	308(13)	998(6)	740(4)
H(12.1)	189(6)	952(5)	937(2)
H(12.2)	328(7)	927(5)	994(2)
H(13.1)	35(7)	845(5)	1013(2)
H(13.2)	173(5)	739(4)	1006(2)
H(14.1)	−206(7)	621(5)	924(2)
H(14.2)	−148(8)	680(5)	996(2)
H(14.3)	−24(7)	574(5)	963(2)
H(15.1)	510(8)	730(5)	829(2)
H(15.2)	375(9)	674(6)	776(3)
H(15.3)	449(8)	579(5)	828(3)

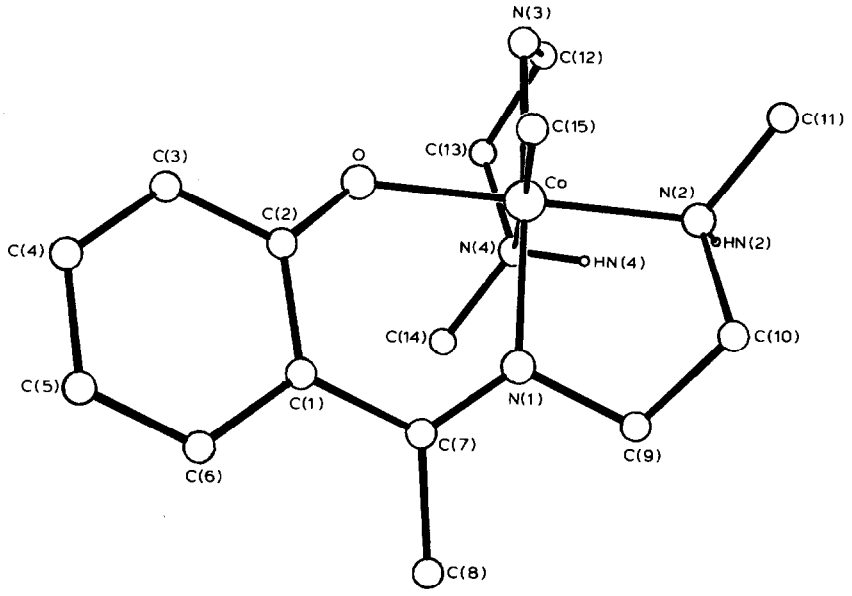


Fig. 1. Structure of the cation in crystals of [MeCo(7-Me-salen-*N*-Me)(*N*-Me-en)]I. The only H atoms shown are those bound to nitrogen in secondary amino groups.

Table 5

Bond lengths (Å) and angles (°) in complex IV

Co–O	1.887(3)	N(1)–C(9)	1.469(6)	C(1)–C(7)	1.468(6)
Co–N(1)	1.890(4)	N(2)–C(10)	1.483(6)	C(2)–C(3)	1.410(6)
Co–N(2)	1.974(4)	N(2)–C(11)	1.490(6)	C(3)–C(4)	1.366(6)
Co–N(3)	1.970(4)	N(3)–C(12)	1.477(6)	C(4)–C(5)	1.382(7)
Co–N(4)	2.146(4)	N(4)–C(13)	1.476(6)	C(5)–C(6)	1.379(7)
Co–C(15)	1.972(5)	N(4)–C(14)	1.479(6)	C(7)–C(8)	1.503(7)
O–C(2)	1.304(5)	C(1)–C(2)	1.442(6)	C(9)–C(10)	1.498(7)
N(1)–C(7)	1.301(6)	C(1)–C(6)	1.411(6)	C(12)–C(13)	1.500(7)
OCoN(1)	93.6(1)	CoOC(2)	122.4(3)	OC(2)C(1)	122.7(4)
OCoN(2)	179.0(1)	CoN(1)C(7)	127.8(3)	OC(2)C(3)	119.5(4)
OCoN(3)	84.1(1)	CoN(1)C(9)	111.2(3)	C(1)C(2)C(3)	117.7(4)
OCoN(4)	88.5(1)	C(7)N(1)C(9)	120.0(4)	C(2)C(3)C(4)	121.5(4)
OCoC(15)	89.6(2)	CoN(2)C(10)	106.7(3)	C(3)C(4)C(5)	121.0(4)
N(1)CoN(2)	86.7(2)	CoN(2)C(11)	120.6(3)	C(4)C(5)C(6)	119.9(5)
N(1)CoN(3)	173.9(2)	C(10)N(2)C(11)	110.9(3)	C(1)C(6)C(5)	121.1(4)
N(1)CoN(4)	91.1(1)	CoN(3)C(12)	111.1(3)	N(1)C(7)C(1)	120.5(4)
N(1)CoC(15)	94.0(2)	CoN(4)C(13)	105.4(3)	N(1)C(7)C(8)	120.8(4)
N(2)CoN(3)	95.5(2)	CoN(4)C(14)	117.1(3)	C(1)C(7)C(8)	118.6(4)
N(2)CoN(4)	90.6(1)	C(13)N(4)C(14)	111.3(3)	N(1)C(9)C(10)	106.8(4)
N(2)CoC(15)	91.3(2)	C(2)C(1)C(6)	118.6(4)	N(2)C(10)C(9)	107.8(4)
N(3)CoN(4)	83.2(1)	C(2)C(1)C(7)	121.8(4)	N(3)C(12)C(13)	107.8(4)
N(3)CoC(15)	91.6(2)	C(6)C(1)C(7)	119.4(4)	N(4)C(13)C(12)	108.0(4)
N(4)CoC(15)	174.6(2)				

cycle, N(1), is displaced from this mean plane towards the alkyl ligand by 0.30 in V and 0.52 Å in IV. To explain such a large difference, both the conformational non-rigidity of the chelate ring [4] and the repulsion of the N(1) atom by methyl group of the bidentate ligand must be taken into account.

In our view, the most interesting features of the structure IV are those related to potential isomerism of the complex cation. First, the methylamino group of the bidentate ligand in IV is located *trans* to R. Analysis of the ^{1}H NMR spectra enabled us to conclude [8] that *N*-methylethylenediamine is coordinated in the same manner even if amino group of the tridentate ligand is a primary one, i.e. in the case of [MeCo(7-Me-salen)(*N*-Me-en)]$^+$. These facts agree well with molecular models which suggest that bulky groups will be sterically hindered from entering the equatorial plane, viz. the position *cis* to R.

Second, the methyl group bound to nitrogen in the tridentate ligand of complex IV occupies the one of the two feasible sites which is more remote from the chelating diamine. Again, molecular models are helpful in revealing that this specificity is due to a steric effect in that Van der Waals repulsion near the equatorial plane would be much stronger in the alternative diastereomer. Moreover, in the case of the complexes derived from *N*,*N*-disubstituted ethylenediamine, such a hindrance becomes a major factor which affects their composition. In this case the *cis*-R-position apparently lacks space even for a primary amino group, so that the template synthesis results in the formation of alkylcobalt chelate II, with the anionic residue of hydroxyketone as bidentate ligand. Although steric requirements of the latter are not as large as those of a diamine, the complexes in question are rather labile (thus they decompose in the air), probably owing to overcrowding of the coordination sphere.

Unlike IV, the related complexes with monodentate Lewis bases, [MeCo(7-Me-salen-*N*-Me)L^1L^2]$^+$ where L^1, $L^2 = NH_3$ or H_2O, consist of nearly equal amounts of diastereomeric species [8,9]. Hence, if the Lewis base in the *cis*-R-position is small enough, the tridentate ligand may adopt either configuration.

Steric effects in the *trans*-R-position are generally weaker, so that it may be accessible to rather bulky donors. Thus, *N*,*N*-Me_2en proved capable of displacing pyridine ligands in [MeCo(7-Me-salen)$(py)_2$]$^+$. On the basis of the above discussion, we conclude that the dimethylamino group has entered that site in the resulting complex [MeCO(7-Me-salen)(*N*,*N*-Me_2en)]$^+$. Nevertheless, structure IV reveals certain stereospecificity even here, the methyl group of the bidentate ligand occupying that of two feasible positions which is less liable to Van der Waals repulsions; viz. its projection on the equatorial plane falls upon the six- rather than five-membered chelate ring of the tridentate ligand. An analysis of the NMR data, in particular the ^{13}C data for [MeCo(7-Me-salen)(*N*-Me-en)]$^+$ *, indicates that the methylcobalt chelate with *N*-methylethylenediamine exists in solution as a single species, which must be the diastereomeric form found in the crystal.

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* In CD_3OD, with NO_3^- as counter-ion. Assignment of the spectrum is given below, with chemical shifts (in ppm) relative to TMS. Methyl ligand: −0.17, br. Bidentate ligand: CH_3, 35.0; CH_2, 41.9 and 44.1. Tridentate ligand (concerning the numbering of carbon atoms, see Fig. 1): (1), 122.6; (2), 165.8; (3), 114.3; (4) and (6), 131.9 and 130.3; (5) 123.7; (7), 169.9; (8), 18.3; (9), 56.5; (10), 51.6. ^{13}C NMR data for several closely related complexes [8] were taken into account in making these assignments.

3. Reaction route

To elucidate the series of reactions leading to formation of alkylcobalt chelates with tridentate ligands, a further study was attempted, generally with ethylenediamine and *o*-hydroxyacetophenone as chelating agents. First, it was shown that the 'symmetrical' organometallic compounds (III), exemplified by EtCo{(7-Me-sal)$_2$en}, are stable under the conditions of the template synthesis and so they are only by-products rather than intermediates in the formation of the 'unsymmetrical' complexes under consideration. (In the case of starting diamines with a secondary or tertiary amino group the formation of 'symmetrical' compounds is, of course, impossible.)

Second, work-up of the reaction mixtures produced in some template syntheses of the [RCo(7-Me-salen)(en)]$^+$ complexes allowed the bis-chelate of Co^{III} with two tridentate ligands 7-Me-salen to be identified as a by-product; it was isolated as crystal solvate of a salt, [Co(7-Me-salen)$_2$]I $\cdot \frac{1}{2}$MeOH $\cdot \frac{1}{2}H_2O$ [4]. This complex was obtained when the reaction was not sufficiently prolonged or when either the reducing or alkylating agent was absent, or the procedure failed to yield organometallic products, e.g. in the case of the phenylcobalt complex (see Section 1). A polarographic study of the bis-chelate showed it to undergo a reversible one-electron reduction at -0.98 V * with apparent conversion to the corresponding complex of Co^{II}, [Co(7-Me-salen)$_2$]. The latter is an analogue of the known bis-chelates of Co^{II} with Schiff bases derived from aromatic *o*-hydroxyaldehydes and *N*-substituted ethylenediamines. These complexes prepared by Sacconi et al. by direct template synthesis are readily oxidized by air [25]. Hence, it can be concluded that [Co^{III}(7-Me-salen)$_2$]$^+$ was formed from the corresponding complex of Co^{II} when the reaction mixtures were worked up in the air. Further, we have found that the bis-chelate of Co^{III} is converted into the organometallic complex [EtCo(7-Me-salen)(en)]$^+$ under the conditions of the template synthesis. It should be recalled here that the maximum yield of the latter complex was obtained with a ratio of the reagents Co^{2+}/diamine/hydroxyketone of 1/2/2, reflecting the stoichiometry of the bis-chelate rather than that of the product. These observations suggest that Co^{II}(7-Me-salen)$_2$] is an essential intermediate in formation of the organocobalt complexes in question. Obviously, similar bis-chelates of Co^{II} with tridentate Schiff bases may be involved in template syntheses of the organocobalt chelates I as well as those of II.

With such intermediates, one of two Schiff base ligands must undergo hydrolysis (or alcoholysis) at a later stage. There are many examples of partial ('template') solvolysis of C=N bonds in metal complexes with polydentate Schiff bases (see e.g. [12]), the reactions probably proceeding by the same mechanism that applies in the case of the free ligand [26]. Solvolysis may be favoured by steric effects, which mostly affect complexes with large coordination numbers, and by a substantial positive charge at 'azomethine' carbon, and hence by a high oxidation state of metal. Consequently, hydrolysis of a Schiff base ligand must occur in a complex of Co^{III}, i.e. after the formation of a Co–C bond. Vacated coordinated sites are then

* In an 0.1 *M* solution of Et_4NBF_4 in MeCN at 20 °C. The reversibility of the process was established by the Kalousek commutator technique. Here and below, potentials are referred to a standard calomel electrode.

occupied by a product of the hydrolysis, either diamine or ketoenolate, depending on steric requirements of the remaining tridentate ligand (see Section 2).

The most difficult task is elucidating the mid stage of the synthesis, i.e. the reduction and alkylation steps. Two alternative mechanisms can be suggested: (**A**) reduction of the bis-chelate of Co^{II} to the corresponding complex of Co^{I} which is then alkylated by organic halide, and (**B**) one-electron reduction of the latter

A $$Co^{II} \xrightarrow{e} (Co^{I})^{-} \quad (3)$$

$$(Co^{I})^{-} + RX \rightarrow RCo^{III} + X^{-} \quad (4)$$

compound followed by attack of the resulting free radical on the Co^{II} complex. In all the cases studied so far, the formation of metal–carbon bond through interaction

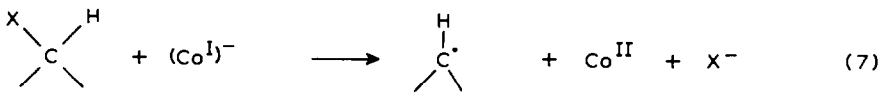
B $$RX \xrightarrow{e} R^{\cdot} + X^{-} \quad (5)$$

$$Co^{II} + R^{\cdot} \rightarrow RCo^{III} \quad (6)$$

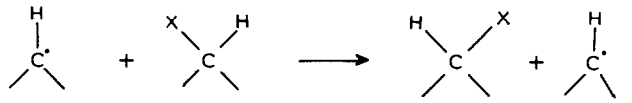
of simple alkyl halides and inorganic cobalt complexes under reductive conditions evidently proceeds via the route **A**, with an S_N2 mechanism for the alkylation step (eq. 4) [18,27]. Nevertheless, we must also consider the other possibility (**B**), since the reduction of the bis-chelate of Co^{II} proved difficult. Thus, the polarographic study of $[Co^{III}(7\text{-Me-salen})_2]^{+}$ showed that the 2nd wave evidently related to this process was located at -2.15 V, i.e. in the potential range typical of the reduction of alkyl bromides [28], while polarographic reductions of corresponding iodides [28] as well as Co^{II} chelates with α-dioximes and tetradentate Schiff bases [29] proceed much more readily.

An attempt was made to solve this problem by means of a stereochemical approach using either *cis*- or *trans*-1,4-dibromocyclohexane as the alkylating agent.

C

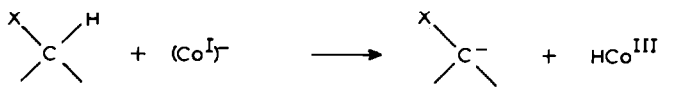


(7)



(8)

D



(9)

(10)

Whichever one was used as starting material, we found that its excess was converted into the equilibrium (1/1) mixture of both isomers, even when the experiment was carried on for only one-third as long as a standard template synthesis. Check runs showed the isomerization did not occur unless all the other reagents (and Pd catalyst) used in the template synthesis were also present. These findings indicate that a low-valent cobalt complex is involved into the isomerization. Two mechanisms, **C** and **D**, can be tentatively proposed for such a process. They involve intermediate formation of either an alkyl-free radical or a (*gem*-halogeno)carbanion through either electron or proton exchange between the halide and a Co^{I} complex. The loss of the preferential configuration must then be due either to inversion in the carbanion or to abstraction of halogen atom by the radical (a degenerate chain propagation step (eq. 8).

Despite a very high basicity of the Co^{I} complex, the carbanion mechanism **D** seems less plausible because of the use of a protolytic solvent. To enable a firm choice, we carried out a template synthesis (using c-$C_6H_{11}Br$ as alkylating agent) in the deuterated solvent CH_3OD. The ^1H NMR spectrum of the organocobalt product, [c-HexCo(7-Me-salen)(en)]$^+$, indicated that it contained protium rather than deuterium in the α-position of cyclohexyl ligand. This rules out the participation of carbanions, and thus supports the alternative mechanism (**C**) involving the electron transfer from a Co^{I} complex to the alkyl halide *.

Thus, the intermediate formation of both Co^{I} complexes and simple alkyl radicals under the conditions of the template synthesis has been established. Unfortunately, the results do not show whether the electron transfer from Co^{I} to RX (eq. 7) is a consecutive step preceding the alkylation of Co^{II} complex (eq. 6) or a competitive (essentially blind-alley) reaction with respect to the alternative alkylation of Co^{I} species (eq. 4); i.e. the mechanism of the reduction-alkylation stage remains uncertain. However, the involvement of Co^{I} species in the template synthesis of the organometal complexes under consideration is now proved.

Experimental

General

Organocobalt complexes were protected from light. The template syntheses were carried out under anaerobic conditions. Contact with air was also avoided in handling oxygen-sensitive complexes II. Aqueous or alcoholic solutions of complexes I with a s-alkyl ligand were stabilized with added alkali (NaOH or NH_3) or the corresponding diamine. Evaporation of solutions of organocobalt complexes was carried out under vacuum, with the bath temperature kept below 40 °C.

Materials

A mixture of *cis*- and *trans*-1,4-dibromocyclohexanes (with positional isomers as minor components) was prepared and resolved by a standard procedure [31] which was improved by introduction of an extra operation, viz. phase separation at 40 °C (slightly above the eutectic temperature), after fractional distillation. A single crystallisation of each combined solid was then sufficient to give the corresponding

* Then the *cis-trans*-isomerization of 1,4-dibromocyclohexanes can be regarded as an example of catalysis by electron transfer reagents (see e.g. [30]).

isomer containing less than 0.3% of impurities (data from GC analysis). The products were characterized by their m.p.'s: 50.0–50.5 and 114.0–114.2°C, respectively.

Other materials were either commercially available reagent grade chemicals or were prepared (*N*-Me-en, *N*-Ph-en, *N*,*N*-Me_2en, tn, Et_4NBF_4) or purified (MeCN, anhydrous MeOH) by standard procedures.

Spectral and electrochemical studies

^{1}H NMR spectra were recorded at room temperature on a Bruker spectrometer WP-200 with sodium 3-trimethylsilylpropanesulphonate (DSS) (in D_2O) or TMS (in other solvents) as internal standard. The $^{13}C\{^1H\}$ NMR spectrum was obtained at ambient temperature on the same instrument at 50.31 MHz, the signal of the CD_3OD solvent being used as internal standard; digital resolution was 2 Hz per channel.

IR spectra were taken on a Carl Zeiss spectrometer UR-20 with solid samples, either as KBr pellets (in the wide range of 400–3800 cm^{-1}) or hexachlorobutadiene mulls (in the region of N–H and O–H stretches)

The polarographic study of the complexes $[Co(7\text{-Me-salen})_2]X$, where X is I or ClO_4, was performed with a potentiostatic polarograph OH-102 (Radelkis, Hungary), a three-electrode cell, and a dropping mercury electrode, with its tip sloping at 45° to the axis. The characteristics of this d.m.e. were: m 1.24 mg/s, and t_1 0.88 s (while dropping into water, with the circuit open).

X-Ray structural study of [MeCo(7-Me-salen-N-Me)(N-Me-en)]I

Crystals were obtained by slow evaporation of an acetone solution.

Crystal data. Monoclinic system, space group $P2_1/n$, $Z = 4$; at −120°C a 7.372(2), b 11.165(4), c 22.468(8) Å, β 91.15(2)°.

Data collection. −120°C, Syntex $P2_1$ diffractometer, Mo-K_α radiation (graphite monochromator), $\theta - 2\theta$ scan ($\theta \leqslant 25°$). 2528 reflections with $|F^2| \geqslant 4\sigma(F^2)$; the data uncorrected for absorption (μ(Mo-K_α) 26.6 cm^{-1}).

Structure analysis. The structure was solved by direct methods; non-hydrogen atoms were refined in the anisotropic approximation. All hydrogen atoms were located in the difference map and included in the subsequent refinement with isotropic thermal parameters. The final discrepancy factors are $R = 0.042$, $R_w = 0.057$.

Analyses

'Acidolysis' of organocobalt chelates with tridentate Schiff bases, as well as the following head-space GC analyses for gaseous products, extraction of the resulting emulsion with CH_2Cl_2, and TLC or GC analysis of the extract was performed as previously described [8]. The aqueous layer was passed through Amberlite CG-400 with diluted (1/1) hydrochloric acid as eluent. The eluate collected before a coloured zone (containing Co^{2+}) reached the bottom of the column was evaporated to dryness under vacuum, the residue was dissolved in a small amount of water, and $NaHCO_3$ was added; the resulting solution was analysed for diamine(s), as described in earlier work [8].

For TLC identification of organocobalt complexes, 'Silufol' plates were used in association with the following eluents: CH_2Cl_2/py (19/1) (A) or 0.1 *M* solutions of

NaOAc in $MeOH/H_2O$ 4/1 (B) and $HCONH_2/H_2O$ (1/1) (C) in the case of chelates III (with tetradentate ligands) or I (with tridentate ones) respectively. Complexes of both the types gave distinctive spots on the chromatograms; they were either yellow or orange (I) or dark green (III), and all turned grey in light or on heating.

Isomeric dibromocyclohexanes were analysed by GC with a trifluoropropylmethylsilicone elastomer as the liquid phase.

Syntheses

A. Template syntheses.

These were carried out with constant stirring.

(1) [EtCo(7-Me-salen)(en)]Br. *o*-Hydroxyacetophenone (3.4 ml, 28 mmol), ethylenediamine (2.4 ml of its 70% aqueous solution, 28 mmol) and $CoCl_2 \cdot 6H_2O$ (3.3 g, 14 mmol) were dissolved successively in MeOH (100 ml) and 50% aqueous NaOH (4.5 ml) was added with cooling by a water bath. After 10 min, ca. 1/10 of a solution of $NaBH_4$ (in toto, 0.75 g, 20 mmol) in 5 ml of 5% aqueous sodium alkali was introduced, followed by 0.25 ml of a 2% solution of $PdCl_2$ in 1 *M* aqueous KCl. After 15 min, EtBr (5 ml, 65 mmol) was added, and the cooling bath was removed. The remaining $NaBH_4$ solution then was continuously added during 5 h at such a rate that gas evolution was maintained throughout. Stirring was continued for 1 h, then NaBr (5.8 g) was added. The suspension was filtered, and the precipitate was washed with a small amount of methanol and then with water (50 ml). The filtrate, combined with these washings was concentrated under vacuum to a volume of 40 ml and the precipitate thus formed was combined with the previous one, and the solid was washed with water, a small amount of acetone and ether, then extracted with CH_2Cl_2 until the solvent no longer became green *. The residue was dried by suction, to give 5.0 g (86%) of an orange-red crystalline powder. Recrystallization from MeOH at room temperature (by partial evaporation of the solvent or precipitation with NaBr) gave red prisms.

Other complexes of the series [RCo(7-Me-salen)(en)]X, where R is a primary or secondary alkyl, and X = Br or I, were prepared similarly and in comparable yields starting from corresponding halides RX (n-BuBr and n-BuI, n-AmBr, n-OctBr, i-PrBr and i-PrI, c-HexBr, 4-Br-c-HexBr and s-OctBr). In the cases of RX = MeBr and MeI, mixtures of [MeCo(7-Me-salen)(en)]X and [MeCo(7-Me-salen)(*N*-Me-en)]X were obtained, the ratio of these species being ca. 2/1 for X = Br and 1/2 for X = I **. Gaseous MeBr was passed through the reaction mixture during the addition of $NaBH_4$. In the preparation of the 4-bromocyclohexylcobalt complex, both the dibromide (either *cis*- or *trans*-isomer) and NaBr were added prior to the reducing agent. In the case of higher alkyl halides (from C_5 and above), crude products were extracted with mixtures of CH_2Cl_2 with C_6H_6 or C_6H_5Cl rather than with pure CH_2Cl_2. For washing of precipitates of the s-alkylcobalt complexes, water and methanol were slightly alkalified with NaOH.

* The dichloromethane washings contained the complex $EtCo\{(7\text{-Me-sal})_2en\}$, in a yield of ca. 1%.

** Procedures for the conversion of these mixtures into either of the individual complexes have been described [8].

(2), (3) Complexes of the series [RCo(7-Et-salen)(en)]Br with R = Et, i-Pr and c-Hex, and *[EtCo(7-Me-salpn)(pn)]Br* were prepared as described for (1) starting from the appropriate ligand sources.

(4) [EtCo(7-Me-saltn)(tn)]I was prepared as described previously [2].

(5) [RCo(7-Me-salen-N-Me)(N-Me-en)]X (with R = Me and X = I, or R = Et and X = Br). These syntheses were carried out as described for (1) (with *N*-Me-en used instead of en) up to the end of the final 1-h stirring. The precipitate was then filtered off, and washed with alkaline methanol, and the coloured liquor was combined with the filtrate. The solution was diluted with water, the corresponding sodium halide was added and the methanol was removed under vacuum, and the product allowed to crystallize at 0 °C. It was filtered off, washed with cold water, a small amount of acetone, and ether, and then air-dried. The yields of both the complexes were ca. 50%.

(6) [MeCo(7-Me-salen-N,N-Me$_2$)(o-OC$_6$H$_4$COMe)]. *o*-Hydroxyacetophenone (3.4 ml, 28 mmol), *N,N*-Me$_2$en (2.9 ml, 28 mmol) and $CoCl_2 \cdot H_2O$ (3.3 g, 14 mmol) were dissolved successively in anhydrous methanol (100 ml), and NaOH (3.4 g) was then added to the suspension. After the alkali had dissolved, ca. one-tenth of a solution of $NaBH_4$ (in toto, 0.75 g, 20 mmol) was introduced with cooling in a water bath. (The solvent for $NaBH_4$ had been prepared by dissolving sodium (0.25 g) in anhydrous methanol (10 ml)). Next, the solution of K_2PdCl_4 was added to the reaction mixture as in synthesis (1). After 15 min MeI was introduced, and the cooling bath was removed and the remaining solution of $NaBH_4$ was added as described in synthesis (1). Stirring was continued for 2 h and the suspension was filtered. The precipitate was washed with methanol and water, both of which had been made slightly alkaline with NaOH, and then dried under vacuum. The resulting solid was extracted with CH_2Cl_2. Then the solvent was removed under vacuum to leave brown crystals. Yield 4.7 g (80%). Found (calc.), %: C, 59.46 (60.87); H, 6.58 (6.57); N, 7.10 (6.76); Co, 13.95 (14.22).

Other complexes of the series [RCo(7-R^1-salen-N,N-Me$_2$)(o-OC$_6$H$_4$COR^1)] with R,R^1 = Me, Et were prepared and characterized in a similar manner.

(7) [EtCo(acacen)(en)]Br. This preparation differed from (1) in two ways: (a) *o*-HOC_6H_4COMe was replaced by $CH_2(COMe)_2$, and (b) the minimal amount of water (made alkaline with NaOH) was used to wash the product. After vacuum-drying, an orange-red powder was obtained. Yield 3.2 g (62%).

B. Syntheses via ligand exchange

(8) [EtCo(acacen)(phen)]Br. *o*-Phenanthroline (120 mg, 0.6 mmol), concentrated HBr acid (1.1 mmol of HBr) and [EtCo(acacen)(en)]Br (180 mg, 0.5 mmol) were successively dissolved in MeOH (5 ml). Gradual precipitation of en · 2HBr (identified in the form of the Schiff base $(salH)_2$en) occurred, and after 1 h the precipitate was filtered off. The filtrate was diluted with water (3 ml), and methanol was removed under vacuum, and the product allowed to crystallize out at 0 °C. It was separated by filtration, washed with water and air-dried. Yield 84 mg (40%), orange powder. Products detected after acidolysis were C_2H_6, C_2H_4, n-C_4H_{10}, $CH_2(COMe)_2$, en, and phen.

(9) [MeCo(7-Me-salen)(N,N-Me$_2$en)]NO$_3$. To a solution of [MeCo(7-Me-salen)$(py)_2$]NO_3 (242 mg, 0.5 mmol) in MeOH (5 ml) was added *N,N*-Me$_2$en (78 μl, 0.75 mmol). After 1.5 h, the volume of the solution was reduced by half under

vacuum, and the product allowed to crystallize out at 0 °C. It was filtered off and dried by suction to give an orange powder. The products detected after acidolysis were CH_4, C_2H_6, *o*-HOC_6H_4COMe, en and *N*,*N*-Me_2en.

^1H NMR spectrum in CD_3OD (δ, ppm vs. TMS): *o*-C_6H_4 - (6), 7.52, dd; (4), 7.01, ddd; (3), 6.74, dd; (5), 6.47 ddd; CH_3-C, 2.56, s; CH_3-Co, 2.09, s; $N(CH_3)_2$, broad complex signals at 2.3–2.8 ppm, suggesting equilibrium decoordination of the dimethylamino group to be appreciable and established on the NMR time scale.

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