

# Solution- and solid-state NMR study of intermediate $\eta^3$ -allyl-cobalt tricarbonyl type complexes in 3-methyl-1,2-butadiene polymerization

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Dedicated to: Professor László Markó on the occasion of his 70th birthday.

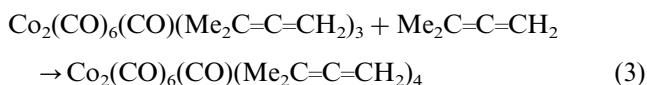
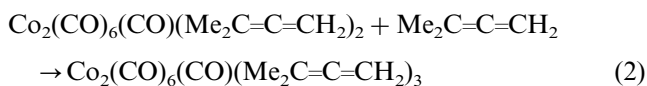
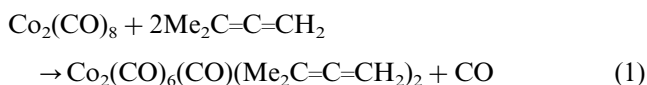
## Abstract

<sup>1</sup>H- and <sup>13</sup>C-NMR of  $\eta^3$ -allyl-cobalt tricarbonyl complexes  $\{\text{Co}(\text{CO})_3\}_2\{(\eta^3\text{-Me}_2\text{CCCH}_2)_2\text{CO}\}$  (**1**),  $\{\text{Co}(\text{CO})_3\}_2\{(\eta^3\text{-Me}_2\text{CCCH}_2)_3\text{CO}\}$  (**2**) and  $\{\text{Co}(\text{CO})_3\}_2\{(\eta^3\text{-Me}_2\text{CCCH}_2)_4\text{CO}\}$  (**3**) were studied. The X-ray structures obtained for **1** and **2** suggested that the 1,2-polymer chain would grow in a helical manner. Due to the coordination of the  $\text{Co}(\text{CO})_3$  units to the chain-closing prochiral dimethylallylic planes and/or to the hindered rotation of the dimethylallylic units conjugated to some extent with the ketonic carbonyl several diastereomers and even more rotamers can be envisaged. In solution, however, only two symmetric forms in different ratio could be detected in all cases studied so far. We have undertaken a detailed NMR study on these compounds both in solution- and solid-state, in order to assign the resonances unambiguously and understand clearly the nature of the isomers present in solutions. The results obtained suggest the presence of *meso* and *rac* diastereomers due to the coordination of the  $\text{Co}(\text{CO})_3$  units to the prochiral allyl planes. These dimethylallylic groups rotate relatively free around the ketonic carbonyl. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Diastereomeric  $\eta^3$ -allyl-cobalt complexes; Solution- and solid-state NMR

## 1. Introduction

Complexes formed in the reaction of  $\text{Co}_2(\text{CO})_8$  and 3-methyl-1,2-butadiene in *n*-octane at room temperature with different molar ratios have a composition according to Eqs. (1)–(3) [1]:



Based on spectroscopic evidence, complexes **1–3** are members in a series of binuclear  $\eta^3$ -allyl-type complexes that contain  $2 + n$  ( $n = 0, 1, 2, \dots, 8, \dots, 38$ ) five-carbon units in form of a 1,2-polymer chain divided by a ketonic carbonyl in the middle and closing the chain on each side by a  $\eta^3$ -3,3-dimethylallyl cobalt tricarbonyl group. Solid-state structures of complexes **1** and **2** suggested that the 1,2-polymer chain of 3-methyl-1,2-butadiene grows in a helical manner [1].

For the first three members of this series of complexes preliminary solution-state NMR data have also been given [1] noting the existence of two isomers (interpreted as diastereomers). Data obtained for **1** and **2** were taken as if in support of asymmetric structures in solution too.

Now we have undertaken a more detailed NMR study on these compounds in order to correct the assignments of certain resonances and the interpreta-

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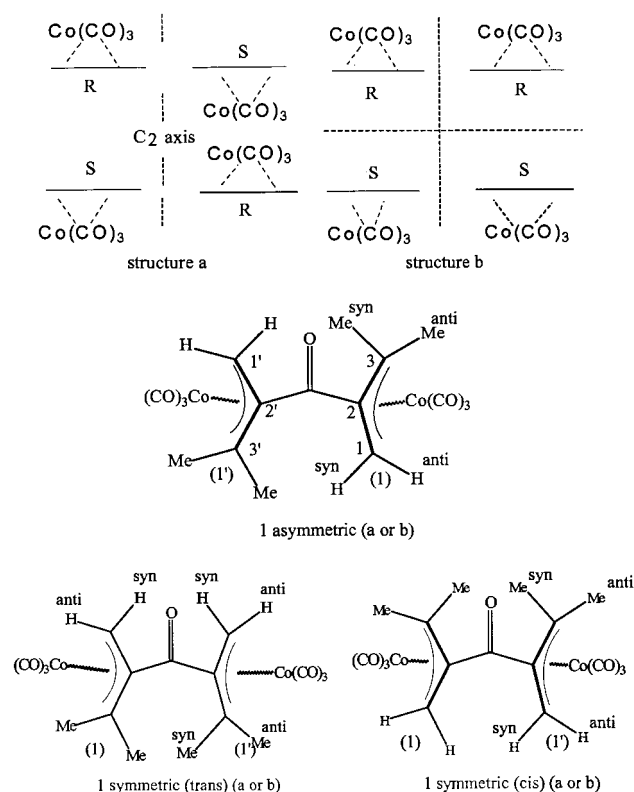
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tion and understand more clearly the nature of the isomers present in solutions.

Concerning the plausible structures of these isomers several possibilities must be considered (see Scheme 1).

On one hand, since the 3,3-dimethylallyl units are prochiral, coordination of the  $\text{Co}(\text{CO})_3$  moiety, which can occur from two directions, leads to enantiomer pairs ( $R$ - $S$ ;  $S$ - $R$ ; and  $R$ - $R$ ;  $S$ - $S$ ), two of these pairs being diastereomers (see structures **a** (*meso*) and **b** (*rac*), respectively in Scheme 1). Such diastereomers have already been observed and assigned, e.g. in mononuclear Pd(II)  $\pi$ -allyl complexes [2]. It is noteworthy that the X-ray structures obtained for **1** and **2** proved the *meso* structure (**a**) for both.

On the other hand, restricted rotation, if significant, of the allylic moieties around the  $\text{C}=\text{O}-\text{C}2$  and  $\text{C}=\text{O}-\text{C}2'$  bonds can result in *cis* (the methyl end of both dimethylallylic group is close to the ketone carbonyl) and *trans* forms (the methyl end of both dimethylallylic group is far from the ketone carbonyl) i.e. in rotamers (see Scheme 1 for *symmetric cis* and *trans* and *asymmetric* structures). It is known that  $\alpha,\beta$ -unsaturated ketones prefer planar arrangement with substantial rotational barrier, however, the extent of change of delocalization due to the  $\text{Co}(\text{CO})_3$  coordination cannot be easily estimated. Although not a strictly similar problem, examples of restricted rotation of two phenyl groups attached to an allyl moiety in Pd(II) complexes were



reported with a fairly large phenyl rotational barrier of about  $60 \text{ kJ mol}^{-1}$  [3].

Considering the asymmetric rotameric forms as well, in principle we may have two diastereomers in four possible conformations for **1**, four diastereomers in eight possible conformations for **2** and eight diastereomers in 16 different conformations for **3**.

Furthermore, based on the crystal structure of **1** and **2**, for the larger members of the series the possibility of a helical asymmetry axis has to be considered as well [1].

## 2. Experimental

Complexes studied were prepared according to reported procedures [1]. All NMR spectra were recorded on a Varian UNITY 300 spectrometer at the NMR Laboratory of the Veszprém University using the standard Varian software. (Switchable 5 mm probe;  $^1\text{H}$ , 300 MHz, width of the  $90^\circ$  pulse, 17  $\mu\text{s}$ ;  $^{13}\text{C}$  75.42 MHz, width of the  $90^\circ$  pulse 14  $\mu\text{s}$ ). The  $^1\text{H}$ -FID-s were processed with Gaussian weighting functions. Data size was normally 32K.

Unfortunately we were unable to get rid of the paramagnetic impurities, presumably Co(II) ions of the samples. To be able to achieve sufficient resolution in the proton spectra rather diluted samples ( $0.5$ – $0.7 \text{ mg } 0.75 \text{ ml}^{-1}$ ) were used, whereas for the carbon measurement even much higher concentrations ( $20$ – $35 \text{ mg ml}^{-1}$ ) did without significant line broadening effects, however, the fast relaxation of the proton and carbon nuclei prevented any experiments which involved evolution times longer than  $100$ – $150 \text{ ms}$ , such as e.g. NOESY or long range carbon–proton correlations.

$^{13}\text{C}$ -CP/MAS: Varian UNITY 300 spectrometer, Doty XC5 probe, thin wall 5 mm  $\text{Si}_3\text{N}_4$  rotors, Kel-F end caps, relaxation delay 5 s, contact time 2.5 ms, room temperature, spinning speed 8100 Hz, pulse sequence: xpolar.

## 3. Results and discussion

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of **1**–**3** are collected in Tables 1 and 2, respectively. A remarkable general feature of both the  $^1\text{H}$  and  $^{13}\text{C}$  spectra is the high symmetry of the two isomers present. In complex **1**, in crystalline state, one allylic system and the ketone carbonyl group are nearly coplanar, but this plane approaches orthogonality ( $81^\circ$ ) with the other  $\eta^3$ -3,3-dimethylallyl group, in complex **2** the helical twist of the molecular backbone is even more pronounced [1].

In solution, however, only two chemically different vinyl protons or methyl groups are observed in each form containing even number of the allylic group, i.e.

Table 1  
<sup>1</sup>H-NMR data of complexes 1–3 ( $\delta$  in ppm relative to TMS, 300 MHz, CDCl<sub>3</sub>, 293 K)

Compound	Vinyl protons				Methylene protons				Vinyl methyls				Propylene methyls			
	<i>Syn</i>		<i>Anti</i>		H <sub>A</sub> <sup>a</sup>		H <sub>B</sub> <sup>a</sup>		Ext.		Int.		<i>Syn</i>		<i>Anti</i>	
	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>	A <sup>b</sup>	B <sup>b</sup>
<b>1</b> (1:2) = A:B	3.42	3.13	2.79	2.76									1.86	1.88	1.42 (overlapped)	
<b>2</b> (A:B = 45:55)																
Coordinated allyl (1)	3.14	3.10	2.64	2.64									1.79	1.77	1.32	1.28
Coordinated allyl (2)	3.35	3.24	2.73	2.76									1.96	2.06	1.43	1.46
Non-coordinated allyl (3)					3.56	3.60	3.02	3.04	1.82 *	1.80	1.79 *	1.8				
<b>3</b> (A:B ~ 5:95)																
Non-coordinated allyl (3, 3')						3.43		3.10		1.84 *		1.82 *				
Coordinated allyl (1, 1')		3.06		2.61										1.78		1.30

<sup>a</sup> H<sub>A</sub> and H<sub>B</sub> are not assigned.

<sup>b</sup> A, minor; B, major.

\* Tentative assignments, may be interchanged.

Table 2  
<sup>13</sup>C-NMR data of complexes 1–3 ( $\delta$  in ppm relative to TMS, 75 MHz, CDCl<sub>3</sub>, 293 K)

Compound	=CH <sub>2</sub> (C1) (CH <sub>2</sub> )		=C(CH <sub>3</sub> ) <sub>2</sub> (C3)		–C= (C2)		Me* syn (ext)		Me* anti (int)		C=O (ketone)		(CO) ( <i>n</i> )
	A	B	A	B	A	B	A	B	A	B	A	B	
<b>1</b> (1:2) <sup>a</sup>	45.3	46.2	87.0	85.8	97.2	97.2	28.4	29.1	27.8	27.3	198.1	199.6	201.8
<b>2</b> (45:55) <sup>a</sup>	49.1	49.6	89.6	88.7	91.5	90.3	29.1 <sup>b</sup>	28.1 <sup>b</sup>	27.0 <sup>b</sup>	26.7 <sup>b</sup>	201.7		203.6,
Coordinated allyl (1)													201.5
Coordinated allyl (2)	46.5	45.9	88.4	86.7	99.7	90.3	28.4	28.3	28.2	28.0			
Non-coordinated allyl (3)	CH <sub>2</sub> * 38.2	CH <sub>2</sub> * 38.9	135.6 *	134.9 *	135.0 *	134.7 *	22.9 *	22.8 *	20.5 *	20.2 *			
<b>3</b> (~ 5:95) <sup>a</sup>	CH <sub>2</sub> * 36.1	CH <sub>2</sub> * 36.2	135.7	135.8	141.1	141.2	n.o. <sup>c</sup>	30.9	n.o.	28.3	201.5	203.7	
Non-coordinated allyl (3, 3')													
Coordinated allyl (1, 1')	48.9	49.0	87.5	87.8	n.o.	100.8	n.o. <sup>c</sup>	27.3	22.5	22.4			

<sup>a</sup> Ratio of the minor (A) and major (B) diastereomers.

<sup>b</sup> Overlapped signals.

<sup>c</sup> n.o., not observed.

\* Tentative assignments, may be interchanged.

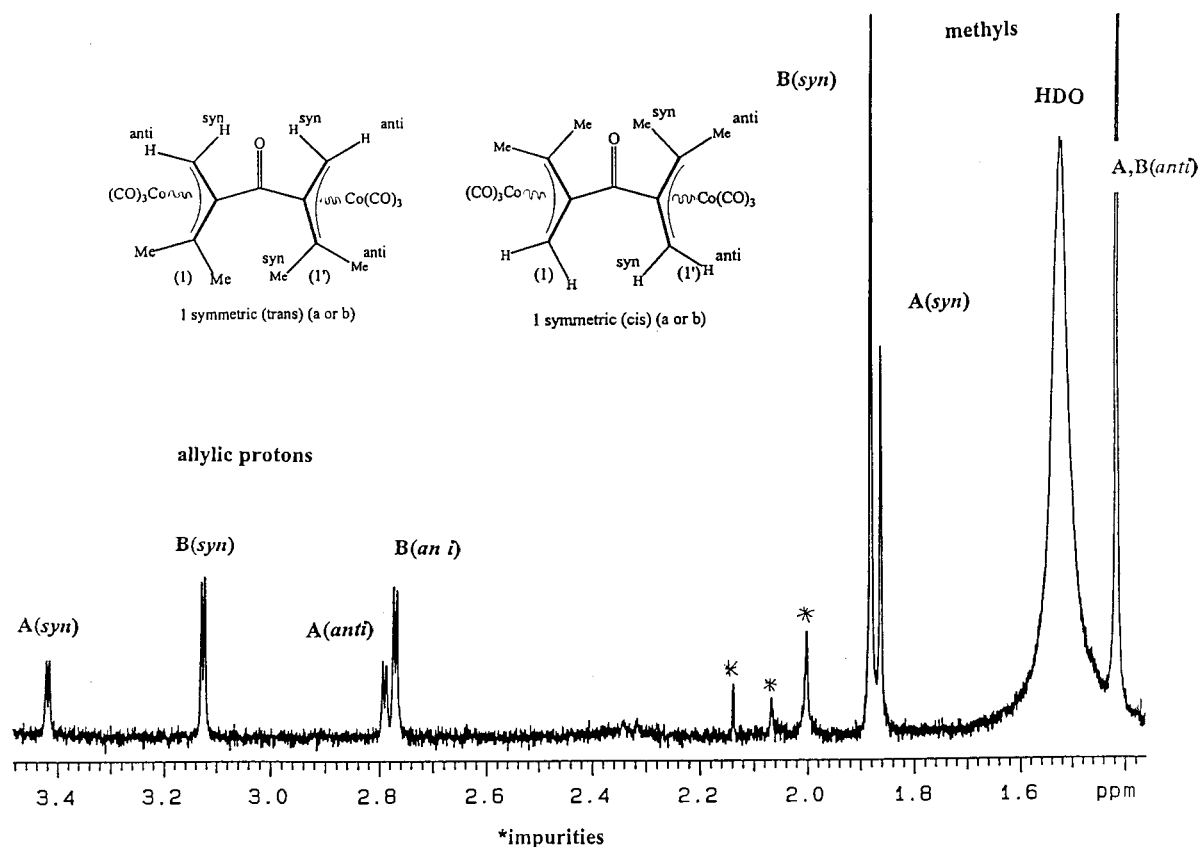


Fig. 1.  $^1\text{H-NMR}$  spectrum of **1** ( $\text{CDCl}_3$ , 293 K, 300 MHz,  $\sim 0.6 \text{ mg ml}^{-1}$ ).

for **1** and **3**, therefore asymmetric structures such as shown in Schemes 1 and 3 can be excluded.

This assumes structures with  $C_2$  symmetry (time-averaged or static) or structures with a mirror plane (at least on the NMR timescale), otherwise the observed identity of the two allylic groups cannot be explained. Although inherently asymmetric, the same phenomena are observed in **2** as well (see below), indicating that the origin of the isomeric forms must be similar in all cases.

#### $\{\text{Co}(\text{CO})_3\}_2\{(\eta^3\text{-Me}_2\text{CCCH}_2)_2\text{CO}\}$ (complex **1**)

The  $^1\text{H-NMR}$  spectrum of this compound (Fig. 1) clearly indicates the presence of two isomers (referred to as **A** and **B**) with an approximate ratio of 1:2. The assignment of the signals to the *syn* and *anti* positions (Scheme 1) is based on chemical shift considerations and possible steric and/or anisotropic effects of the ketone carbonyl group and is in agreement with the general observation that the proton resonance frequency of  $\text{H}^{\text{syn}}$  is higher than that of  $\text{H}^{\text{anti}}$ , such phenomena have already been reported for  $\text{Pd}(\text{II})$ - [4a] and  $\text{Pt}(\text{II})$   $\pi$ -allyl complexes as well [4b]. The chemical shift difference of the corresponding *syn* and *anti* protons/groups is quite substantial in the minor form (**A**) but less significant in the major (**B**) form (0.63 and 0.37 ppm for  $\Delta\delta_{\text{H}}^{\text{syn-anti}}$  in the two forms, respectively). At

the same time signals of the *anti* protons of the two isomers almost overlap.

It is noteworthy that no remarkable change was detected in the spectrum in the temperature range going from 213 K (in  $\text{CD}_2\text{Cl}_2$ ) till 363 K (toluene- $d_8$ ), i.e. no support was obtained for the existence of rotamers of medium energies.

Steady-state differential NOE experiments [5] revealed only the trivial spatial proximity of the geminal *syn* and *anti* protons in both diastereomers, however, it is very likely that the paramagnetic impurities quench the long-distance NOE enhancements.

The  $^{13}\text{C}$  spectrum confirmed the symmetric nature of both forms. The terminal carbonyls attached to the cobalt gave one exchanged broadened signal at 201.8 ppm, whereas the ketone signals of the two isomers appeared at 198.1 and 199.6 ppm as sharp singlets. These high values indicate very moderate extent of delocalization of the  $\pi$  electrons along the  $\text{C}=\text{O}-\text{C}_2$  bonds, consequently the rotational barriers cannot be high either.

The assignments are based on DEPT spectra [6] and on the literature data of compounds containing a similar moiety [7]. Nevertheless assignment of the *syn* and *anti* methyl signal is tentative only. In order to prove unambiguously that the bulk sample contains the two

forms even in solid-state, we have carried out  $^{13}\text{C}$  measurements in solid-state too. The CP/MAS spectra, although not resolved for all signals, prove sufficiently the existence of isomers, observed earlier in solution, in the crystalline form too. (Spectral data:  $\sim 200$  ppm,  $\text{C}=\text{O}$  ketone, A and B together;  $\sim 196$  ppm CO carbonyls, broad signal; 105 ppm C2, A and B together; 85 and 82 ppm C3, A and B well resolved; 46 ppm, broad line, C1, A and B together; 29.3 ppm methyl, *syn* and *anti* (A); 28.8 ppm methyl, *anti* or *syn* (B); 27.7 ppm methyl, *anti* or *syn* (B).)

$\{\text{Co}(\text{CO})_3\}_2\{(\eta^3\text{-Me}_2\text{CCCH}_2)_3\text{CO}\}$  (complex 2)

The addition of one more  $\eta^3$ -3,3-dimethylallyl group to the molecule resulted in the loss of the symmetry, consequently here we have well resolved signals for all allylic protons and methyl groups. Furthermore, like **1** practically all signals are doubled due to the presence of isomeric forms (A and B) in a near 45:55 ratio. This ratio did not change between room temperature and 230 K as proved by low-temperature  $^{13}\text{C}$ -NMR spectra. The carbonyls, however, do show some temperature dependence. The two relatively broad signals became much sharper at low temperatures indicating the slowdown of the carbonyl fluxionality around the cobalt atoms, whereas the sharp ketone signal at relatively high frequency (201.7 ppm) did not change.

Assignment of protons and methyl groups belonging to the same  $\eta^3$ -3,3-dimethylallyl group was possible through standard 1D and 2D techniques [8] (see e.g. Fig. 2 for the  $^1\text{H}$ ,  $^1\text{H}$  COSY spectrum of **2**). Distinction between the two terminal allylic groups (Scheme 2, allyl (1) and allyl (2)) is based on steady-state differential NOE measurements. These experiments suggest the spatial vicinity of the geminal methylene protons of the allyl (3) group and the methyls of one of the terminal allyl groups (numbered 1) as depicted in Scheme 2. (Unfortunately, it was not possible to saturate selectively the individual lines of the different isomers.)

Assignment of resonances to the isomers observed in the  $^{13}\text{C}$ -NMR spectrum is not unambiguous (Table 2), especially those of the allyl group (3) is tentative at best owing to the small chemical shift differences of these signals. Again, no  $^1\text{H}$ - $^{13}\text{C}$  chemical shift correlation spectrum could be obtained due to the relatively fast  $T_2$  relaxation of the carbon atoms.

$\{\text{Co}(\text{CO})_3\}_2\{(\eta^3\text{-Me}_2\text{CCCH}_2)_4\text{CO}\}$  (complex 3)

The addition of a fourth  $\eta^3$ -3,3-dimethylallyl group to the molecule resulted in the re-establishment of the symmetry axis or plane already seen in **1**; we observed again only one pair of signals for the *anti* and *syn* allylic protons and likewise for the methylene and methyl

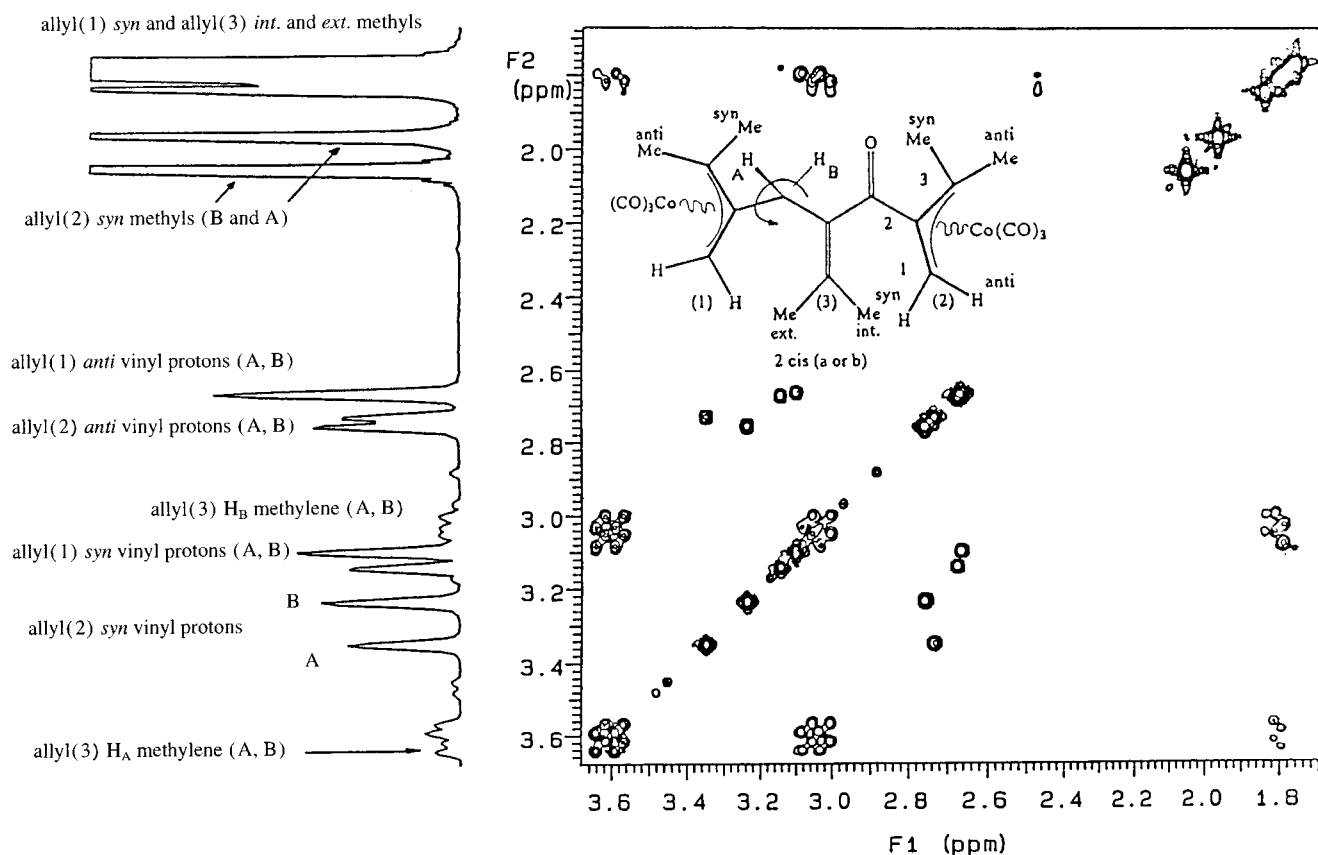
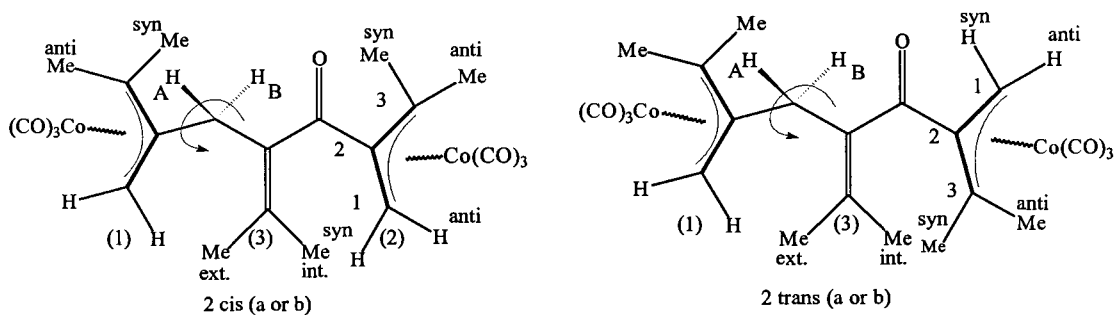
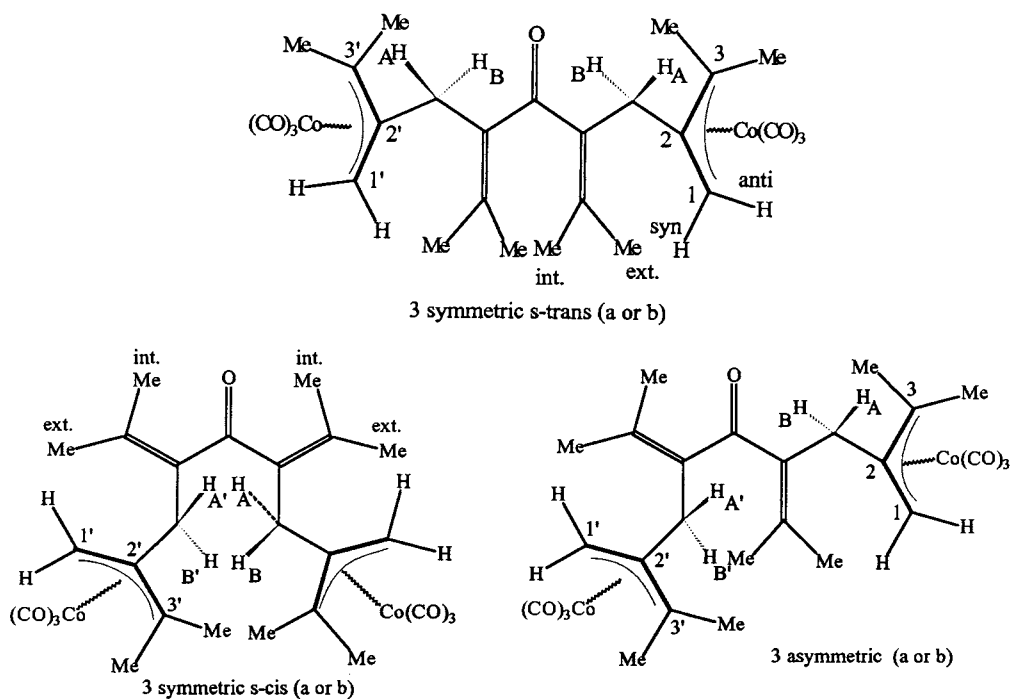


Fig. 2.  $^1\text{H}$ ,  $^1\text{H}$  chemical shift correlation map (COSY spectrum) of **2** ( $\text{CDCl}_3$ , 293 K, 300 MHz).



Scheme 2.



Scheme 3.

groups in each form. Two isomers exist even here, however, the quantity of the minor form now hardly exceeds 5% (Scheme 3).

Based on the data obtained for **1** and **2**, assignment of the  $^1\text{H}$  spectrum is more straightforward now. Methyls of the (3, 3') allyl groups (referred to as ext. and int.), however, heavily overlap.

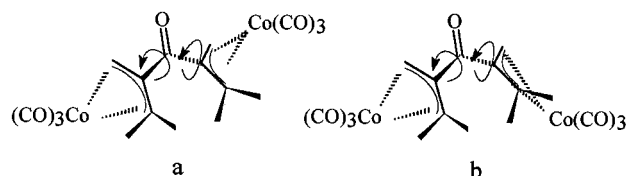
Certain signals of the minor isomer remained unobserved or overlapped (methyl signals) in the somewhat noisy  $^{13}\text{C}$  spectrum (see Table 2) due, most probably, to their low intensity (Scheme 4).

#### 4. Conclusions

The experimental evidence gathered and outlined in the previous section suggests the following interpretation. No support for hindered rotation around the

ketonic  $\text{C}=\text{O}-\text{C}_2$  bonds has been obtained, such barriers, if they exist, must be low. Therefore at room temperature and even below, the rotation must be relatively free. The observed high chemical shift values of the ketone carbonyls (199 ppm and above) are in accordance with the low extent of  $\pi$ -delocalization.

Also, the so far unexplained symmetry of the isomers observed in the solution spectra can be better understood in terms of a  $\text{C}=\text{O}-\text{C}_2$  rotation that is fast on the NMR timescale.



Scheme 4.

All these suggest that the isomers we observe correspond to the **a** and **b** structures (see below), i.e. to the *meso* and *rac* diastereomers resulting from the coordination of the  $\text{Co}(\text{CO})_3$  units to the same or different sites of the prochiral allyl planes.

Concerning the origin of the substantial chemical shift difference of the *syn* and *anti* protons of the coordinated allylic groups, it may well be caused by the anisotropy of the  $\text{Co}(\text{CO})_3$  units. At the same time we have not sufficient proof to assign these signals to the **a** and **b** diastereomers.

#### Acknowledgements

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