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Authors' Review

Intramolecular Cyclization Reactions in Haloalkyl-Cobalt Complexes with Macrocyclic Equatorial Ligands*

Renata Dreos,[a,] Lucio Randaccio,[a,**] Patrizia Siega,[a] and Višnja Vrdoljak[b]**

[a]*Dipartimento di Scienze Chimiche, Università di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy*
[b]*Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia*

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Abstract. Organocobalt complexes containing axial haloalkyl groups afford metallacycles of different size by N or O alkylation of the macrocyclic equatorial ligands. The reaction mechanism involves the intramolecular nucleophilic attack of a negatively charged atom of the equatorial ligand on the axial XCH_2 haloalkyl group with simultaneous detachment of a halide ion, X^-. In imino/oxime and amino/oxime derivatives, the generation of the negatively charged nitrogen requires the abstraction of a proton and the reaction occurs only in alkaline medium. In bis(dimethylglioximato) and Schiff base complexes, a negatively charged oxygen is present in the equatorial ligand and the reaction occurs even in neutral medium. Three-, six- and seven- membered metallacycles are obtained, with the common feature that the Co–C bond is shorter and more resistant toward homolysis than in parent complexes or in closely related derivatives.

Keywords: intramolecular metallacyclization, haloalkyl-cobalt, reaction mechanism, X-ray structures

INTRODUCTION

Cleavage of the carbon-cobalt bond in organocobalt complexes coordinated with different equatorial ligands has been extensively investigated since Co–C bond breaking is a key step in all the currently known reactions of B_{12}-dependent enzymes.[1–4] In some cases, rearrangement of the organocobalt complexes have been induced by Co–C bond cleavage followed by subsequent migration of the alkyl group to a carbon[5] or a nitrogen[6] of the chelate. In contrast, the chemistry of the carbon bound to cobalt has been scarcely explored and pertinent studies are limited to the reactivity of the haloalkyl derivatives. For instance, it has been shown that α-chloro- and α-bromo-alkylcobaloximes afford non-halogenated alkyl-derivatives by reaction with sodium borohydride[7] (Eq. (1), DH_2 = bis(dimethylglyoximato), X = halogen)).

$$R(X)CHCo(DH)_2py \xrightarrow[\text{excess}]{NaBH_4} RCH_2Co(DH)_2py \quad (1)$$

Trifluoromethylcobamides (CF_3Cb) treated with chemical reductants, such as zinc or sodium borohydryde, or subjected to controlled-potential reduction, give the corresponding (difluoromethyl) cobamides (CF_2HCb) and dealkylated cobamides.[8] Alkylcobaloximes containing a $-CH_2OCH_3$ group are obtained through a reaction which again involves the participation of a haloalkyl derivative[9]

$$BrCH_2Co(DH)_2py + CH_3O^- \rightarrow CH_3OCH_2Co(DH)_2py + Br^- \quad (2)$$

In this context, a number of reactions has been discovered in recent years in which the nucleophilic attack of a negatively charged nitrogen or oxygen of different equatorial ligands on the axial haloalkyl group bound to cobalt leads to the formation of metallacycles of various size. All the previously reported metallacycles containing a cobalt-carbon bond were obtained by intramolecular Co alkylation either by an opportunely functionalized pending arm of the equatorial ligand[10–12] or by photodecarboxylation of chelated amino acids.[13]

In this review we summarize the synthesis, reactivity and structural aspects of complexes containing metallacycles of different size formed by N or O alkylation of the macrocyclic equatorial ligands in haloalkyl-cobalt complexes. In our investigations we were focused only on the synthesis and characterization of three-, six-

* Dedicated to Professor Emeritus Drago Grdenić, Fellow of the Croatian Academy of Sciences and Arts, on the occasion of his 90th birthday.

** Author to whom correspondence should be addressed. (E-mail: dreos@units.it; randaccio@units.it)

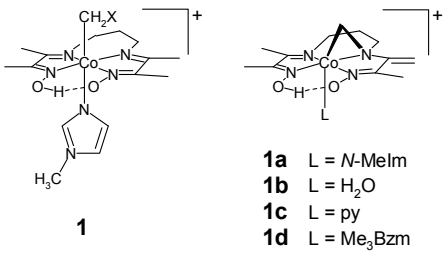
and seven-membered metallacycles. The important findings highlighted here can serve as useful guide for future investigations such as four and five membered metallacycles.

THREE-MEMBERED RINGS

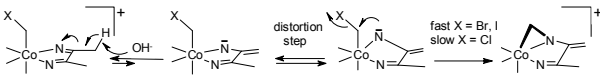
The reaction of [*N*-MeImCo((DO)(DOH)pn)CH_2X]$^+$ (**1**, *N*-MeIm = *N*-methylimidazole, (DO)(DOH)pn = N^2,$N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime)), an imine/oxime complex, with base afforded as the major product the cyclizated species [*N*-MeImCo(*N*-CH_2-CHEL)]$^+$ (**1a**) (Scheme 1) which contains a methylene bridge from the cobalt to an equatorial nitrogen.[14,15] The ring closure causes the simultaneous conversion of the imine group (N=C–CH_3) involved in the cyclization into an enamine moiety (N–C=CH_2). The corresponding [H_2OCo(*N*-CH_2-CHEL)]$^+$ (**1b**) (where CHEL is an equatorial chelating system) was obtained by treatment of an aqueous solution of **1a** with an exchange resin and the derivatives **1c** and **1d**, containing pyridine and 1,5,6-trimethylbenzimidazole (Me_3Bzm), respectively, from **1b** by axial ligand substitution.

The X-ray structures of **1a**, **1c**, and **1d** show similar features. Ring closure leads to a distortion of the six-coordinate geometry of the complexes, mainly concentrated in the Co–C and Co–N ring linkages. The C–Co–N angle is acute (43.6–43.8°) and the Co–C and Co–N bonds are distorted from the direction normally found for [LCo((DO)(DOH)pn)CH_2X]$^+$. In addition, the Co–N_{ax} bond lengths, ranging from 2.036 to 2.068(5) Å, are significantly shorter than in other imine/oxime-type alkyl complexes with corresponding axial ligands (range 2.060–2.133(4) Å).[3,4] Furthermore, the Co–C bond lengths, in the range 1.913–1.932(5) Å, are not only shorter than those in normal imine/oxime type structures (range 2.003–2.011(3) Å), but shorter than almost all examples of organocobalt(III) compounds.[3,4] Correspondingly, the C–Co–N_{ax} angle in the latter is close to 180°, whereas in the cyclizated species it decreases to about 150°.[14,15]

Qualitative observations under conditions for which Co–C bond cleavage is normally observed suggest that this bond is relatively inert in the cyclizated species.[14] A mechanism has been proposed for the cyclization of **1**,[14] consistent with the observation that: (i) the ring closure rate at pH = 10 shows a slight dependence on the leaving halogen for X = Br and I, whereas for X = Cl no ring closure could be detected under comparable conditions and (ii) for X = Br and I, ring closure is competitive with deuteration. The proposed mechanism (Scheme 2) involves the formation of a short-lived deprotonated intermediate in a slow step followed by a fast distortion step, which leads to the ring closure. The observation that ring closure and deuteration are competitive suggests that the distortion occurs in a fast equilibrium process that follows deprotonation and precedes ring closure. This mechanism can also account for the slight dependence of the rate on the halogen for X = Br and I, if in these two cases the final C–N bond formation step is fast compared to the reverse of the distortion step. The fact that the cyclization of the $ClCH_2$ derivative is much slower can be explained if the C–N bond formation step is slow compared to the reverse of the distortion step.

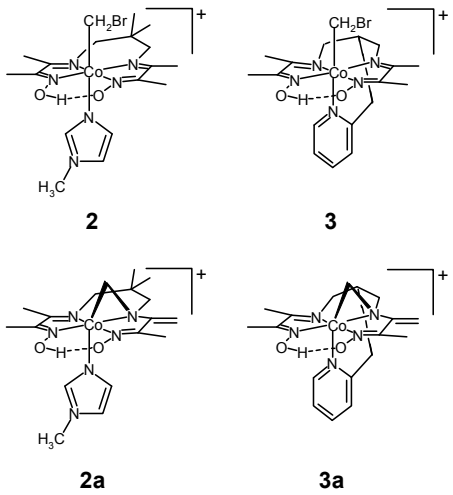


Scheme 1.

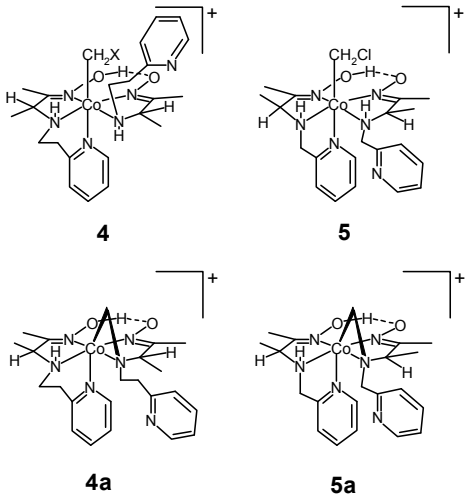


Scheme 2. Mechanism proposed for the formation of **1a**.

Cyclization of two closely related complexes, [*N*-MeImCo((DO)(DOH)Me_2pn)CH_2Br]$^+$ (**2**, (DO)(DOH)-Me_2pn = N^2,$N^{2'}$-2,2-dimethylpropanediylbis(2,3-butanedione 2-imine 3-oxime)) and [$BrCH_2$Co(C_1py)]$^+$ (**3**) (C_1py = 2,3,9,10-tetramethyl-6,2-pyridylmethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1,11-diolo), affords [*N*-MeImCo(*N*-CH_2-Me_2CHEL)]$^+$ (**2a**) and [Co(*N*-CH_2-C_1pyCHEL)]$^+$ (**3a**), respectively, (Scheme 3) which have been characterized by ^{1}H NMR spectroscopy.[15] Indeed, the ^{1}H NMR spectra of the cyclizated derivatives show two peculiar features, *i.e.* two one-proton olefinic doublets and two one-proton singlets due to the



Scheme 3.



Scheme 4.

geminal *N*-CH_2 protons. The *N*-CH_2 protons are not coupled, suggesting that the *N*-CH_2 carbon has considerable sp^2 character.[15]

Complexes containing an η^2-aminomethylene group have also been obtained starting from two kinds of amine/oxime complexes. In fact, $[XCH_2Co(LNH\text{-}py)(HLNH\text{-}py)]^+$ (**4** (LNH-py = 2-((2-pyridylethyl)amino)-3-butanone oxime)) and $[ClCH_2Co(L_1NH\text{-}py)(HL_1NH\text{-}py)]^+$ (**5**) (L_1NH-py = 2-((2-pyridylmethyl)amino)-3-butanone oxime), which differ in the length of the arm linking the pyridyl group to the equatorial moiety (-CH_2-CH_2- in **4** and -CH_2-in **5**, Scheme 4), afforded **4a** and **5a**, respectively, by treatment with diluted alkali at room temperature.[16,17]

X-ray structures of complexes **4a** and **5a** show a methylenic bridge from the cobalt to the equatorial amine nitrogen which is linked to the pendent pyridine. The acute C–Co–N angles of 42.8° and 43.4°, respectively, are very close to those found for complexes **1a-c**. As in the case of **1a-c**, a significant shortening of the Co–CH_2 and Co–N_{py} axial bonds and a decrease of about 25° in the C–Co–N_{py} angle are observed in **4a**, when compared to the corresponding values in the methyl analogue of **4**.[18] In the case of **5a**, only a significant shortening of the Co–CH_2 bond is observed with respect to the methyl analogue of **5**.[19] The Co–N_{py} axial distance in **5a** is significantly shorter than that in **4a**, but comparable to that found in the methyl analogue of **5**. The difference has been ascribed to the different constraints required for a five-membered ring closure in **5** and **5a** in comparison to those required for a six-membered ring closure in **4** and **4a**.[17]

Complexes **4a** and **5a** differ in the configuration of the C and N chiral centers. In fact, in **5a** both the C^*-Me bonds lie in the half-plane containing the three-membered cycle and both the N^*-CH_2py in the opposite half-plane. On the contrary, in **4a**, the two C^*-Me bonds and the two N^*-CH_2CH_2py residues lie in opposite half-planes.

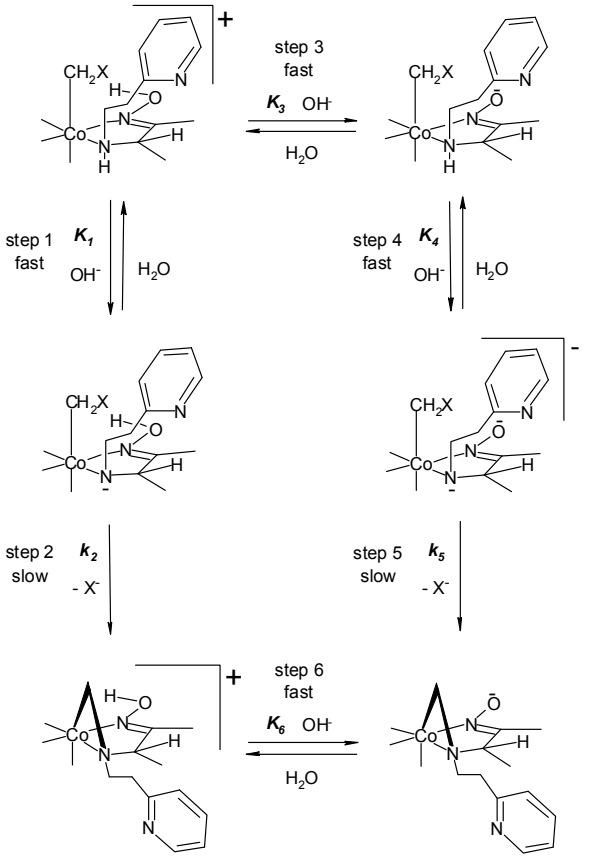
The metallacycle formation is faster in **4** and **5** than in **1**. In both cases, the generation of a nucleophilic negatively charged nitrogen is required, but in **4** and **5** the deprotonation occurs by removal of a proton from the nitrogen itself, whereas in **1** the proton is removed from an equatorial CH_3 group, far from the reactive center.

Kinetic studies of the formation of **5a** starting from $[(XCH_2Co(LNH\text{-}py)(HLNH\text{-}py)]^+$ in alkaline solution showed that the metallacycle formation rate increases in the order Cl < Br < I. The observed rate constants, k_{obsd}, corresponding to kinetics of first-order with respect to the complex, depend on $[OH^-]$ according to a two-term equation

$$k_{obsd} = a[OH^-] + b[OH^-]^2 \quad (3)$$

The results have been interpreted according to the mechanism reported in Scheme 5 for complex **4**.[16]

An analogous mechanism has been proposed for **5**.[17] The quadratic term in Eq. (3) is consistent with the presence of a fast acid-base pre-equilibrium, tentatively



Scheme 5. Mechanism proposed for the formation of **4a**. Steps are numbered according to the original paper (see Ref. 16).

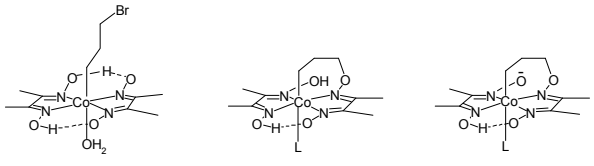
identified with the reversible deprotonation of the O–H···O bridge (step 3). Similar pre-equilibria have been observed in cobaloximes and in related complexes containing hydrogen bonds in the chelating systems.[20,21] Scheme 5 requires that both the protonated and the deprotonated species undergo fast deprotonation of the nitrogen bearing the pendant pyridyl group (step 1 and 4, respectively), followed by the slow nucleophilic attack of the equatorial nitrogen on the axial carbon (step 2 and 5). The latter step requires an inversion of configuration at the deprotonated nitrogen in **4** but not in **5**. The re-protonation of the equatorial oximato group occurs in the fast final step 6.

Compound **4** has been found to be light resistant even in aerobic conditions. The increased stability of the Co–C toward homolysis has been ascribed to the geometry of the system, which forces the initially formed radicals close to each other, so that they react preferentially together rather than with oxygen.[16]

SIX-MEMBERED RINGS

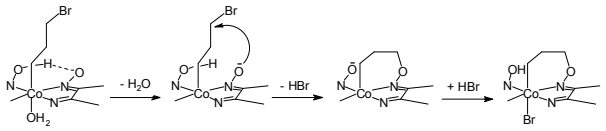
In general, XCH_2 groups of organocobaloximes are quite inert toward alkaline hydrolysis under relatively mild conditions,[21] so that the syntheses of the haloalkyl cobalt complexes are generally performed in alkaline media and no problems are encountered in obtaining pure products. The intermolecular nucleophilic substitution shown in Eq. (2) requires drastic experimental conditions. On the other hand, the cyclizated species **6a** was obtained by simple heating of an aqueous solution of aqua(3-bromopropyl)cobaloxime (complex **6**) at 80 °C (Scheme 6).[22,23]

The suggested cyclization mechanism involves an intramolecular nucleophilic attack at the γ carbon by an oximato group, elimination of HBr and formation of a six-membered ring (Scheme 7). In **6a**, the sixth coordination position is occupied by bromide; removal of bromide by reaction with $AgNO_3$ and addition of a suitable L ligand allowed to obtain **6b** (L = H_2O), **6c** (L = py; pyridine), **6d** (L = Bzm; 5,6-dimethylbenzimidazole) and **6e** (L = Im; imidazole).[23] Complex **6f**



6 **6a** L = Br; **6b** L = H_2O; **6c** L = py; **6d** L = Bzm; **6e** L = Im; **6f** L = Im

Scheme 6.



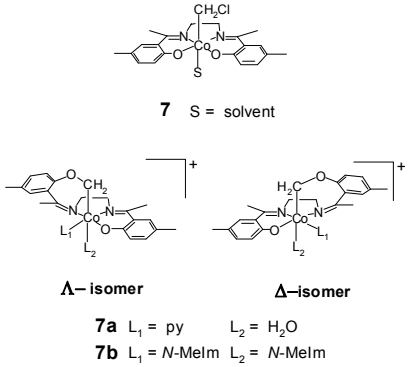
Scheme 7. Mechanism proposed for the formation of **6a**.

arises from **6e** by deprotonation of the O–H···O bridge involved in the formation of the six-membered ring. All these complexes were structurally characterized.[22,23] In contrast to complexes with three-membered rings, the formation of the six-membered cycle does not significantly affect the geometry of the axial fragment. In fact, the axial Co–C and Co–N distances as well as the Co–N_{ax} are very similar to those found in $RCH_2Co(DH)_2L$ complexes with L = py, Me_3Bzm, and Im.[4]

Photolysis studies on the bridged alkylcobaloximes showed that cobalt-carbon bond cleavage is slower than in the corresponding aqua-(3-bromopropyl)-cobaloxime.[24]

SEVEN-MEMBERED RINGS

A quite common way to obtain the organometallic derivatives of the cobalt Schiff base complexes involves the "*in situ*" generation of a Co^I species by reduction with $NaBH_4 / PdCl_2$ in alkaline methanolic solution, followed by the oxidative addition of the appropriate alkyl halide. The attempts to synthesize with standard methods $[ClCH_2Co(tmsalen)]_2$ (**7**) (tmsalen = 4,4',7,7'-tetramethyl-bis-(salicylidene)ethylenediamine) (Scheme 8), led, besides the expected *trans* organometallic species, to the β *cis* organometallic derivative **7a**, by intramolecular reaction of the axial chloromethyl group with the equatorial chelate.[25] In this complex the tetradentate ligand assumes a β *cis* configuration, with the formation of a seven-membered ring, the other two positions being occupied by one py and one water molecule. The resulting complex is chiral, due to the helical arrangement of the quadridentate ligand, even if the reaction product is a racemic compound. The two monodentate ligands of



7 S = solvent

Λ– isomer **Δ–isomer**

7a L_1 = py L_2 = H_2O

7b L_1 = *N*-MeIm L_2 = *N*-MeIm

Scheme 8.

7a can be easily replaced by other ligands. The addition of a 1:1 amount of *N*-MeIm to a solution of **7a** causes the almost complete replacement of pyridine, whereas in presence of a tenfold excess of *N*-MeIm both the monodentate ligands are replaced (complex **7b**).

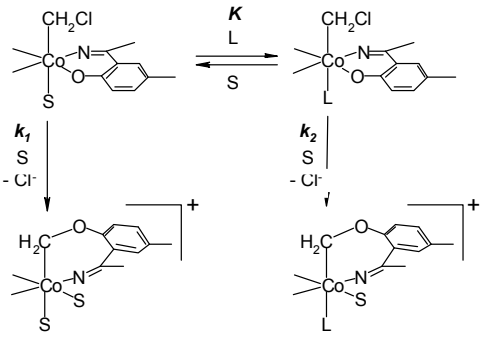
The cyclizated complexes are not light sensitive, even in aerobic conditions, in contrast to the other complexes of the RCo(tmsalen) series.[26] In this case, the stability toward photolysis does not reflect a shortening of the cobalt carbon bond. In fact, the Co–C distance of 1.965(4) Å in **7a** and 1.964(6) Å in **7b** are very close to those of 1.951(2)[26] and 1.963(7) Å[27] found in the [MeCo(chel)]$_2$ dimeric species, where chel = Schiff base. However, the Co–C bond in **7a** is shorter than that of 1.996(6) Å found in EtCo(acsalen)H_2O (acsalen = *N*,*N*'-ethylene (acetylacetonylideneiminato) (salicylideneiminato)), while the Co–O distance of 2.213(3) in **7a** does not differ significantly from that of 2.219(4) Å found in the latter complex.[28] Analogously, the Co–C bond in **7b** is shorter than those found in complexes RCo(chel)py (chel = Schiff base) which vary in the range 1.99(1)–2.042(6) Å.[3] Although in **7b** the ligand *trans* to the carbon is imidazole, the latter comparison is meaningful, since it is known that the Co–C bond length is not influenced by the *trans* N donor ligand.

The cyclization reaction of [$ClCH_2$Co(tmsalen)]$_2$ in CD_3OD can be easily monitored by ^{1}H NMR spectroscopy, because the loss of symmetry causes a doubling of the number of signals arising from the macrocycle. It is noteworthy that the product of the cyclization of [$ClCH_2$Co(tmsalen)]$_2$, which presumably contains two solvent molecules as monodentate ligands, is not stable in methanolic solution, and further reactions occur after the cyclization is complete. On the contrary, **7a**, which contains pyridine in equatorial position, is stable in methanolic solution.

To investigate the effect of different nucleophiles on the cyclization rate,[29] the cyclization of [$ClCH_2$Co(tmsalen)]$_2$, which in methanol is present as $ClCH_2$Co(tmsalen)S (S = solvent), has been carried out in the presence of an excess of several different monodentate ligands. The kinetic traces reveal perfect first order behaviour. The plots of k_{obs} versus [L] show non-zero intercept and significant curvature at high nucleophile concentration.

Kinetic data show that the cyclization rate is independent of pH in the range 5.6–11, increases at pH > 11, and is almost double at pH = 13.[30] Therefore, in this case the cyclization also occurs in neutral medium, as the negative charge present on the oxygen atom makes it prone to a nucleophilic attack on the CH_2 group.

The results have been interpreted in terms of the mechanism reported in the Scheme 9. This scheme



Scheme 9. Mechanism proposed for the formation of **7a**.

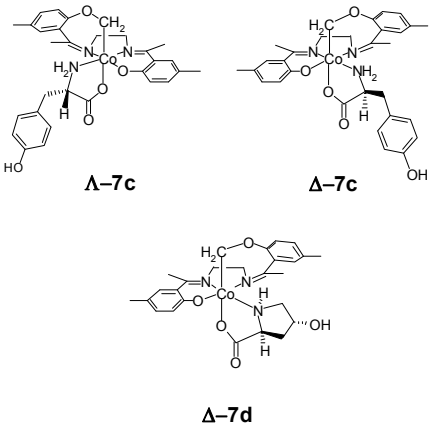
involves the substitution of the solvent by L in a fast pre-equilibrium step, both [$ClCH_2$Co(tmsalen)(S)] and [$ClCH_2$Co(tmsalen)(L)] undergoing the attack of the negatively charged oxygen of the equatorial ligand on the axial chloromethyl group, with the loss of a chloride from the latter and formation of the monocationic complex containing a seven membered ring.

The N-donor ligands increase the cyclization rate. The accelerating effect is mainly due to the electron-donor power of the ligand, which increases the electron density on the equatorial chelate and, in particular, makes the oxygen atoms more nucleophilic.

The cyclization of **7** in the presence of py and *N*-MeIm has been studied at various temperatures in the range 16.2–34.5 °C.[29] The most relevant feature of the activation parameters is the considerably negative activation entropy. As the cyclization involves the formation of ions from neutral **7**, the activated complex may be described almost as an ion pair or an exceedingly polar complex approaching an ion pair. The large negative value of the activation entropy is attributed to the freezing of the solvent around the incipient ions, in agreement with this picture.

As pointed out above, the two monodentate ligands of **7a** can be easily replaced. The reaction of **7a**, racemic compound of Δ and Λ enantiomers (Scheme 8), with enantiomerically pure L-tyrosine afforded a mixture of the two diastereoisomers **Δ-7c** and **Λ-7c**, which, owing to the lower solubility of **Δ-7c**, could be separated by fractional crystallization.[31] The absolute configuration of the two diastereomers was unequivocally assigned from the X-ray structure, using the known absolute configuration of the asymmetric carbon of the amino acid as internal reference. The reaction of racemic **7a** with *trans*-4-hydroxy-L-proline afforded only the diastereoisomer with a Δ configuration of the tetradentate ligand (**Δ-7d**), as revealed, by X-ray diffractometric analysis (Scheme 10).

Parallel experiments carried out by UV-visible and CD spectroscopy evidenced that, both for L-tyrosine and



Scheme 10.

trans-4-hydroxy-L-proline, the amino acid initially coordinates to both the Δ and Λ enantiomers of **7a**, leading to an approximately equimolar mixture of diastereoisomers. In the case of L-tyrosine the diastereoisomers have about the same energy, so that the successive isomerization is negligible. In the case of *trans*-4-hydroxy-L-proline, **Δ-7d** is much more stable than **Λ-7d** and the isomerization reaction **Λ-7d** → **Δ-7d** goes practically to completion.

CONCLUSION

In this review article, our goal is to underline important findings on the synthesis, reactivities and structural characteristics of three-, six- and seven- membered metallacycles. In all cases, the metallacyclization occurs through the intramolecular nucleophilic attack of a negatively charged atom of the equatorial ligand (a neighbouring group)[32] on the axial haloalkyl group with the detachment of a halide ion. In imino/oxime and amino/oxime derivatives, the generation of the negatively charged nitrogen requires the abstraction of a proton and the reaction occurs only in alkaline medium. In bis(dimethylglioximato) and Schiff base complexes, a negatively charged oxygen is present in the equatorial ligand and the reaction also occurs in neutral medium. Cycles of different size are obtained, according to the statement that "a neighbouring group may be located at any distance from the center of substitution, provided that in the transition state it can get near enough to the reaction center and can be suitably disposed geometrically to give a transition state approximating that of an S_N2 reaction".[32]

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SAŽETAK

Unutarmolekulske reakcije ciklizacije haloalkilnih kompleksa kobalta s makrocikličkim ekvatorijalnim ligandima

Renata Dreos,[a] Lucio Randaccio,[a] Patrizia Siega[a] i Višnja Vrdoljak[b]

[a]*Dipartimento di Scienze Chimiche, Università di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy*
[b]*Laboratorij za opću i anorgansku kemiju, Kemijski odsjek, Prirodoslovno-matematički fakultet, Sveučilište u Zagrebu, Horvatovac 102a, 10000 Zagreb, Hrvatska*

Alkilacijom N ili O iz makrocikličkog ekvatorijalnog liganda organokobaltovi kompleksi s aksijalnim haloalkilnim skupinama daju metalocikličke spojeve različite veličine. Reakcijski mehanizam uključuje unutarmolekulski nukleofilni napad negativno nabijenog atoma iz ekvatorijalnog liganda na aksijalnu XCH_2 haloalkilnu skupinu uz istovremeno otcjepljenje halogenidnog iona, X^-. U imino/oksimskim ili amino/oksimskim derivatima, stvaranje negativno nabijenog dušika zahtijeva oduzimanje protona i reakcija se zbiva samo u alkalnoj sredini. U bis(dimetilglikosimato) kompleksima i kompleksima sa Schiffovim bazama, negativno nabijeni kisik prisutan je u ekvatorijalnom ligandu te se reakcija zbiva i u neutralnoj sredini. Tro, šestero i sedmeročlani metalocikli nastaju sa zajedničkom karakteristikom da je Co–C veza kraća i otpornija prema homolizi nego odgovarajući kompleksi ili slični derivati.