

C_1 -insertion reactions at cyclodimeric (η^2 -acetaldehyde) zirconocene complexes \star

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Abstract

Carbonylation of dimethylzirconocene, followed by treatment with zirconocene dihydride, benzyl chloride and then methyllithium, gave the (η^2 -acetaldehyde)zirconocene dimer (**9**) as a mixture of *trans*- and *cis*-isomers isolated in a 1.5 : 1 ratio under kinetic control and in a 1 : 1.7 ratio under thermodynamic control, respectively. Complexes *trans*-**9**/*cis*-**9** were treated with carbon monoxide to give the *trans*-**10**/*cis*-**10** monoinsertion products, and with isonitriles RNC (R = CH₂SiMe₃ (**a**), CMe₃ (**b**)) to give the mono- and bis-insertion products *trans*- and *cis*-**11(a, b)** and **12(a, b)**, respectively. Complex **12a** was characterized by X-ray diffraction. In all cases the *trans/cis* stereochemical information was predominantly retained in the products, which indicates that dimetallic pathways are favoured in these insertion reactions of the metallatricyclic (η^2 -aldehyde)metallocene dimers.

Keywords: (η^2 -Aldehyde)zirconocenes; Carbonylation; Isonitrile insertion; Iminoacyl complexes; CO insertion

1. Introduction

(η^2 -Formaldehyde)zirconocene-dimer (**1**) has been discussed to serve as a molecular model mimicking certain aspects ascribed to the chemistry of methylene groups at a metal oxide surface [1]. One may consider the cyclodimeric structure of **1** to be composed of a Zr₂O₂ molecular metal oxide core with CH₂ groups attached to its edges and the remaining coordinative vacancies at zirconium saturated with the η^5 -cyclopentadienyl ligands. Indeed, complex **1** exhibits a variety of unique reaction patterns that one might consider to be in some way related to Fischer–Tropsch-type chemistry at a heterogeneous catalyst surface [2]. Such typical reactions include the removal and oligomerization of CH₂ group from the molecular metal oxide core and formation of oligomeric (–CH₂–)_n chains upon treatment of **1** with catalytic quantities of triethylborane [3].

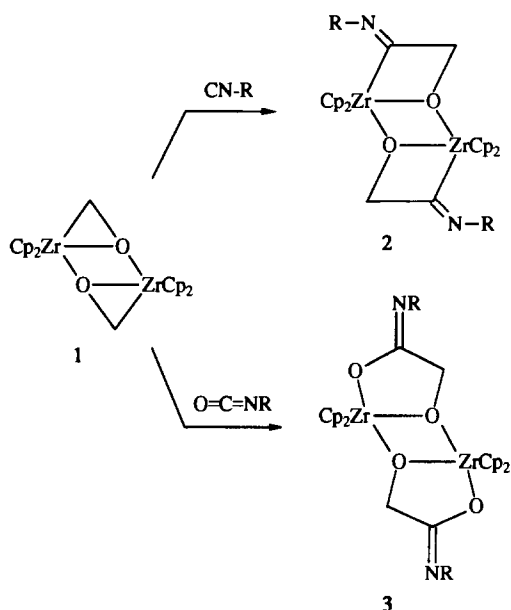
Also, complex **1** inserts a variety of reactive monomers into the zirconium to carbon bonds. This includes carbon monoxide, isonitriles, ketones and alde-

hydes, heterocumulenes, olefins and acetylenes and even metal halides and hydrides [4]. In most cases complexes (such as **2** or **3**) are obtained that still contain two zirconium atoms per molecule [5]. This renders the question of whether these insertion reactions generally occur at the stage of the dinuclear oxygen-bridged complexes or if dissociative pathways via intermediate monomer formation are favoured. In this case the observed stable dinuclear products would have resulted from a subsequent recombination of monomeric insertion products.

A way to distinguish between these possible pathways is to make use of stereochemical labels introduced at the stage of the (η^2 -aldehyde)zirconocene complexes. When each of the three-membered metallacycles of the [(η^2 -aldehyde)ZrCp₂]₂ dimetallatricyclic structure contains a single chirality element, then two diastereoisomers are possible whose relative ratios can be retained or lost during the insertion reaction. This then indicates whether the two organometallic subunits stay together and their stereochemical information remains dependent on each other or become separated during the reaction and thus lose their relationship. A first study of this type was recently described by Askham et al. [6] that indicated that (η^2 -O=CHCH₂SiMe₃)ZrCp₂ groups stay together in the course of carbon monoxide insertion. We

\star Dedicated to Professor Henri Brunner on the occasion of his 60th birthday.

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have now completed a related study using the diastereomeric (η^2 -acetaldehyde)zirconocene dimers in different ratios and investigated the stereochemical course taken in CO and in alkylisocyanide insertion reactions.

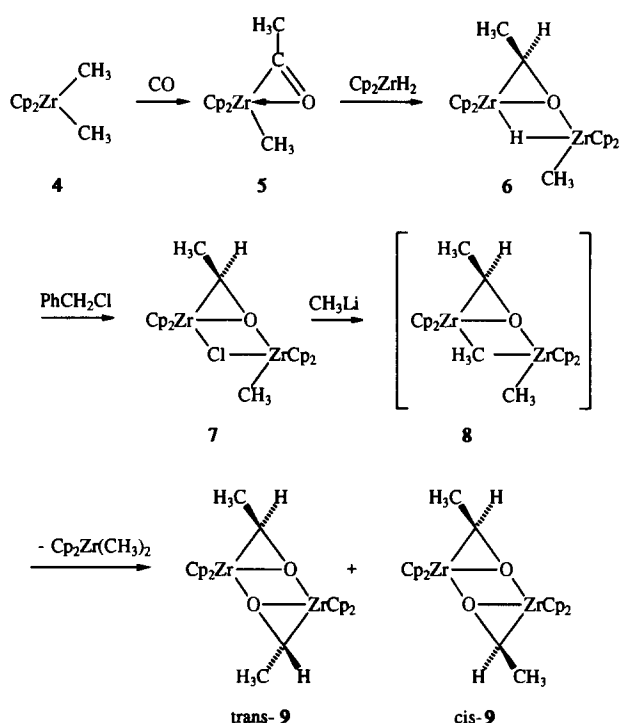
2. Results and discussion

The (η^2 -formaldehyde)zirconocene dimer **1** was prepared by first reacting hydrido-zirconocene chloride with carbon monoxide and then treating the resulting dinuclear (μ - η^1 -O : η^2 -C,O-formaldehyde)(Cp_2ZrCl)₂ product [7] with two molar equivalents of methyl-lithium. This led to the production of a mixture of one equivalent of dimethylzirconocene and 0.5 molar equivalent of **1** that was easily separated owing to their drastically different solubilities of these organometallic products [1].

The (η^2 -acetaldehyde)zirconocene dimer **9** needed for this study was synthesized in a related way. We first carbonylated dimethylzirconocene (**4**) to give the “O-inside” (η^2 -acetyl)methylzirconocene isomer **5**, as described by Floriani and co-workers [8]. Then this product was treated with one molar equivalent of dihydrido-zirconocene. This resulted in the addition of one hydride to the acyl ligand, thereby reducing it to a (μ - η^1 -O : η^2 -C,O-acetaldehyde) moiety [9]. The remaining hydride ended up in a second bridging position to give the product **6**, which was isolated in 82% yield. Next we exchanged the μ -hydride ligand for chloride by reacting complex **6** with benzyl chloride to give **7** in 94% yield. The **6** to **7** conversion can also be achieved by treatment with chloroform; in this case methylene chloride is the stoichiometric organic product. The (μ -

acetaldehyde)(μ -chloride)dizirconium complex **7** was then treated with one molar equivalent of methyl-lithium. We assume that this may initially generate the (μ -methyl)dizirconium complex **8** that is thermally unstable and rapidly loses dimethylzirconocene to give (η^2 -acetaldehyde)zirconocene, which is recovered and isolated as a dimetallatricyclic dimer in ca. 50% yield. Two diastereoisomers are formed. After crystallization from toluene at -30°C they are obtained in a 1.5 : 1 ratio. These diastereomeric complexes have different symmetries. The *cis*-**9** isomer is C_2 symmetric and the *trans*-**9** isomer is of C_i symmetry. Thus each of them contains a pair of symmetry-equivalent (η^2 -acetaldehyde)ZrCp₂ units in the dimeric structure. Each of the monomeric subunits then exhibits a diastereotopic pair of η^5 -cyclopentadienyl ligands. Hence the NMR spectra could not allow us to decide which isomer had a *cis* and which a *trans* arrangement of methyl substituents at the planar dimetallatricyclic central (ZrOC)₂ framework. From an X-ray crystallographic analysis of a stereochemically related product (see below), we deduced that the major diastereomer of **9** obtained from the toluene recrystallization as described above is *trans*-**9**.

The major component *trans*-**9** exhibits ¹H/¹³C NMR signals at δ 5.77, 5.68/108.2, 108.0 (Cp), 2.70/73.2 (CH) and 1.66/23.9 (CH₃) in benzene-*d*₆. The minor *cis*-**9** diastereoisomer shows the corresponding ¹H/¹³C NMR signals at δ 5.76, 5.68/108.4, 108.1 (Cp), 2.61/73.3 (CH) and 1.66/24.2 (CH₃). For this stereochemical study, it was important to monitor the



stereochemistry during the insertion reactions and to distinguish clearly between kinetic and thermodynamic stereocontrol. For this reason, it would have been ideal to study and follow each insertion reaction starting from each of the pure **9** diastereoisomers in separate experiments. Unfortunately, this could not be done because

we were not able to separate and isolate the pure *cis*- and *trans*-**9** complexes. However, we succeeded in obtaining a mixture of the (η^2 -acetaldehyde)zirconocene dimers enriched in the *cis*-**9** diastereoisomer that was reproducibly formed under conditions of thermodynamic control. Keeping the kinetic 1.5:1 *trans*-**9**/*cis*-**9**

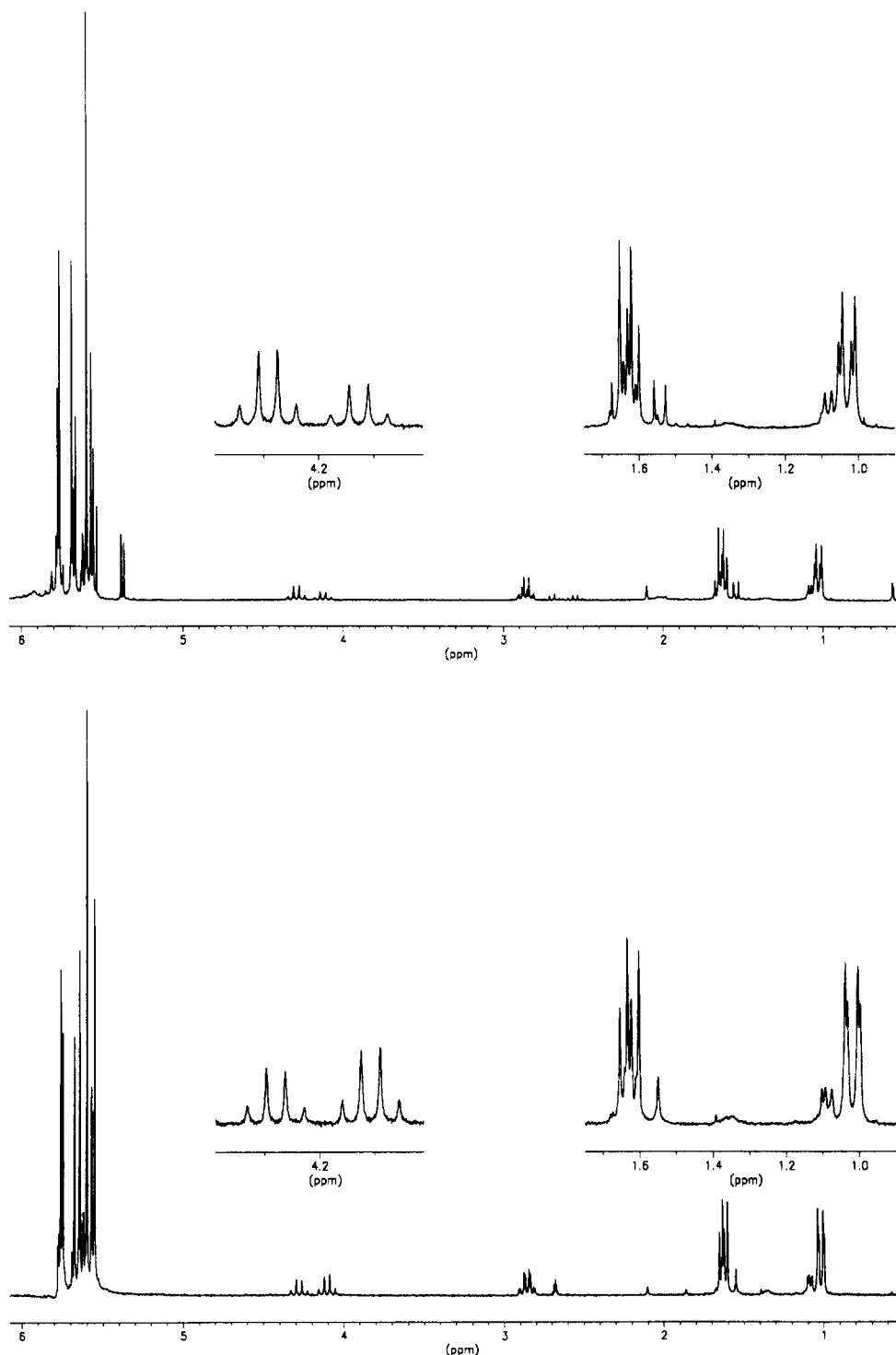


Fig. 1. ^1H NMR spectra of the mixture of moncarbonylation products *trans*-**10** and *cis*-**10** obtained from the 1.5:1 (top) and 1:1.7 mixtures (bottom) of the diastereomeric (η^2 -acetaldehyde)zirconocene dimers *trans*-**9** and *cis*-**9**.

mixture (obtained as described above) for 24 h in toluene solution at reflux temperature produced a 1 : 1.7 mixture of the **9** diastereoisomers, that was obtained pure after crystallization.

Both the *trans-9*/*cis-9* mixtures were subjected to carbonylation at ambient temperature and pressure in benzene-*d*₆ solution and the product mixtures obtained were directly analysed by NMR without work-up. In this way the stereochemical relationship between the (η^2 -acetaldehyde)zirconocene system and its carbonylation products was determined. Under these conditions, one CO molecule is inserted in each (η^2 -acetaldehyde)-zirconocene dimer. A dimetallatricyclic (η^1 -acyl)metallocene complex is formed. Starting from the kinetic 1.5 : 1 *trans-9*/*cis-9* mixture, two diastereoisomeric acyl complexes are also obtained in a 1.5 : 1 mixture. We assign these product complexes the *trans-10* and *cis-10* acylmetallocene structures. The major product is characterized by ¹H/¹³C NMR features at δ 2.85/77.3 (CH) and 1.64/24.3 (CH₃) of the (η^2 -acetaldehyde)ZrCp₂ moiety that is coordinated to the four-membered metalacyclic (η^1 -acyl)ZrCp₂ unit (see Fig. 1) [δ 4.28/101.4 (CH), 1.01/18.7 (CH₃), ¹³C NMR acyl carbon signal at δ 316.4; IR (KBr): $\tilde{\nu}$ (CO) = 1652 cm⁻¹]. The *trans-10* complex is chiral and thus exhibits the signals of two pairs of diastereotopic Cp ligands (¹H NMR signals at δ 5.75, 5.68, 5.60, 5.57). This is also observed for the minor component of the monocarbonylation product mixture (¹H NMR Cp signals at δ 5.76, 5.65, 5.60, 5.55). Carbonylation of the 1 : 1.7 mixture of *trans-9* and *cis-9* gave the same products, now formed in a 1 : 1.7 ratio.

We then treated the (η^2 -acetaldehyde)zirconocene dimer **9** with isonitriles. Both (trimethylsilyl)methyl isocyanide and tert-butyl isocyanide were used. First we employed the kinetic 1.5 : 1 mixture of the (η^2 -acetaldehyde)zirconocene dimers and reacted it with the (trimethylsilyl)methyl isocyanide reagent under preparative conditions in a 1 : 2 molar ratio. After 24 h at room temperature in toluene solution the reaction is complete and the double insertion product (**12a**) is recovered in 44% yield as a pale-yellow crystalline material. This isolated product contains the two diastereoisomers *trans-12a* and *cis-12a* in a 2.4 : 1 ratio. This is evident

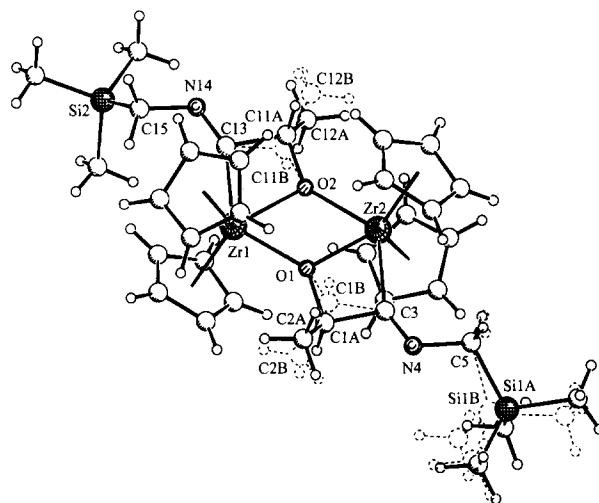
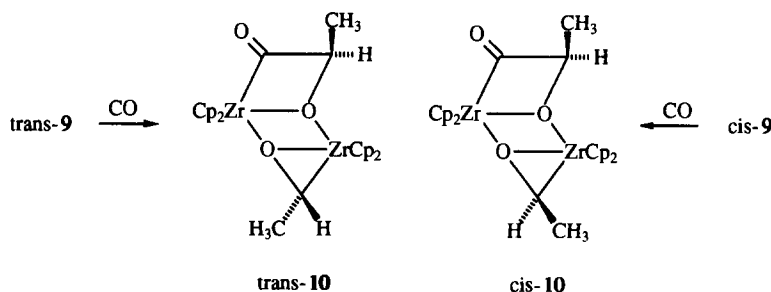


Fig. 2. A projection of **12a** in the crystal. The disordered structural moieties are indicated.

from the ¹H/¹³C NMR spectra that exhibit two sets of typical signals of the two isomeric compounds in this ratio. The major component (that was identified as *trans-12a*, see below) shows Cp singlets at δ 5.81 and 5.80/109.0 and 108.6, respectively. The “acetaldehyde” moiety gives rise to signals at δ 4.82 (broad quartet)/95.1 (¹J_{CH} = 134 Hz, CH) and 1.37 (d, ³J = 6.5 Hz)/21.7 (¹J_{CH} = 124 Hz, CH₃). The SiMe₃ resonance is at δ 0.36/−1.6 (¹J_{CH} = 117 Hz). Owing to the neighbouring chiral carbon centre, the methylene group of the −CH₂SiMe₃ substituent at the iminoacyl moiety gives rise to diastereotypic ¹H NMR resonances (δ 3.20 and 3.02, ²J = 13.2 Hz, with a further set of ⁵J coupling constants of 2.0 and 1.2 Hz, respectively). The corresponding ¹³C NMR signal is observed at δ 49.6 (¹J_{CH} = 122 Hz) and the iminoacyl carbon resonance is at δ 221.7 (IR at $\tilde{\nu}$ = 1599 cm⁻¹). The minor isomer (*cis-12a*) shows an equivalent set of ¹H/¹³C NMR signals at δ 5.80, 5.79/109.0, 108.9 (Cp), 3.16, 3.07 (²J = 13.1 Hz, ⁵J = 1.8 and 1.2 Hz)/49.3 (CH₂Si), 0.37/−1.5 (SiMe₃).

The bis-isonitrile insertion product **12a** was characterized by X-ray diffraction (see Fig. 2, and Tables 1 and 2). The X-ray crystal structure analysis was carried out by using a single crystal of the 2.4 : 1 mixture of



diastereoisomers that was obtained as described above. ^1H NMR spectra of representative samples of that material had already indicated that each of the single crystals

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of **12a**

Atom	x	y	z	U_{eq}^a
Zr(1)	2115(1)	1748(1)	3937(1)	30(1)
Zr(2)	2124(1)	-1114(1)	2110(1)	28(1)
Si(1A) ^b	3156(6)	-2440(8)	-1861(6)	50(2)
Si(1B) ^c	3361(16)	-2102(25)	-1596(22)	83(6)
Si(2)	2878(1)	3402(2)	8382(1)	45(1)
O(1)	2206(3)	583(3)	2347(3)	33(1)
O(2)	2063(3)	57(3)	3714(3)	30(1)
C(1A) ^d	2604(7)	585(6)	1463(6)	35(3)
C(2A) ^d	1940(14)	1169(8)	915(8)	70(6)
C(1B) ^e	1886(13)	413(10)	1220(9)	31(5)
C(2B) ^e	2531(35)	1317(12)	1113(17)	83(12)
C(3)	2305(6)	-689(5)	704(5)	48(2)
N(4)	2281(5)	-993(4)	-278(4)	53(2)
C(5)	2163(5)	-2159(5)	-1014(5)	45(2)
C(6A) ^b	4588(12)	-2339(24)	-1028(15)	112(8)
C(7A) ^b	3231(18)	-1485(14)	-2454(16)	84(8)
C(8A) ^b	2600(20)	-3879(10)	-2971(12)	92(7)
C(6B) ^c	4746(20)	-1370(54)	-538(36)	134(18)
C(7B) ^c	3041(32)	-1396(25)	-2448(23)	55(12)
C(8B) ^c	3437(51)	-3548(31)	-2463(42)	136(19)
C(11A) ^f	1748(11)	72(7)	4634(7)	38(4)
C(12A) ^f	2442(12)	-486(8)	5205(8)	56(4)
C(11B) ^g	2258(14)	180(8)	4811(8)	36(5)
C(12B) ^g	1482(15)	-694(9)	4866(11)	50(5)
C(13)	1980(5)	1340(5)	5356(5)	39(2)
N(14)	1847(5)	1653(4)	6303(4)	47(1)
C(15)	1842(5)	2799(5)	6963(4)	38(2)
C(16)	4313(5)	3885(6)	8388(5)	67(2)
C(17)	2942(6)	2360(7)	8885(6)	85(3)
C(18)	2410(6)	4603(6)	9280(5)	73(2)
C(20)	3789(8)	2863(8)	3875(6)	79(3)
C(21)	3426(6)	3629(6)	4689(7)	68(2)
C(22)	3609(6)	3356(6)	5522(6)	57(2)
C(23)	4099(6)	2450(7)	5234(8)	68(2)
C(24)	4203(6)	2156(7)	4214(9)	82(3)
C(25)	835(6)	3096(6)	4306(6)	64(2)
C(26)	819(6)	2749(7)	3224(7)	66(2)
C(27)	259(6)	1633(7)	2625(6)	58(2)
C(28)	-36(5)	1294(6)	3347(5)	48(2)
C(29)	303(5)	2197(6)	4376(6)	52(2)
C(30)	788(5)	-2944(5)	813(6)	56(2)
C(31)	651(5)	-2652(5)	1852(6)	50(2)
C(32)	170(5)	-1727(5)	2121(5)	46(2)
C(33)	9(5)	-1460(5)	1263(5)	48(2)
C(34)	398(5)	-2215(6)	457(5)	54(2)
C(35)	3311(6)	-2533(6)	2053(7)	63(2)
C(36)	3738(6)	-1958(7)	1587(6)	60(2)
C(37)	4243(5)	-870(7)	2428(7)	62(2)
C(38)	4064(6)	-835(7)	3365(6)	64(2)
C(39)	3481(6)	-1862(7)	3117(7)	64(2)
C(40)	1557(8)	-5370(7)	2031(7)	72(2)
C(41)	640(11)	-5098(8)	2369(10)	104(3)
C(42)	651(13)	-4427(9)	3370(11)	116(4)
C(43)	1707(14)	-3962(8)	4130(9)	111(4)
C(44)	2711(11)	-4150(8)	3904(9)	95(3)
C(45)	2590(10)	-4915(8)	2759(10)	95(3)
C(46)	3534(9)	-5158(10)	2503(12)	158(6)

contained the 2.4:1 mixture of the *trans*-**12a** and *cis*-**12a** diastereoisomers, the ratio of which apparently was not determined by either kinetic control of the reaction or thermodynamic equilibration of the product, but was due solely to the crystal properties. This led to a peculiar disorder of the molecular crystal structure, as *trans*-**12a** and *cis*-**12a** molecules seem to occupy almost the same positions in the crystal, and the diastereomeric molecules are anchored at the Si2 end of the system. Thus the surrounding of Si2 shows no detectable disorder whereas the distant Si1 atom exhibits a 68:32 positional disorder which is also found at the carbon centres C1 and C2 (both ca. 71:29 disordered). The resulting situation at C11, C12 is more complicated owing to overlapping effects of positional disorder in the crystal and the presence of a minor (*cis*) isomer, and a ca. 59:41 disorder was calculated.

The major isomer probably has the ‘acetaldehyde’-derived methyl groups *trans* arranged at the dimetalla-tricyclic framework. The basic skeleton containing three fused four-membered heterocyclic ring systems is very similar in structure to analogous products derived by twofold isonitrile insertion into the zirconium to carbon bonds of the (η^2 -formaldehyde)zirconocene dimer [4]. In **12a** the iminoacyl groups are also η^1 -coordinated with the Zr centre and the substituent at the iminoacyl nitrogen being Z-oriented.

The reaction of the 1.5:1 mixture of the diastereomeric (η^2 -acetaldehyde)zirconocene dimers with tert-butyl isonitrile in a 1:2 ratio under preparative conditions gives a similar result. Crystallization of the product at -30°C from toluene in this case yields a single bisinsertion product (60% isolated) to which we ascribe the *trans*-**12b** structure ($^1\text{H}/^{13}\text{C}$ NMR in benzene- d_6 : δ 5.83, 5.82/109.5, 109.2 (Cp), 4.78/97.4 (CHMe), 1.43/31.6, 21.5 (CMe₃), 1.38/21.5 (CHCH₃), C=N ^{13}C NMR resonance at δ 215.5; IR (KBr): $\bar{\nu}$ = 1594 cm^{-1}). Again, the apparent diastereoselectivity was not due to any characteristics of the mode of product formation but only to physical separation during the crystallization process.

This became evident when we carried out the CNCH₂SiMe₃ and CNCMe₃ insertion reactions of (η^2 -acetaldehyde)zirconocene dimer under direct ^1H NMR control. In the monoinsertion regime the situation is clear: like monocarbonylation, the insertion of the

Notes to table 1:

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b S.o.f. = 0.68(3).

^c S.o.f. = 0.32(3).

^d S.o.f. = 0.71(1).

^e S.o.f. = 0.29(1).

^f S.o.f. = 0.59(1).

^g S.o.f. = 0.41(1).

first isonitrile molecule into the (η^2 -acetaldehyde)-zirconocene dimer takes place with complete conservation of the stereochemical information. This we deduced from the following series of experiments. We first allowed the 1.5:1 mixture of *trans*-9 and *cis*-9 to react with a ca. threefold excess of $\text{CNCH}_2\text{SiMe}_3$ at ambient temperature in benzene- d_6 solution in a sealed NMR tube under direct ^1H NMR observation. After 30 min a clear yellow solution is obtained that contains the two mono-insertion products *trans*-11a (typical ^1H NMR signals at δ 5.91, 5.82, 5.63, 5.59 (Cp), 4.59 (C(N)CHMe), 2.81 (η^2 -acetaldehyde CHMe); for others, see the Experimental Section) and *cis*-11a (^1H NMR Cp singlets at δ 5.90, 5.81, 5.62 and 5.59), again in a 1.5:1 ratio. With time more and more of the bisisonitrile insertion products *trans*-12a and *cis*-12a appear. Under these reaction conditions it takes about 16 h until most of the mono-insertion products have inserted a second isonitrile molecule. The final *trans*-12a : *cis*-12a ratio is 1.3:1, which is close to the initial diastereomeric ratio but not identical. The complementary experiment was carried out by reacting the 1:1.7 mixture of *trans*-9 and *cis*-9 with $\text{CNCH}_2\text{SiMe}_3$ under similar conditions. The *trans*-11a/*cis*-11a mixture of monoinsertion products is now formed within 30 min in a 1:1.7 ratio, as expected. After 16 h the eventually observed mixture of the final bis- $\text{CNCH}_2\text{SiMe}_3$ insertion products is *trans*-12a : *cis*-12a = 1 : 1.5 (see Fig. 3).

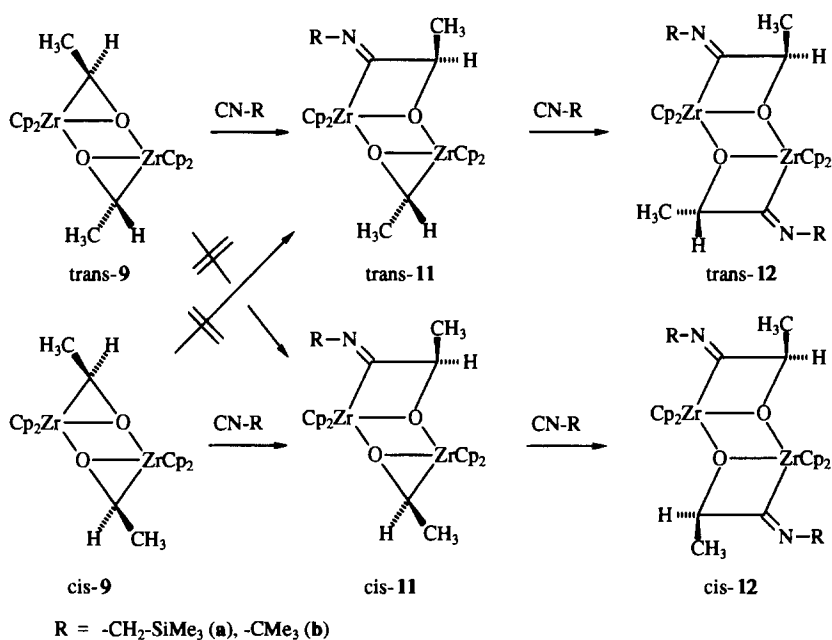
The reaction of the (η^2 -acetaldehyde)zirconocene dimers *trans*-9 and *cis*-9 (1.5:1) with tert-butyl isonitrile proceeds much faster. Under similar conditions to those described above we observe a mixture of two mono-insertion and two bis-insertion products after 20

min. The mono-insertion products are probably *trans*-11b and *cis*-11b, which are obtained in ca. 1.7:1 ratio. The bis-insertion products then have to be *trans*-12b and *cis*-12b, which are initially observed in a ca. 1.9:1 ratio. After 1.5 h the mono-insertion products can no longer be clearly observed; the major amount of these primary products has reacted further. Now the bis-insertion products *trans*-12b and *cis*-12b are seen in a ratio as high as 2.4:1. After 24 h at ambient temperature the reaction has gone to completion and then a 1.5:1 ratio of the bis-insertion products *trans*-12b and *cis*-12b is eventually obtained.

In a separate experiment we reacted a 1:1 mixture of *trans*-9 and *cis*-9 (which we had available from an incomplete thermal equilibration experiment) with CNCMe_3 under similar conditions. After 20 min, the mono-insertion products *trans*-11b and *cis*-11b are found in a 1:1 ratio and the bis- CNCMe_3 insertion products *trans*-12b and *cis*-12b in a 1.4:1 ratio. After 2 h only the signals of the bis-insertion products are monitored, now in a *trans*-12b : *cis*-12b ratio of ca. 1.3:1 that eventually even changes to 1.2:1 (after 4 h).

3. Conclusions

The (η^2 -acetaldehyde)zirconocene dimers *trans*-9 and *cis*-9 were prepared and their insertion reactions studied to clarify whether CO and isonitrile insertion reactions are taking place at the dinuclear dimetallic moiety or if monomeric metallaoxiranes might be involved as intermediates. For mono-insertion there is a clear answer. Starting from mixtures containing differ-



Scheme 1.

ent *trans*-**9**:*cis*-**9** ratios this diastereomeric information is strictly retained when one equivalent of carbon monoxide, (trimethylsilyl)methyl isonitrile or tert-butyl isonitrile is inserted. These reactions clearly proceed at the dinuclear systems, analogously to the reactions observed in Askham's study [6]. In these reactions there is no indication for preceding dissociation to generate (η^2 -aldehyde)ZrCp₂ monomers.

The situation is less clear in the cases of the subsequent bisisonitrile insertion reactions since in all examples examined complicated changes in product ratios became evident, although most of these are most likely

still occurring within the regime of dominating kinetic control. Among these the CNCH₂SiMe₃ insertions are rather slow. Therefore, we suspect that the slight deviations from the expected *trans*-**12a**:*cis*-**12a** product ratios (i.e. 1.3:1 instead of 1.5:1 in the first experiment and 1:1.5 instead of 1:1.7 in the second) might be due to a slow subsequent thermally induced (intermolecular) product equilibration. However, it is likely that in this case also the second CNCH₂SiMe₃ insertion is initially taking place with complete retainment of the diastereomer ratio, but this second insertion is so slow that the system is close to go to thermodynamic control which

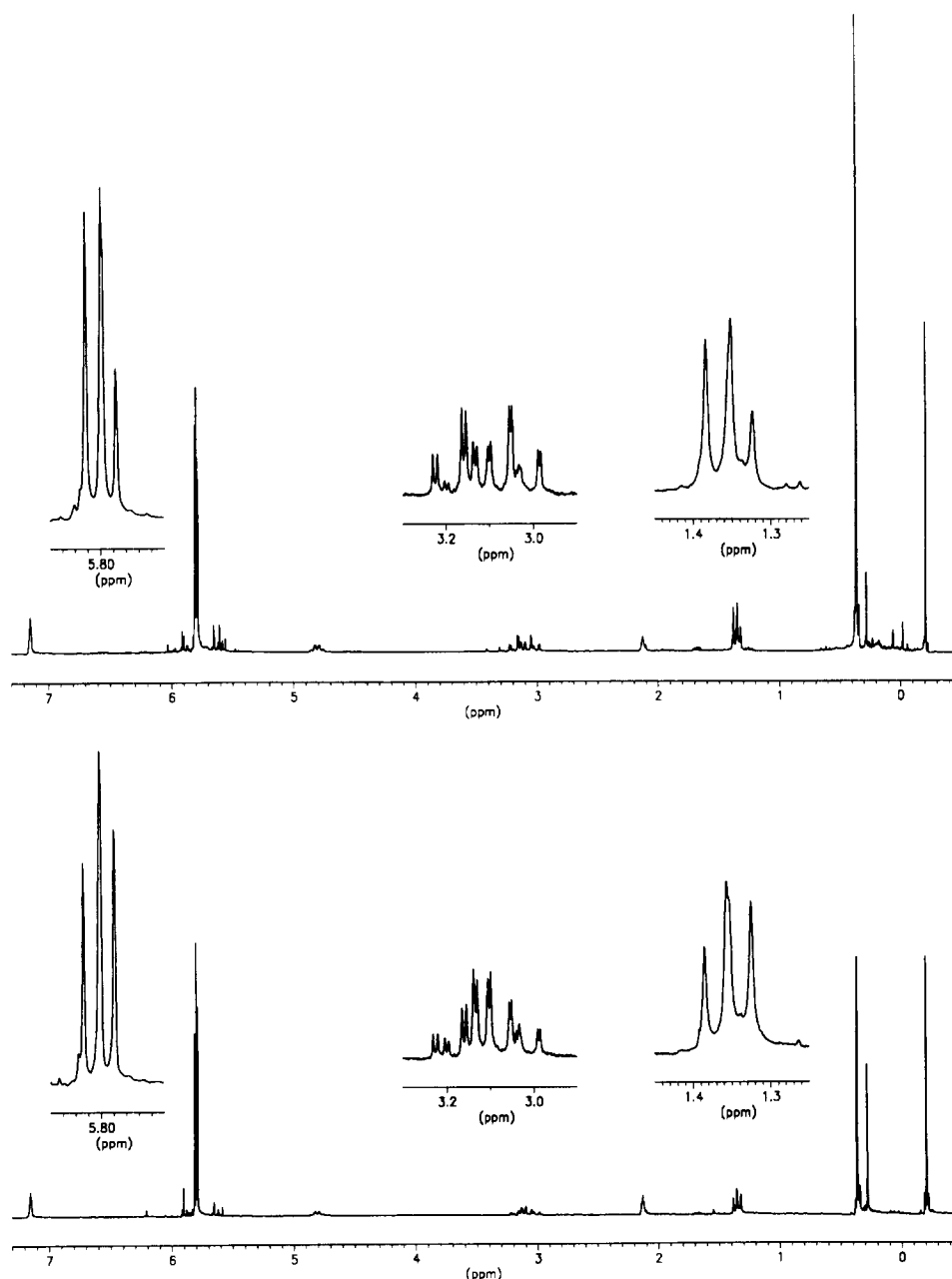


Fig. 3. ¹H NMR spectra of the mixture of diastereomeric bis-insertion products *trans*-**12a** and *cis*-**12a** obtained upon reacting the 1.5:1 (top) and 1:1.7 (bottom) mixtures of *trans*-**9** and *cis*-**9** with CNCH₂SiMe₃ (in benzene-*d*₆).

leads to some small deviation from the expected product ratios. In the formation of the bis-CNCMe₃ insertion products, the deviations from the expected values are more pronounced and much more difficult to rationalize. From the experimental observation it is again clear that the system is not yet under thermodynamic control. It appears that in this very reactive system the situation is complicated by the fact that the diastereomers both of the starting materials (*trans*-**9**/*cis*-**9**) and of the monoinsertion products (*trans*-**11b**/*cis*-**11b**) have different reactivities towards CNCMe₃ and that, therefore, some diastereomeric discrimination takes place during the reaction. This leads to unpredictable ratios at intermediate stages of the reaction but eventually produces bis-insertion product mixtures (*trans*-**12b**/*cis*-**12b**) that come close to those of the respective mixtures of *trans*-**9**/*cis*-**9** starting materials employed in these experiments, as expected for non-dissociative pathways. Hence it appears that in the examples examined the insertion reactions involve only intramolecular mechanisms, leaving the (η^2 -acetaldehyde)zirconocene subunits of the respective diastereomers and their insertion products connected throughout the reaction. Pathways resulting in diastereomeric crossover seem to be disfavoured.

This raises the question as to what types of binuclear intermediates might be involved in these reactions. It is likely that at least one of the four Zr–O bonds present has to be opened to allow CO or CNR addition and insertion. There are two possibilities to do that: one would either have to cleave a lateral (a) or a central (b) (see Scheme 2) zirconium to oxygen linkage of the central Zr₂O₂ core to open up a viable insertion pathway. Askham et al. [6] favoured and proposed the former, but it maybe that central Zr–O bond opening

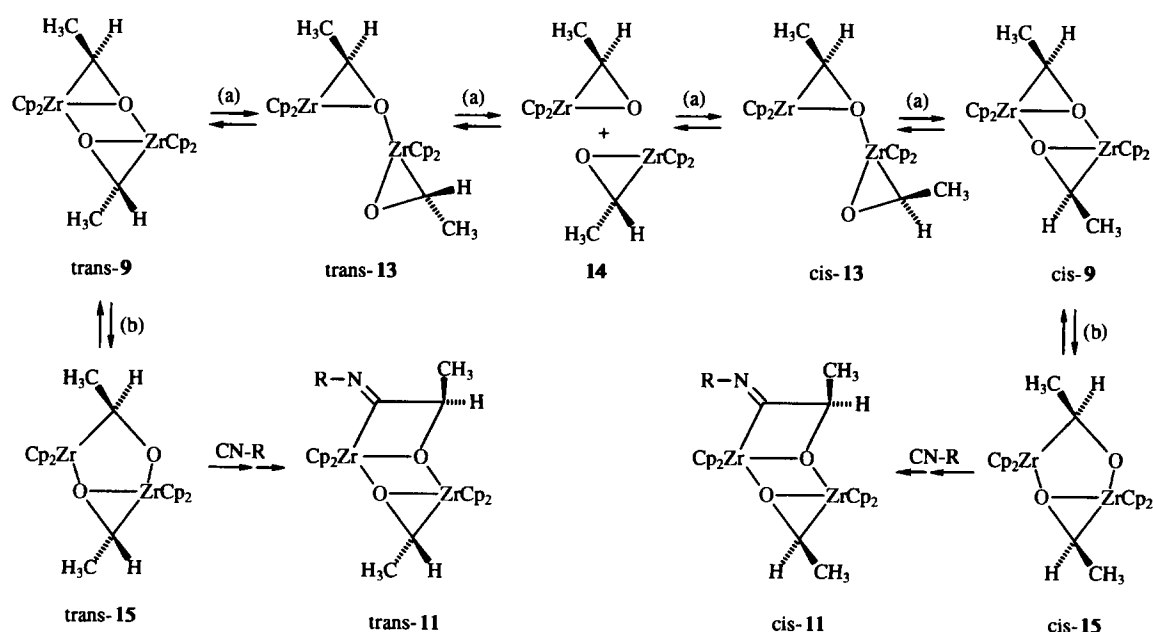
(b), here leading to **15**, is more likely. There are many examples known in related larger Zr₂O₂-derived dimetallacycles where central Zr–O rupture can be directly observed experimentally [5]. Also, lateral Zr–O bond cleavage would inevitably create a situation prone to entering the intermolecular pathways. Subsequent cleavage of a second Zr–O bond after lateral ring opening leads to monomers (and probably represents the pathway actually being followed under thermodynamic control, i.e. in the thermal equilibration of the starting material diastereomers *trans*-**9**/*cis*-**9**, as is observed at higher temperatures; see above), whereas central ring opening automatically activates a repair mechanism as any subsequent central Zr–O bond rupture would leave the dimetallic system intact.

4. Experimental section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. Solvents were dried with the usual reagents and distilled under argon prior to use. Experiments under direct ¹H NMR control were performed in sealed 5 mm NMR tubes using an FT NMR spectrometer (Bruker AC 200 P) at 200 MHz. The complexes **5** and **6** were prepared analogously to published procedures [9].

4.1. Preparation of η -(*O*- η^1 :*C*,*O*- η^2 -acetaldehyde)- μ -chloro-[bis(η^5 -cyclopentadienyl)methylzirconium][bis(η^5 -cyclopentadienyl)zirconium] (**7**)

To a solution of 14.8 g (29.5 mmol) of **6** in 600 ml of toluene was added 3.8 ml (33.0 mmol) of benzyl



Scheme 2.

Table 2
Selected bond lengths (Å) and angles (°) of **12a** in the crystal

Zr(1)–O(1)	2.178(3)
Zr(1)–O(2)	2.181(3)
Zr(1)–C(13)	2.343(6)
Zr(2)–O(1)	2.180(3)
Zr(2)–O(2)	2.181(3)
Zr(2)–C(3)	2.355(6)
O(1)–C(1A)	1.459(7)
O(1)–C(1B)	1.462(11)
O(2)–C(11A)	1.446(8)
O(2)–C(11B)	1.450(10)
C(1A)–C(2A)	1.502(13)
C(1A)–C(3)	1.555(9)
C(1B)–C(2B)	1.50(2)
C(1B)–C(3)	1.566(12)
C(3)–N(4)	1.266(7)
N(4)–C(5)	1.455(7)
C(5)–Si(1A)	1.885(7)
C(5)–Si(1B)	1.890(10)
C(11A)–C(12A)	1.511(12)
C(11A)–C(13)	1.545(10)
C(11B)–C(12B)	1.512(12)
C(11B)–C(13)	1.550(11)
C(13)–N(14)	1.284(7)
N(14)–C(15)	1.441(7)
C(15)–Si(2)	1.890(6)
O(1)–Zr(1)–O(2)	66.0(1)
O(1)–Zr(1)–C(13)	126.3(2)
O(2)–Zr(1)–C(13)	60.4(2)
O(1)–Zr(2)–O(2)	65.9(1)
O(1)–Zr(2)–C(3)	60.3(2)
O(2)–Zr(2)–C(3)	126.2(2)
Zr(1)–O(1)–Zr(2)	114.1(2)
Zr(1)–O(2)–Zr(2)	114.0(2)
C(1A)–O(1)–Zr(1)	139.6(4)
C(1B)–O(1)–Zr(1)	139.2(5)
C(1A)–O(1)–Zr(2)	103.7(3)
C(1B)–O(1)–Zr(2)	101.5(5)
C(11A)–O(2)–Zr(1)	103.8(4)
C(11B)–O(2)–Zr(1)	103.5(4)
C(11A)–O(2)–Zr(2)	140.3(4)
C(11B)–O(2)–Zr(2)	140.5(4)
O(1)–C(1A)–C(2A)	111.3(7)
O(1)–C(1A)–C(3)	98.4(5)
C(2A)–C(1A)–C(3)	110.6(7)
O(1)–C(1B)–C(2B)	111.7(10)
O(1)–C(1B)–C(3)	97.8(7)
C(2B)–C(1B)–C(3)	110.4(10)
N(4)–C(3)–C(1A)	116.1(6)
N(4)–C(3)–C(1B)	113.7(6)
N(4)–C(3)–Zr(2)	150.6(5)
C(1A)–C(3)–Zr(2)	93.3(4)
C(1B)–C(3)–Zr(2)	91.3(5)
C(3)–N(4)–C(5)	120.3(5)
N(4)–C(5)–Si(1A)	114.5(5)
N(4)–C(5)–Si(1B)	101.5(10)
O(2)–C(11A)–C(12A)	114.0(8)
O(2)–C(11A)–C(13)	99.2(6)
C(12A)–C(11A)–C(13)	111.9(8)
O(2)–C(11B)–C(12B)	113.2(10)
O(2)–C(11B)–C(13)	98.8(6)
C(12B)–C(11B)–C(13)	111.6(9)
N(14)–C(13)–C(11A)	115.6(5)
N(14)–C(13)–C(11B)	117.2(6)
N(14)–C(13)–Zr(1)	149.1(4)

chloride (dried over Sicapent) at -10°C and the mixture was stirred for 6 days at room temperature. After filtration from a small amount of precipitate, the resulting yellow solution was concentrated in vacuo. The yellow viscous product was washed twice with 15 ml of pentane and dried in vacuo to yield 14.9 g (94%) of **7**, m.p. $125\text{--}128^{\circ}\text{C}$. ^1H NMR (benzene- d_6): δ 5.95, 5.88, 5.68, 5.67 (4s, each 5 H, Cp-H), 3.13 (q, $^3J = 6.3$ Hz, 1 H, OCH), 1.51 (d, $^3J = 6.3$ Hz, 3 H, CHCH_3), 0.44 (s, 3 H, ZrCH_3). ^{13}C NMR (benzene- d_6): $\delta = 112.8, 112.5, 109.0, 108.6$ (Cp), 85.0 ($^1J_{\text{CH}} = 149$ Hz, OCH), 34.6 ($^1J_{\text{CH}} = 120$ Hz, CH_3), 25.2 ($^1J_{\text{CH}} = 123$ Hz, CH_3). IR (KBr): $\bar{\nu}$ 3091, 2929, 2878, 1441, 1133, 1016, 847, 813, 805, 799, 792, 740, 735, 510, 506 cm^{-1} . Anal. Found: C, 49.82; H, 4.82. $\text{C}_{23}\text{H}_{27}\text{ClOZr}_2$ (537.4) Calc. C, 51.41; H, 5.06%.

4.2. Preparation of bis[μ -(O - η^1 : C,O - η^2 -acetaldehyde)bis(η^5 -cyclopentadienyl)zirconium] (**9**)

A solution of 11.9 g (22.1 mmol) of **7** in 500 ml of tetrahydrofuran was treated with 13.8 ml of a 1.6 M solution of methyllithium in diethyl ether (22.1 mmol) at -30°C . The reaction mixture was allowed to warm up to room temperature during 16 h. The solution was evaporated to dryness in vacuo and the residue was extracted with pentane (5×50 ml) and then with toluene (4×150 ml) at 80°C . From the combined pentane fractions was isolated 5.50 g (quantitative) of dimethylzirconocene after removal of the solvent. The combined toluene extracts were concentrated to 200 ml and the product was crystallized at -30°C . After concentration of the mother liquor and subsequent crystallizations at -30°C , *trans*-**9**/*cis*-**9** was isolated as a pale-yellow powder in a total yield of 3.1 g (52%). According to the ^1H NMR spectrum the product consists of a mixture of the *trans*-**9**/*cis*-**9** isomers in a ratio of 1.5:1, m.p. 252°C (decomp.). *trans*-**9**: ^1H NMR (benzene- d_6): δ 5.77, 5.68 (2s, each 10 H, Cp-H), 2.70 (q, $^3J = 6.2$ Hz, 2 H, OCH), 1.66 (d, $^3J = 6.2$ Hz, 6H, CH_3); ^{13}C NMR (benzene- d_6): δ 108.2, 108.0 (Cp), 73.2 (OCH), 23.9 (CH_3). *cis*-**9**: δ 5.76, 5.68 (2s, each 10 H, Cp-H), 2.61 (q, $^3J = 6.2$ Hz, 2 H, OCH), 1.66 (d, $^3J = 6.2$ Hz, 6H, CH_3). ^{13}C NMR (benzene- d_6): δ 108.4, 108.1 (Cp), 73.3 (OCH), 24.2 (CH_3). IR (KBr): $\bar{\nu} = 3089, 2951, 2915, 2833, 1440, 1335, 1328, 1262, 1131, 1093, 1069, 1043, 1019, 876, 810, 792, 754, 740\text{ cm}^{-1}$. Anal. Found: C, 52.94; H, 5.17. $\text{C}_{24}\text{H}_{28}\text{O}_2\text{Zr}_2$ (530.9) Calc.: C, 54.29; H, 5.32%.

Table 2 (continued)

C(11A)–C(13)–Zr(1)	93.8(4)
C(11B)–C(13)–Zr(1)	93.5(4)
C(13)–N(14)–C(15)	120.2(5)
N(14)–C(15)–Si(2)	112.5(4)

4.3. Thermal isomerization of the *trans-9* / *cis-9* mixture

(a) A solution of 10 mg (0.02 mmol) of the acetaldehyde zirconocene complexes *trans-9*/*cis-9* (1.5 : 1) in 0.5 ml of THF-*d*₈ was kept at 100°C for 22 h in a sealed NMR tube. The ¹H NMR spectrum clearly showed the change of the isomeric mixture from 1.5 : 1 to 1 : 1.7.

(b) Preparative isomerization: a suspension of 500 mg of the acetaldehyde zirconocene complexes *trans-9*/*cis-9* (isomeric mixture in a ratio of 1.5 : 1) in 40 ml of toluene in a sealed ampoule was heated for 24 h at 120°C in an autoclave. After crystallization 420 mg of *trans-9*/*cis-9* as a isomeric mixture in a ratio of 1 : 1.7 was isolated.

4.4. Reaction of bis[μ-(*O-η*¹:*C,O-η*²-acetaldehyde)-bis(η⁵-cyclopentadienyl)zirconium] (**9**) with carbon monoxide

(a) A suspension of 10 mg (0.02 mmol) of the acetaldehyde zirconocene complexes *trans-9*/*cis-9* (1.5 : 1) in 0.5 ml of benzene-*d*₆ was stirred for 1 h in a carbon monoxide atmosphere. During this time the solution turned intensely yellow. The reaction mixture was transferred to an NMR tube. The ¹H NMR spectrum showed the presence of the acyl complexes *trans-10*/*cis-10* in a 1.5 : 1 ratio.

Analogously, 10 mg (0.02 mmol) of the acetaldehyde zirconocene complex mixture *trans-9*/*cis-9* in a 1 : 1.7 ratio in 0.5 ml of benzene-*d*₆ was stirred for 1 h under carbon monoxide. The bright yellow solution was transferred to an NMR tube and the ¹H NMR spectrum revealed the formation of *trans-10*/*cis-10* in a 1 : 1.7 ratio.

(b) A suspension of 197 mg (0.37 mmol) of the acetaldehyde zirconocene complexes *trans-9*/*cis-9* (1.5 : 1) in 20 ml of toluene was stirred for 1 h in an atmosphere of carbon monoxide. During the reaction the solution became bright yellow. Pentane (100 ml) was added and the solution was cooled for 3 h at –78°C. The solution was decanted from a precipitate and dried in vacuo. Washing with 5 ml of pentane followed by drying in vacuo gave the *trans-10*/*cis-10* isomers (yield 160 mg (77%)) in a ratio of 1.5 : 1, m.p. 148°C (DSC). *trans-10*: ¹H NMR (benzene-*d*₆): δ 5.75, 5.68, 5.60, 5.57 (4s, each 5 H, Cp-H), 4.28 (q, ³*J* = 6.8 Hz, 1 H, C(O)CH), 2.85 (q, ³*J* = 6.2 Hz, 1 H, OCH), 1.64 (d, ³*J* = 6.2 Hz, 3 H, OC(H)CH₃), 1.01 (d, ³*J* = 6.8 Hz, 3 H, C(O)C(H)CH₃); *cis-10*: δ = 5.76, 5.65, 5.60, 5.55 (4s, each 5 H, Cp-H), 4.11 (q, ³*J* = 6.9 Hz, 1 H, C(O)CH), 2.86 (q, ³*J* = 6.2 Hz, 1 H, OCH), 1.62 (d, ³*J* = 6.2 Hz, 3 H, OC(H)CH₃), 1.02 (d, ³*J* = 6.9 Hz, 3 H, C(O)C(H)CH₃). ¹³C NMR (benzene-*d*₆): δ 316.4 (C=O), 109.4, 109.2, 107.9, 107.8, 107.7 (each Cp, *trans* + *cis*), 101.4 (C(O)CH, *trans*), 108.8 (C(O)CH,

cis), 77.3 (OCH, *trans*), 76.8 (OCH, *cis*), 24.3 (OC(H)CH₃, *trans*), 24.2 (OC(H)CH₃, *cis*), 18.7 (C(O)C(H)CH₃, *trans*), 18.4 (C(O)C(H)CH₃, *cis*). IR (KBr): $\tilde{\nu}$ 3091, 2961, 2917, 2856, 2826, 1652 (vs, CO), 1440, 1355, 1262, 1079, 1037 (sh), 1015, 924, 873, 808, 796, 640, 511 cm⁻¹. Anal. Found: C, 51.13; H, 5.01. C₂₅H₂₈O₃Zr₂ (558.9) Calc.: C, 53.72, H, 5.05%.

4.5. Reaction of bis[μ-(*O-η*¹:*C,O-η*²-acetaldehyde)-bis(η⁵-cyclopentadienyl)zirconium] (**9**) with (trimethylsilyl)methyl isonitrile

(a) To 12 mg (0.023 mmol) of an isomeric mixture of 1.5 : 1 of the aldehyde complexes *trans-9*/*cis-9* in 0.5 ml of benzene-*d*₆ was added 9 μl (0.06 mmol) of (trimethylsilyl)methyl isonitrile. During the reaction in a sealed NMR tube the solution became bright yellow. After 1 h at room temperature the mono-insertion products **11a** were detected in the NMR spectrum in a 1.5 : 1 ratio. *trans-11a*: ¹H NMR (benzene-*d*₆): δ 5.91, 5.82, 5.63, 5.59 (4s, each 5 H, Cp-H), 4.59 (q, ³*J* = 6.5 Hz, 1 H, C(N)CH), 3.05 (m, 2 H, CH₂), 2.81 (q, ³*J* = 6.2 Hz, 1 H, OCH), 1.70 (d, ³*J* = 6.2 Hz, 3 H, OC(H)CH₃), 1.26 (d, ³*J* = 6.5 Hz, 3 H, C(N)C(H)CH₃), 0.36 (s, 9 H, SiMe₃). *cis-11a*: ¹H NMR (benzene-*d*₆): δ 5.90, 5.81, 5.62, 5.59 (4s, each 5 H, Cp-H), 4.49 (q, ³*J* = 6.5 Hz, 1 H, C(N)CH), 3.05 (m, 2 H, CH₂), 2.87 (q, ³*J* = 6.2 Hz, 1 H, OCH), 1.67 (d, ³*J* = 6.2 Hz, 3 H, OC(H)CH₃), 1.24 (d, ³*J* = 6.5 Hz, 3 H, C(N)C(H)CH₃), 0.36 (s, 9 H, SiMe₃).

After an additional 16 h at room temperature, only the signals belonging to the bis-insertion products *trans-12a*/*cis-12a* (1.3 : 1) were detected in the ¹H NMR spectrum (see below).

(b) To a suspension of 19 mg (0.036 mmol) of the aldehyde complexes *trans-9*/*cis-9* in a 1 : 1.7 ratio in benzene-*d*₆ was added at room temperature 10 μl (0.071 mmol) of (trimethylsilyl)methyl isonitrile and then the NMR tube was sealed. The resulting bright-yellow product solution was investigated by ¹H NMR spectroscopy. The ratio of the mono-insertion products *trans-11a*/*cis-11a* was 1 : 1.7. Further reaction to the bis-insertion product **12a** resulted in an isomeric mixture in a ratio of 1 : 1.5.

(c) Reaction on a preparative scale: to a suspension of 257 mg (0.48 mmol) of *trans-9*/*cis-9* (1.5 : 1) in 30 ml of toluene was added at room temperature 110 mg (0.14 ml, 0.82 mmol) of (trimethylsilyl)methyl isocyanide. The reaction mixture was stirred for 24 h. The solution became bright yellow during the reaction. Compound **12** was crystallized at –30°C. After concentration of the mother liquor and subsequent crystallizations at –30°C, a total 160 mg (44%) of *trans-12a*/*cis-12a* was isolated as pale-yellow crystals in a 2.4 : 1 ratio, m.p. 99°C (DSC). *trans-12a*: ¹H NMR (benzene-*d*₆): δ 5.81, 5.80 (2s, each 10 H, Cp-H), 4.82

(br, q, $^3J = 6.5$ Hz, 2 H, CH), 3.20, 3.02 (each dd, $^2J = 13.2$ Hz, $^5J = 2.0$ Hz; $^5J = 1.2$ Hz, each 1 H, CH₂), 1.37 (d, $^3J = 6.5$ Hz, 6 H, CH₃), 0.36 (s, 18 H, SiMe₃). ¹³C NMR (benzene-*d*₆): δ 221.7 (s, C=N), 109.0, 108.6 (Cp), 95.1 (d, $J = 134$ Hz, CH), 49.6 (t, $J = 122$ Hz, NCH₂Si), 21.7 (q, $J = 124$ Hz, C(H)CH₃), -1.6 (q, $J = 117$ Hz, Si(CH₃)₃). *cis*-**12a**: ¹H NMR (benzene-*d*₆): δ 5.80, 5.79 (2s, each 10 H, Cp-H), 4.82 (br. q, $^3J = 6.5$ Hz, 2 H, CH), 3.16, 3.07 (each dd, $^2J = 13.1$ Hz, $^5J = 1.8$ Hz, $^5J = 1.2$ Hz, each 1 H, CH₂), 1.34 (d, $^3J = 6.4$ Hz, 6 H, CH₃), 0.37 (s, 18 H, SiMe₃). ¹³C NMR (benzene-*d*₆): δ 223.9 (s, C=N), 109.0, 108.9 (Cp), 95.7 (d, CH), 49.3 (t, NCH₂Si), 22.5 (q, C(H)CH₃), -1.5 (q, Si(CH₃)₃). IR (KBr): $\tilde{\nu}$ 2948, 2817, 1599 (CN), 1439, 1349, 1241, 1073, 1020, 990, 938, 867, 800, 736, 699, 643, 605, 519, 471, 426 cm⁻¹. Anal. Found: C, 57.66; H, 6.95; N, 3.08. C₃₄H₅₀N₂O₂Si₂Zr₂ · C₇H₈ (849.5) Calc.: C, 57.97; H, 6.88; N, 3.30%.

4.6. X-ray crystal structure analysis of **12a**

Suitable crystals were obtained by crystallization from toluene. Data were collected from a crystal of 0.40 × 0.25 × 0.20 mm, which was mounted in inert oil (RS 3000, Riedel-de Haën) on a glass fibre and transferred to the cold nitrogen stream of an Enraf–Nonius CAD4 diffractometer. Graphite-monochromated Mo K α radiation was used and the diffractometer was operating in the $\omega - 2\theta$ scan mode. The intensities were corrected for Lorentz and polarization effects and absorption correction was done using empirical ψ -scans. The structure was solved by direct methods using SHELXS-86 [10] and refined by full-matrix least-squares against F^2 using the SHELXL-93 program [11]. The figure was drawn by SCHAKAL-92 [12]. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogens were introduced to their calculated positions and refined isotropically as riding atoms. The disordered groups were refined using geometrical restraints (defining bond lengths in A and B sets approximately equal) and by defining the thermal parameters of corresponding atoms to be equal in magnitude. Site occupancy factors of disordered groups were refined simultaneously with the thermal parameters.

Crystal data: C₃₄H₅₀N₂O₂Si₂Zr₂ · C₇H₈, $M = 849.51$, triclinic space group $P\bar{1}$, $a = 12.531(2)$, $b = 13.618(2)$, $c = 14.193(2)$ Å, $\alpha = 115.07(1)$, $\beta = 103.93(1)$, $\gamma = 94.89(1)^\circ$, $V = 2080.4(5)$ Å³, $Z = 2$, $D_c = 1.356$ g cm⁻³, λ (Mo K α) = 0.71073 Å, $\mu = 0.593$ mm⁻¹, $F(000) = 884$, $T = 223(2)$ K. A total of 7646 reflections were measured ($2.73 < \theta < 25.00^\circ$), of which 7310 were independent. The final R indices were $R = 0.049$ and $wR^2 = 0.102$ for 4077 observed ($I > 2\sigma(I)$) reflections and 531 parameters. The goodness of fit on F^2 was 0.942.

Fractional atomic coordinates and thermal parameters are given in Table 1 and selected bond lengths and angles in Table 2. Details of the X-ray crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen quoting the depository number CSD 401774, the names of the authors and the journal citation.

4.7. Reaction of bis[μ -(*O*- η^1 :*C*,*O*- η^2 -acetaldehyde)-bis(η^5 -cyclopentadienyl)zirconium] (**9**) with tert-butyl isonitrile

(a) To a suspension of 15 mg (0.028 mmol) of the aldehyde zirconocene complex **9** (1.5:1 mixture of isomers) in 0.5 ml of benzene-*d*₆ was added 5.88 mg (0.071 mmol) of tert-butyl isonitrile. The reaction mixture was transferred to an NMR tube and sealed. After 20 min at room temperature, a ¹H NMR spectrum of the yellow solution was measured. A mixture of the mono-insertion products *trans*-**11b**/*cis*-**11b** (1.7:1) and the bis-insertion product *trans*-**12b**/*cis*-**12b** (1.9:1) was detected. *trans*-**11b**: ¹H NMR (benzene-*d*₆): δ 5.93, 5.83, 5.62, 5.57 (4s, each 5 H, Cp), 4.53 (q, $^3J = 6.5$ Hz, 1 H, C(N)CH), 2.73 (q, $^3J = 6.3$ Hz, 1 H, OCH), 1.68 (d, $^3J = 6.3$ Hz, 3 H, OC(H)CH₃), 1.41 (s, 9 H, ¹Bu), 1.27 (d, $^3J = 6.5$ Hz, 3 H, C(N)C(H)CH₃). *cis*-**11b**: ¹H NMR (benzene-*d*₆): δ 5.93, 5.83, 5.63, 5.56 (4s, each 5 H, Cp), 4.43 (q, $^3J = 6.4$ Hz, 1 H, C(N)CH), 2.81 (q, $^3J = 6.2$ Hz, 1 H, OCH), 1.66 (d, $^3J = 6.2$ Hz, 3 H, OC(H)CH₃), 1.40 (s, 9 H, ¹Bu), 1.27 (d, $^3J = 6.5$ Hz, 3 H, C(N)C(H)CH₃). After 1.5 h at room temperature the ¹H NMR spectrum showed only the signals of the bis-insertion products **12** (*trans*:*cis* = 2.4:1). *trans*-**12b**: ¹H NMR (benzene-*d*₆): δ 5.83, 5.82 (2s, each 10 H, Cp-H), 4.77 (q, $^3J = 6.5$ Hz, 2 H, OCH), 1.42 (s, 18 H, ¹Bu), 1.38 (d, $^3J = 6.5$ Hz, 6 H, CH₃). *cis*-**12b**: δ 5.84, 5.79 (2s, each 10 H, Cp-H), 4.76 (q, $^3J = 6.5$ Hz, 2 H, OCH), 1.42 (s, 18 H, ¹Bu), 1.39 (d, $^3J = 6.5$ Hz, 6 H, CH₃). The *trans*-**12b**/*cis*-**12b** ratio changed with time. After 24 h at room temperature the final observed ratio was 1.5:1.

(b) To 13 mg (0.024 mmol) of the aldehyde zirconocene complexes *trans*-**9**/*cis*-**9** (1:1) in benzene-*d*₆ was added at room temperature 7.5 μ l (0.072 mmol) of tert-butyl isonitrile. After 20 min the ¹H NMR spectrum showed a mixture of the mono-insertion products **11b** (*trans*:*cis* = 1:1) and of the bis-insertion products **12** (*trans*:*cis* = 1.4:1). After 2 h at room temperature only the signals of the bis-insertion products *trans*-**12b**/*cis*-**12b** were detected in a ratio of 1.3:1. After 4 h the final ratio of these products was 1.2:1.

(c) Reaction on a preparative scale: to a suspension of 246 mg (0.46 mmol) of the aldehyde zirconocene complexes *trans*-**9**/*cis*-**9** (1.5:1) in 30 ml of toluene was added at -10°C 0.11 ml (0.93 mmol) of tert-butyl isonitrile. The mixture was allowed to warm up to room

temperature. During the reaction the colour of the mixture turned to orange. After stirring for 20 h at room temperature the mixture was cooled to -30°C to crystallize the product. After concentrating the mother liquor and subsequent crystallizations at -30°C , a total of 192 mg (60%) of *trans*-**12b** was isolated as a yellow solid, m.p. 170°C (DSC, decomp.). ^1H NMR (benzene- d_6): δ 5.83, 5.82 (2s, each 10 H, Cp-H), 4.78 (q, $^3J = 6.3$ Hz, 2 H, CH), 1.43 (s, 18 H, ^tBu), 1.38 (d, $^3J = 6.3$ Hz, 6 H, CH_3). ^{13}C NMR (benzene- d_6): δ 215.5 (s, C=N), 109.5, 109.2 (Cp), 97.4 ($^1J_{\text{CH}} = 139$ Hz, CHCH_3), 57.8 (s, NMe_3), 31.6 ($^1J_{\text{CH}} = 125$ Hz, $\text{C}(\text{CH}_3)_3$), 21.5 ($^1J_{\text{CH}} = 127$ Hz, CHCH_3). IR (KBr): $\tilde{\nu}$ 2970, 2922, 1594 (CN), 1446, 1354, 1261, 1206, 1084, 1021, 806, 647, 566 cm^{-1} . Anal. Found: C, 58.43; H, 6.77; N, 3.77. $\text{C}_{34}\text{H}_{46}\text{N}_2\text{O}_2\text{Zr}_2$ (697.2) Calc.: C, 58.57; H, 6.65; N, 4.02%.

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