Synthesis, structure, dynamics and first atropisomer-selective cleavage of the chromium tricarbonyl complex of a lactone-bridged biaryl*

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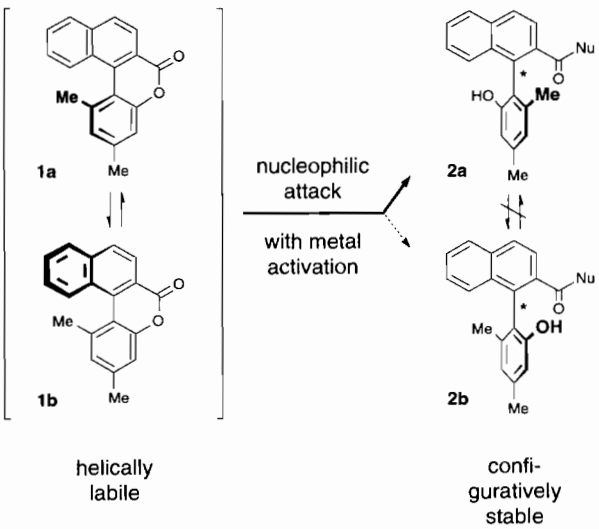
Abstract

The regioselective complexation of the unsymmetric lactone-type bridged biaryl **1** with a chromium tricarbonylfragment is reported. By temperature dependent NMR of the resulting complex **3**, the activation barrier of the helix inversion was determined. This isomerization process is of fundamental importance for the atroposelective opening of the lactone bridge. In the crystal, by contrast, only one diastereomer exists, as determined by X-ray diffraction study. A first experiment on the stereoselective ring opening using the achiral H-nucleophile sodium borohydride leads to only one detectable atropo-diastereomer and demonstrates the great potential utility of chromium tricarbonyl complexes in directed biaryl synthesis and for mechanistic studies of the stereochemically intriguing lactone opening step.

Key words: Crystal structures; Chromium complexes; Carbonyl complexes; Lactone complexes; Stereoselective synthesis; Atropisomerism; Bridged biaryls

Introduction

The stereocontrolled lactone cleavage of configuratively labile bridged biaryl lactones using chiral nucleophiles has become an efficient method for the construction of stereochemically homogeneous, even highly hindered biaryl systems [2]. This concept has already proved its width of application, exemplarily in selected syntheses of naturally occurring biaryls [3]. Especially also for systematic preparative and mechanistic investigations, model systems like **1** (Scheme 1), which are devoid of permanent stereoelements and thus require an external asymmetric induction, have proved to be valuable substrates [4]. Due to the lactone bridge, such biaryls **1** have, compared with their ring opened products **2**, a drastically lowered atropisomerization barrier, thus allowing a rapid interconversion of the two helically distorted atropisomers **1a** and **1b**.



Scheme 1. Principle of the directed ring opening of axial-prostereogenic biaryl lactones, using asymmetric inductors.

Due to the relatively weak reactivity of the carbonyl group of the biaryl lactones, the cleavage of this auxiliary bridge by a nucleophilic attack requires the metal

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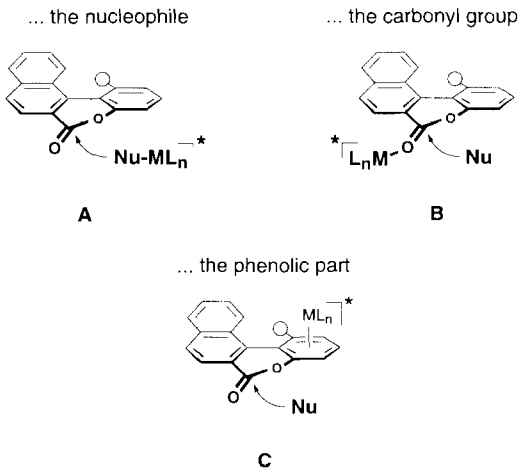


Scheme 2. Different strategies for metal activation to the lactone-bridged biaryl system. Configuratively stable stereogenic elements are denoted by *.

activation either of the nucleophile (**A**) [5] (Scheme 2) or of the carbonyl group (**B**) [6]. A completely different third possibility (**C**) for the chemical activation of the lactone system, combined with the option of achieving asymmetric inductions by an additional element of (planar) chirality [7], might be the use of the configuratively labile lactones **1** in the form of their chromium tricarbonyl complexes.

In this paper, we present investigations on the activation of a phenolic leaving group by complexation of a chromium tricarbonyl fragment to the aromatic ring. Exemplarily for complex **3**, its structure, dynamic behavior and first ring cleavage reactions, and the potential applications of this metal-organic species as a useful intermediate in the asymmetric synthesis of stereochemically homogeneous biaryls is demonstrated.

Experimental

All reactions were performed under inert gas atmosphere in dried glassware. All solvents were purified, dried and thoroughly degassed prior to use. NMR spectra were taken on a Bruker AC 200 instrument, IR spectra were recorded with a Perkin-Elmer 1420 spectrophotometer, mass spectra were measured on a Finnigan MAT MS 8200 and elemental analyses were performed on a Carlo-Erba M 1106 apparatus.

1,3-Dimethyl-6H-{(η^6-chromium tricarbonyl)benzo}-[b]naphtho[1,2-d]pyran-6-one (3)

(a) A solution of 510 mg (2.32 mmol) of $Cr(CO)_6$ and 510 mg (1.86 mmol) of **1** in 50 cm^3 of di-n-butylether and 5 cm^3 of THF was refluxed for 20 h to yield a deep red solution. The solvent was distilled off and the residue chromatographed on silica (petroleum ether/ethyl acetate 4:1). A second chromatography was necessary to obtain a sufficiently pure product. Crystallization from dichloromethane/petroleum ether yielded 54 mg (7%) of **3** as dark red crystals, m.p. 170 °C (decomp.). IR (CH_2Cl_2): ν=1950(s), 1875(s), 1720(s) cm^{-1}. ^{1}H NMR (d_8-THF, −6 °C): δ=2.32 and 2.42 (2 s, 3H overall integration, CH_3), 2.47 (s, 3H, CH_3), 5.43 (br s, 1H, 2- or 4-H), 5.91 and 6.19 (2 br s, 0.65 and 0.40H, 2- or 4-H), 7.6–7.9 (m, 2H, aromatic-H), 8.0–8.3 (m, 3.4H, aromatic-H), 8.70 (d, J=7.3 Hz, 0.66H). Ratio of diastereomers: 56:44. MS (70 eV): *m/z* (%)=410 (14) [M^+], 326 (61) [M^+−3 CO], 51.9 (100) [Cr^+]. *Anal.* Calc. for $C_{22}H_{14}CrO_5$: C, 64.43; H, 3.44. Found: C, 64.23; H, 3.41%.

(b) A degassed solution of 340 mg (1.24 mol) of lactone **1**, 373 mg (1.41 mmol) of (η^6-chromium tricarbonyl)naphthalene [8], 4 cm^3 of diethyl ether and 4 drops of THF was sealed in an ampulla and heated to 70 °C for 65 h. During this time, the lactone did not dissolve completely. After cooling, the solvent was evaporated, the residue was chromatographed once and the product was crystallized as described above. Yield 183 mg (36%) of **3**, spectroscopically identical to the product described above. From the early chromatographic fractions and from the crystallization mother liquor 185 mg (54%) of **1** were recovered.

Temperature-dependent NMR of 3

An NMR tube with 20 mg of **3**, dissolved in d_8-THF and equipped with a capillary containing ethanediol as internal temperature standard, was thoroughly degassed and sealed. NMR measurements were done at intervals of 6–10 °C, in the range from −30 to +70 °C.

exo-2-Hydroxymethyl-1-[2'-acetoxy-4',6'-dimethyl-(η^6-chromium tricarbonyl)phenyl]-naphthalene (4)

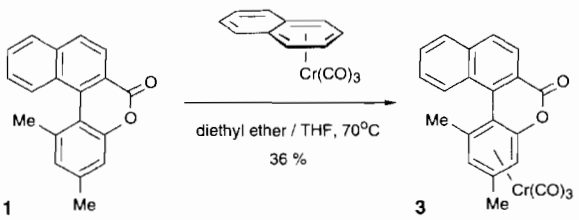
A solution of 80.0 mg (195 μmol) of **3** in THF was reacted with 47.0 mg (1.25 mmol) of $NaBH_4$ at 0 °C. To the resulting bright yellow solution 0.5 ml of acetic anhydride and 30 mg (246 μmol) of 4-*N*,*N*-dimethylaminopyridine were added. The mixture was stirred at room temperature for 1 h, acidified with 2 N HCl and the organic layer extracted with ether. After removal of the solvent, the residue was filtered through silica (methyl-tert-butylether). Yield 47 mg (53%) of **4** as a yellow powder; m.p. 180 °C (decomp.). ^{1}H NMR (C_6D_6): δ=1.63, 1.64 and 1.67 (3 s, 9H, 3 CH_3), 4.08 (s, 1H, 4'- or 6'-H), 4.73 (s, 1H, 4'- or 6'-H), 4.95 and 5.03 (2 d, J=18 Hz, 2H, CH_2OH), 7.25 (m_c, 1H, 6-H), 7.45 (d, J=8.6 Hz, 1H, 4-H), 7.62 (m, 3H, 3-, 5- and 7-H), 10.02 (d, 1H, J=8.9 Hz, 8-H). MS (70 eV): *m/z*=456 (15) [M^+], 372 (100) [M^+−3 CO], 51.9 (37) [Cr^+].

Comparison of the reactivities of 1 and 3

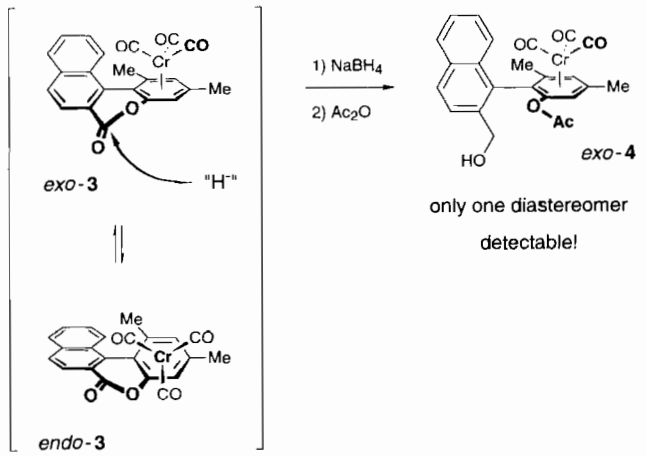
To a mixture of 2 mg of **1** and 2 mg of **3** in 1 cm^3 of THF 0.5 mg of 1-methoxynaphthalene were added as an internal standard. After the addition of 5 mg of sodium borohydride at 0 °C, a sample was taken every minute and analyzed by HPLC (μ-porasil, cyclohexane/ethyl acetate 10:1). After 5 min, the complex had completely disappeared with no sign of conversion of the free lactone **1**, which required 20 h at room temperature.

Crystallography

Suitable crystals of **3** were grown from dichloromethane/petroleum ether. Measurements of the diffraction intensities were performed on a Stoe STADI4 diffractometer by using Mo Kα radiation (0.7107 Å). Cell parameters were determined by least-squares refinement of 25 reflections. The structures were resolved with Siemens SHELXTL PLUS package by using direct methods. All non-hydrogen atoms could be refined anisotropically. The hydrogen positions were calculated by using a riding model and were considered fixed with isotropic U_{eq} in all refinements. For the final residual values R and R_w and further details, see Tables 1 and 2.



Scheme 3. Preparation of the biaryl lactone chromium tricarbonyl complex **3** by ligand exchange reaction.



Scheme 4. Atropo-diastereoseletive ring opening of the lactone tricarbonyl complex **3**.

Results and discussion

Preparation of the chromium tricarbonyl lactone complex 3

Attempts to prepare complex **3** by thermolysis of $Cr(CO)_6$ in the presence of the free lactone ligand **1** using the standard solvent mixture di-n-butylether/THF gave only very insufficient chemical yields, a further disadvantage being the required high reaction temperatures and the difficulty of separating the product from the high boiling solvent mixture. For this reason, alternative methods were tried that might lead to complexation under milder conditions, for which the technique of an aromatic exchange at the $Cr(CO)_3$ unit, as established by Kündig *et al.* [9] proved to be most promising. Thus, at a reaction temperature of 70 °C in the solvent mixture diethyl ether/THF, the desired product **3** was obtained in 36% yield, furthermore allowing the recovery of 54% of unreacted starting material, which constituted a substantial improvement in the preparation of the key compound, sufficient for further investigations with this metal complex (Scheme 3).

Structure and stereochemical dynamics in solution

In solution, the resulting complex **3** undergoes, as expected, in the presence of molecular oxygen, a slow decomposition back to the non-complexed lactone **1**. In the crystalline state, however, **3** is completely air-stable. In the formation of **3**, a high regioselectivity can be observed for both pathways. For the direct reaction of $Cr(CO)_6$ and also for the ligand exchange reaction, only one of three possible regioisomeric products is detected. This is underlined by the NMR spectrum, which shows the expected coordination of the chromium tricarbonyl group to the phenolic (i.e. most electron rich) ring, exclusively. This can clearly be seen from a distinct and characteristic [10] high-field shift of the resonances of the ring protons at C-2 and C-4 (5.43, 5.91 and 6.19 ppm), compared with the non-complexed ligand (7.14 and 7.16 ppm).

The two faces of the oxygenated ring are diastereotopic because of its unsymmetrical substitution and the axial chirality of the molecule. Complexation affords the two diastereomers shown in Scheme 4. Thus, the clearly separated doubled signals for one of the two ring protons at the aromatic core clearly hint at the existence of both atropo-diastereomeric helimers *exo*-**3*** and *endo*-**3** and, simultaneously, can be used for the determination of the interconversion barrier: temperature-dependent NMR shows a coalescence of these

*We propose to denote such an *anti* array of the chromium tricarbonyl fragment to the carbonyl group of **3** or the hydroxymethyl function of **4** as *exo*, the corresponding *syn* array as *endo*, see also ref. 10.

two signals at *c.* 55 °C (200 MHz), which on the basis of the Eyring equation [11] delivers a free activation enthalpy of $\Delta G = 67.6$ kJ mol^{-1}, which corresponds to an very rapid interconversion process ($t_{1/2} = 128$ ms) even at room temperature, so that the two atropo-diastereomers *exo*-**3** and *endo*-**3** are not separable under standard conditions. The value obtained here for the free activation enthalpy of **3** can be considered only as a first hint at the corresponding barrier of the free lactone **1**, as the activation energy can in principle be influenced by the complexation, as Schlögl [12] showed for similar systems.

Structure in the crystal

For an exact knowledge of the geometry of the chromium tricarbonyl complex **3**, we performed an X-ray structure analysis on crystals obtained from dichloromethane/petroleum ether. The resolved structure (Fig. 1) fully confirms the existence of the anticipated regioisomer **3**, with the metal coordinated to the electron-rich phenolic part of the molecule. As expected, the compound crystallizes in a racemic form. Yet, different from its behavior in solution, only one of the two atropo-diastereomeric forms, namely *exo*-**3** (and its enantiomer) is found in the crystal. (Details of the crystal structure determination and atomic coordinates are given in Tables 1 and 2, respectively).

Apparently due to packing effects, two types of conformers with a slightly different degree of molecular distortion can be found in the crystal, an indication for a relatively high flexibility at the biaryl axis. As expected, the biaryl ligand shows a screw-like molecular distortion, similar to that of the free ligand, which can best be seen in some of the dihedral angles of the 'inner spiral loop', compared with the values reported for **1** in the literature [4], see Table 3. Due to the large angle variations already between the two conformers of **3**, only a few significant differences between **3** and **1** can be deduced, such as the angles α at the complexed phenolic ring, which are clearly smaller for both conformers of **3** than for **1**, and the angles γ, which are larger for **3** than for **1**, thus greatly compensating the former effect. Thus, no specific overall planarizing or twisting effect of the chromium fragment can be deduced, and the sum of the overall angles of **1** even ranges between that of the two conformers of **3**.

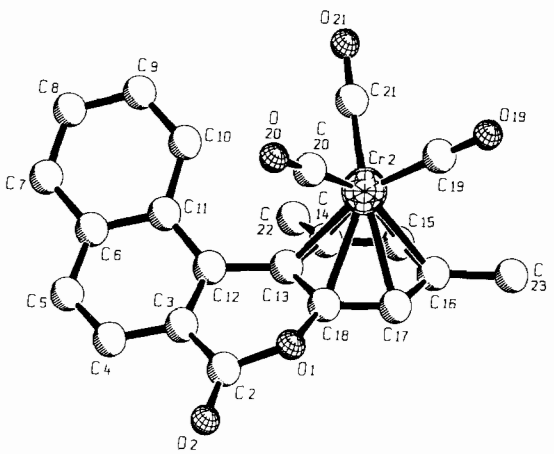


Fig. 1. Stereostructure of **3** in the crystal; only one of the two conformers (and in only one enantiomeric form) is drawn (hydrogen atoms omitted for reasons of clarity).

TABLE 1. Experimental details and results of crystal structure determination of **3**

Empirical formula	$C_{22}H_{14}CrO_5$
Molecular mass	410.35
a (pm)	1779.8(2)
b (pm)	1312.6(1)
c (pm)	1538.8(2)
β (°)	97.51(1)
V (pm^3)	$3564.1(4) \times 10^6$
Z	8
D_{calc} (g cm^{-3})	1.492
Crystal system	monoclinic
Space group	$P2_1/n$
Crystal size (mm)	$0.35 \times 0.35 \times 0.2$
Data collection mode	θ/θ scan
θ Range (°)	1.75–27.5
Reciprocal lattice segment	$h = 0$–21
	$k = 0$–15
	$l = -18$–18
No. reflections measured	6853
No. unique reflections	6285
No. reflections $F > 3\sigma(F)$	4161
Data-to-parameter ratio	8.22
R, R_w	0.057, 0.034
Largest difference peak (e Å^{-3})	0.39
Largest difference hole (e Å^{-3})	0.44

Stereoselective ring opening of the chromium tricarbonyl lactone complex 3

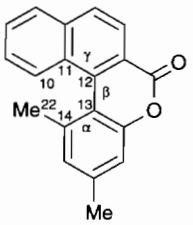
Besides the structure and dynamics of the lactone chromium complex **3**, especially its behavior towards nucleophiles was of crucial interest. Initial reactions of **3** using sodium borohydride show two significant influences of the $Cr(CO)_3$ unit: the enhanced reactivity and a striking stereoselectivity. Thus, the reaction rate of **3**, compared to the non-complexed lactone **1**, is distinctly increased. Whereas complex **3** reacts completely at 0 °C within a few minutes, the reduction of **1** takes place slowly at room temperature and takes 20 h, as monitored by HPLC. A falsification of the results by *de novo* formation of **1** from **3** could be excluded by the use of a quantitative internal standard. The product primarily formed from **3**, a highly sensitive phenolate complex, was subsequently stabilized by *in situ* acctylation of thc phenolic oxygen function, thus

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq} ($\times 10^{-1}$) (pm^2) for **3**

	x	y	z	U_{eq}
Molecule I[a]				
Cr(1)	2802(1)	2304(1)	8250(1)	34(1)
O(1)	1580(2)	635(2)	7261(2)	44(1)
C(2)	873(2)	405(3)	7475(3)	44(2)
O(2)	424(2)	63(2)	6902(2)	66(1)
C(3)	713(2)	710(3)	8347(3)	38(1)
C(4)	−39(2)	538(3)	8537(3)	52(2)
C(5)	−259(2)	928(3)	9279(3)	57(2)
C(6)	207(2)	1619(3)	9792(3)	44(2)
C(7)	−56(3)	2150(4)	10495(3)	62(2)
C(8)	345(3)	2915(4)	10909(3)	61(2)
C(9)	1038(3)	3226(3)	10649(3)	53(2)
C(10)	1331(2)	2686(3)	10000(2)	41(1)
C(11)	949(2)	1840(3)	9589(3)	36(1)
C(12)	1231(2)	1259(3)	8908(2)	32(1)
C(13)	2036(2)	1179(3)	8758(2)	28(1)
C(14)	2690(2)	1249(3)	9390(2)	30(1)
C(15)	3414(2)	1146(3)	9124(3)	35(1)
C(16)	3529(2)	922(3)	8259(3)	37(1)
C(17)	2885(2)	764(3)	7648(3)	36(1)
C(18)	2162(2)	859(3)	7908(3)	33(1)
C(19)	3429(3)	2880(3)	7531(3)	57(2)
O(19)	3830(2)	3219(3)	7079(3)	103(2)
C(20)	2002(3)	2986(3)	7649(3)	56(2)
O(20)	1478(2)	3374(3)	7269(3)	99(2)
C(21)	2978(2)	3383(3)	9012(3)	41(2)
O(21)	3089(2)	4042(2)	9506(2)	71(1)
C(22)	2679(2)	1323(3)	10367(2)	41(2)
C(23)	4319(2)	793(3)	8013(3)	52(2)
Molecule II[a]				
Cr(2)	−6620(1)	−2157(1)	−9291(1)	34(1)
O(1)	−7874(2)	−3782(2)	−10400(2)	43(1)
C(2)	−8537(2)	−4164(3)	−10136(3)	41(2)
O(2)	−8948(2)	−4618(2)	−10675(2)	57(1)
C(3)	−8688(2)	−3883(3)	−9249(3)	33(1)
C(4)	−9426(2)	−4064(3)	−9030(3)	45(2)
C(5)	−9636(2)	−3677(3)	−8292(3)	46(2)
C(6)	−9159(2)	−3007(3)	−7761(3)	40(2)
C(7)	−9410(2)	−2481(3)	−7054(3)	51(2)
C(8)	−8980(2)	−1726(4)	−6621(3)	54(2)
C(9)	−8279(2)	−1459(3)	−6880(3)	48(2)
C(10)	−8007(2)	−1984(3)	−7533(3)	39(1)
C(11)	−8411(2)	−2799(3)	−7979(2)	31(1)
C(12)	−8162(2)	−3349(3)	−8690(2)	32(1)
C(13)	−7368(2)	−3390(3)	−8892(2)	29(1)
C(14)	−6698(2)	−3402(3)	−8272(2)	32(1)
C(15)	−5982(2)	−3431(3)	−8580(3)	36(1)
C(16)	−5899(2)	−3492(3)	−9473(3)	38(1)
C(17)	−6561(2)	−3595(3)	−10075(3)	40(2)
C(18)	−7269(2)	−3583(3)	−9778(3)	34(1)
C(19)	−5985(2)	−1433(3)	−9916(3)	49(2)
O(19)	−5563(2)	−997(3)	−10287(2)	79(2)
C(20)	−7433(3)	−1419(3)	−9825(3)	53(2)
O(20)	−7951(2)	−978(3)	−10139(3)	89(2)
C(21)	−6439(2)	−1196(3)	−8422(3)	46(2)
O(21)	−6317(2)	−585(3)	−7889(2)	81(3)
C(22)	−6709(2)	−3519(3)	−7301(2)	47(2)
C(23)	−5124(2)	−3526(3)	−9774(3)	58(2)

[a]The crystal structure shows two non-identical molecules, slightly different in distortion angles. However, the relative configuration of the stereogenic elements is the same.

TABLE 3. Dihedral angles α[C(22)–C(14)–C(13)–C(12)], β[C(14)–C(13)–C(12)–C(11)] and γ[C(13)–C(12)–C(11)–C(10)] of the two molecules of **3**, present in the elementary unit, compared with the corresponding angles of the uncomplexed lactone **1** [4]



	α	β	γ	Σ[a]
3 (molecule I)	6.11	29.36	24.09	59.56
3 (molecule II)	8.70	35.65	20.13	64.48
1	12.38	34.08	15.00	61.46

[a]Σ = total sum of the dihedral angles α, β and γ.

relatively easily allowing isolation of the resulting product **4**. Moreover, besides the enhanced reaction rate, the ring opening of the lactone complex is extremely stereoselective; only one of the two imaginable diastereomeric reaction products is detectable (NMR, TLC)! The relative configuration of the two stereoelements present in the molecule – the axial and the planar one – was elucidated by two-dimensional NMR experiments. Besides the typical high-field shift of the aromatic protons at the phenolic ring, as caused by the complexation of the metal, an unusually strong low-field shift of a ring proton of the naphthalene part ($\delta = 10$ ppm) is observed. Using homonuclear COSY experiments, this signal could be attributed to the peri-proton (8-H) next to the biaryl axis and hints at an intensive steric interaction with the chromium fragment, thus suggesting the relative configuration as depicted in Scheme 4 to be *exo*.

Conclusions

The high stereocontrol of the ring opening process is not only of preparative but also of mechanistic interest, since it allows a first correlation of the configuration at the axis of the resulting cleavage product with the direction of the initial attack of the nucleophile to the carbonyl group of the lactone [13]: the chromium tricarbonyl fragment does not only, by its steric demand, direct the attack of the nucleophile from only one side of the prostereogenic carbonyl group (apparently only from the less shielded opposite side), but at the same time, being still present in the product, it correlates this attack with the ultimate axial configuration in the final end product.

As in other cases [14], the highly diastereoselective reaction described in this paper, impressingly demonstrates the ability of the chromium tricarbonyl unit to exert stereocontrol not only in α-positions as normally in the literature (e.g. in substituted benzaldehydes) [15], but even over longer distances, on stereocenters in β-positions, here the more remote carbonyl function.

Supplementary material

Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depositary number CSD-400549, the names of the authors and the journal citation.

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