cis-bromination of alkenes

cis-Bromination of Encapsulated Alkenes**

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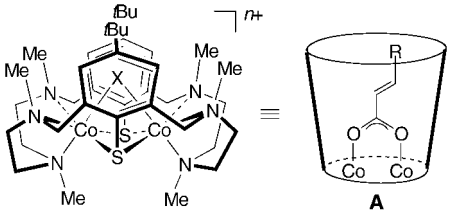
Metalated container molecules are currently attracting much interest, since their properties are often different from those of their constituent components.[1–3] Several groups have already reported that such assemblies show a higher chemical reactivity than their unmodified analogues,[4–6] but so far it is unclear, whether they are also applicable in stereoselective transformations.[7,8] This led us to study the bromination of encapsulated alkene ligands in complexes of the type **A** (Scheme 1); we hoped that the binding pocket would exert an



X = Cl⁻, RCO_2^-, n = 1–3

Scheme 1. Structures of dicobalt complexes $[(L^{Me})Co_2(\mu\text{-}X)]^{n+}$ (X = binding site). The cavity representation of the ligand $(L^{Me})^{2-}$ in **A** should not be confused with the one used for the calixarenes.

effect on the stereochemical course of the reaction. We report here the synthesis and structures of a series of dicobalt complexes of the type $[(L^{Me})Co_2(\mu\text{-}O_2CR)]^{n+}$ bearing α,β-unsaturated carboxylate ligands (Table 1) and demonstrate the remarkable *cis*-bromination of the encapsulated substrates.

The acrylato-bridged dicobalt(III) complex **3** was selected in orienting experiments (Scheme 2). Complex **3** can be readily prepared in high yields by the reaction of the μ-Cl species **1** with sodium acrylate in methanol, followed by a two-electron oxidation of the intermediate $Co^{II}Co^{II}$ species **2**. The kinetically inert complex **3** was subsequently found to undergo the bromination reaction without interference by side reactions. Thus, reaction of **3** with a tenfold excess of Br_2 proceeded smoothly and produced complex **4**, which was identified by IR and NMR spectroscopy, as the sole product.[9]

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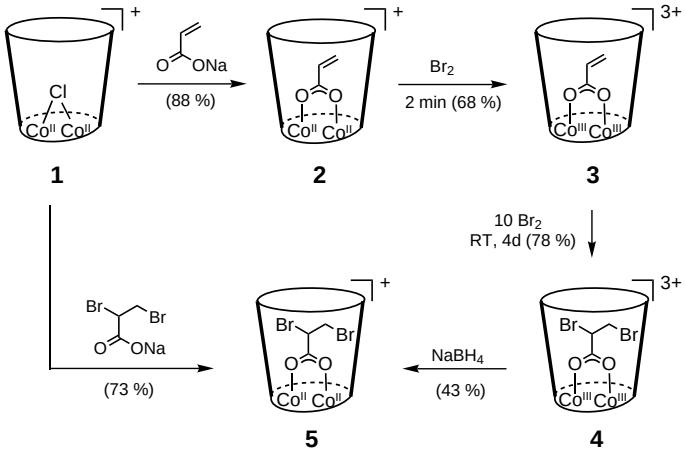
Table 1: Synthesized complexes and selected analytical data.[a]

Complex	$\tilde{\nu}(RCO_2^-)$ [cm^{-1}][b]	E^1, E^2 [V][c]
$[(L^{Me})Co_2^{II}(\mu\text{-}Cl)]^+$ **1**		
$[(L^{Me})Co_2^{II}(\mu\text{-}O_2CCH{=}CH_2)]^+$ **2**	1578, 1430 (1639)	0.22, 0.59
$[(L^{Me})Co_2^{III}(\mu\text{-}O_2CCH{=}CH_2)]^{3+}$ **3**	1519, 1428 (1635)	0.22, 0.60
$[(L^{Me})Co_2^{III}(\mu\text{-}O_2CCHBrCH_2Br)]^{3+}$ **4**	1559, 1386	0.31, 0.70
$[(L^{Me})Co_2^{II}(\mu\text{-}O_2CCHBrCH_2Br)]^+$ **5**	1627, 1394	0.30, 0.69
$[(L^{Me})Co_2^{III}(\mu\text{-}O_2CCH{=}CHPh)]^{3+}$ **6**	1505, 1388 (1631)	0.20, 0.60
$[(L^{Me})Co_2^{III}(\mu\text{-}threo\text{-}O_2CCHBrCHBrPh)]^{3+}$ **7**	1560, 1384	0.32, 0.69
$[(L^{Me})Co_2^{II}(\mu\text{-}threo\text{-}O_2CCHBrCHBrPh)]^+$ **8**	1627, 1390	0.32, 0.70
PhCHBr–CHBr–CO_2H (*threo-dl* pair) **9**		
PhCHBr–CHBr–CO_2H (*erythro-dl* pair) **10**		
$[(L^{Me})Co_2^{II}(\mu\text{-}erythro\text{-}O_2CCHBrCHBrPh)]^+$ **11**	1623, 1393	0.30, 0.68
$[(L^{Me})Co_2^{III}(\mu\text{-}erythro\text{-}O_2CCHBrCHBrPh)]^{3+}$ **12**	1550, 1390	0.30, 0.68

[a] The complexes were isolated as ClO_4^- or BPh_4^- salts. [b] The values in parentheses refer to the IR band poisitions of the C=C stretches. [c] The redox potentials [$E^1(Co^{III,II}/Co^{II,II})$, $E^2(Co^{III,III}/Co^{III,II})$] were determined for the perchlorate salts in CH_3CN and are referenced to the saturated calomel electrode (SCE).

The fact that the reduction of **4** with $NaBH_4$ and the reaction of **1** with sodium 2,3-dibromopropionate yield the same complex **5** (Scheme 2) is also in accord with the formulation of **4**.



Scheme 2. Preparation of dicobalt complexes **2**–**5**. Numbers in parentheses refer to yields of isolated products.

The cinnamato-bridged dicobalt(III) complex **6**, whose synthesis and structure were reported earlier,[10] was examined next. In this case the bromination reaction was complete after 6 h at ambient temperature and yielded a single addition product **7** in nearly quantitative yield (Scheme 3). NMR-spectroscopic studies of **7** and a single-crystal X-ray structure determination of the reduced $Co^{II}Co^{II}$ complex **8** revealed the presence of a bridging 2,3-dibromo-3-phenylpropionato ligand (threo *dl* pair).[9] The expected complex **12** of the *erythro* form of 2,3-dibromo-3-phenylpropionate, which was prepared for comparative purposes according to the route depicted in Scheme 4, is only produced in low yields (< 3 %). Therefore, the bromination of the alkene encapsulated in **6** is a highly diastereoselective *syn* addition.

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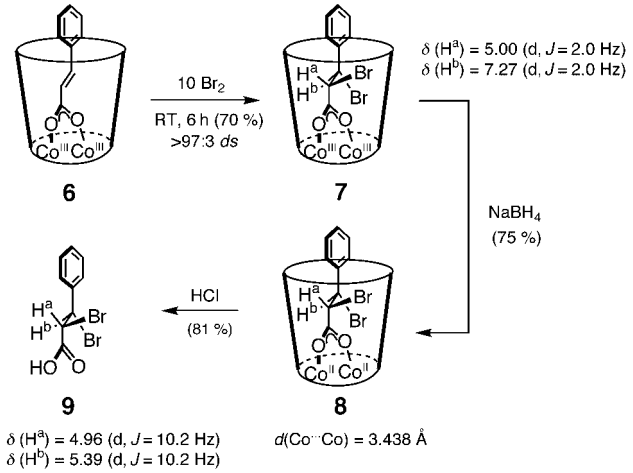
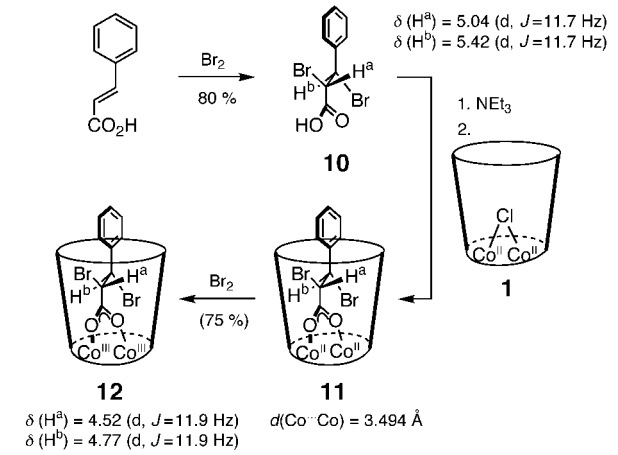


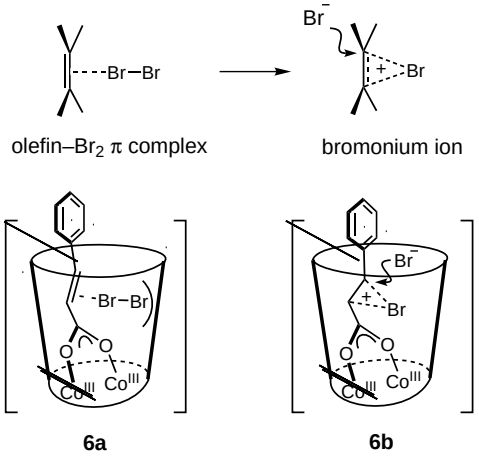
Scheme 3. Preparation of compounds **7**–**9** with details of key NMR data.



Scheme 4. Preparation of compounds **10**–**12** with details of key NMR data.

This is rather unusual and is in striking contrast to the bromination of the free acid, which is an *anti* addition.[9] Also the bromination of the encapsulated alkene is 2–3 orders of magnitude slower. The decrease in the rate can be ascribed to steric effects. This is true in particular, when one recalls that the bromination of free alkenes begins with the formation of olefin–Br_2 π complexes with T-shaped structures.[11] In our case, such a π complex (**6a**) can not form due to steric interactions with the ligand matrix.

To get some preliminary insights into the reaction mechanism, we have carried out the bromination of **6** at four different temperatures.[9] This gave a set of rate constants from which the entropy of activation could be determined. The calculated $\Delta S^{\neq}$ value of $-220\,J\,mol^{-1}\,K^{-1}$ is much more negative than in the case of the free alkenes ($\Delta S^{\neq} \lesssim -80\,J\,mol^{-1}\,K^{-1}$), [12] which indicates a well-ordered transition state. This result nicely corroborates with the observed *syn* addition. The bromination of **6** presumably involves a tight bromonium ion/Br^- contact-ion pair **6b**, in which one face of the olefin is sterically shielded by the aryl ring of the ligand $(L^{Me})^{2-}$. However, a mechanism involving a π complex between the bromonium ion and the arene, in which the soft bromonium ion interacts with a phenyl ring of the spectator ligand, cannot be ruled out at the moment.[13] It should be remembered that Ag^+ or Cs^+ ions can form coordinative bonds with the π electrons of calixarenes.[14]



The electrophilic bromination of olefins almost invariably yields *trans*-1,2-dibromides, and there are currently no reagents available that readily *cis*-brominate olefins.[15] It is therefore worth mentioning that the brominated products can be liberated from the binding pocket of the dicobalt(II) complexes. For example, complex **8** decomposes under acidic conditions to give the hydrochloride salt of the ligand ($H_2L^{Me}\cdot 6\,HCl$), a water-soluble cobalt(II) complex, and the acid **9**, which can be separated from the reaction mixture in analytically pure form by extraction into an organic solvent (Scheme 3). The new method is currently only applicable to olefins with anchoring groups (RCO_2^-), but expansion of the container approach to a general concept for the *cis*-bromination of olefins appears to be in reach.

We have described the stereochemical course of the bromination of α,β-unsaturated carboxylate ligands. The reaction is dictated by the size and form of the binding cavity of the complexes and this results in a highly diastereoselective *syn* addition of the Br_2 molecule to the carbon–carbon double bond. We are currently probing the possibility whether this and related transformations can be made enantioselective.

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Keywords: alkenes · bromination · container molecules · diastereoselectivity · reaction mechanisms

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