Journal of Organometallic Chemistry, 394 (1990) 99–112
Elsevier Sequoia S.A., Lausanne
JOM 20776

Zirconoxycarbene complexes obtained by regioselective coupling of (isoprene)zirconocene with hexacarbonyltungsten and a ketone. Crystal structure of $Cp_2\overline{ZrOC[=W(CO)_5]CH_2CHC(CH_3)CH_2}$ *

Gerhard Erker *, Friedrich Sosna, Ronald Pfaff, Ralf Noe, Christian Sarter, Arno Kraft

Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg (F.R.G.)

Carl Krüger and Roland Zwettler

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a.d. Ruhr (F.R.G.)

(Received January 22nd, 1990)

Abstract

(η^4-Isoprene)zirconocene reacts with hexacarbonyltungsten to give the metallacyclic (π-allyl)zirconoxycarbene complex $Cp_2\overline{ZrOC[=W(CO)_5]CH_2CHC(CH_3)CH_2}$ (**14a**), the structure of which has been determined by an X-ray diffraction study. Only one regioisomer is formed, that with the methyl substituent at the *meso*-position (C2) of the π-allyl-carbene ligand chain. Complex **14a** undergoes insertion of one equivalent of acetone to give the nine-membered metallacyclic zirconoxycarbene complex $Cp_2\overline{ZrOC[=W(CO)_5]CH_2CH=C(CH_3)CH_2CR^1R^2O}$ (**18**, $R^1 = R^2 = CH_3$), which has an *E*-configurated endocyclic C=C double bond. The chiral metallacycle **18** undergoes a thermally induced intramolecular enantiomerization, the activation barrier for which has been determined by dynamic ^1H NMR spectroscopy to be $\Delta G^{\ddagger}_{ent}$ (280 K) = 14.3 ± 0.3 kcal/mol. With pinacolone, **14a** forms an analogous nine-membered metallacyclic zirconoxycarbene complex (only one diastereoisomer observed under thermodynamic control), which undergoes a stereo-unselective base-induced α-alkylation reaction to yield a 55/45 mixture of diastereomeric C6-monomethylated carbene complexes.

---

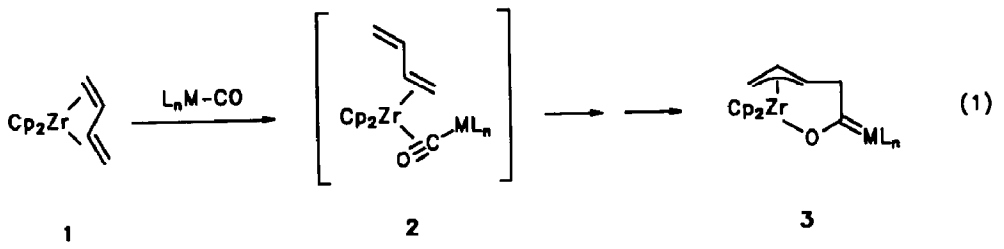
* Dedicated to Professor F. Gordon A. Stone on the occasion of his 65th birthday.

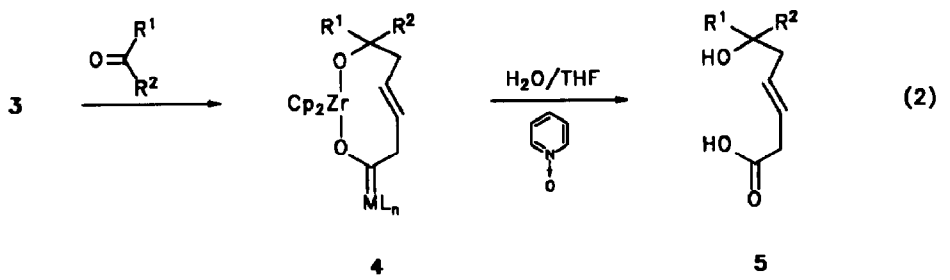
0022-328X/90/$03.50

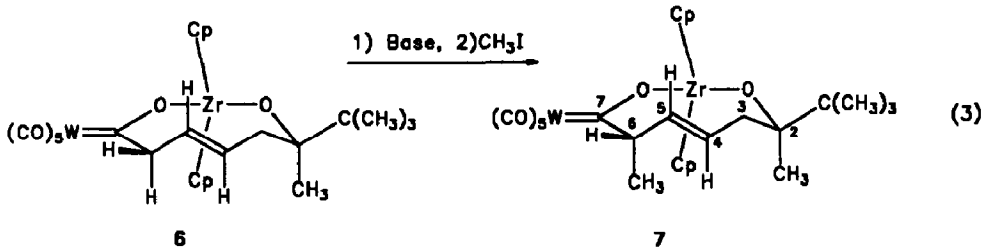
Introduction

We have recently developed a method for coupling butadiene, a metal carbonyl unit and an organic carbonyl compound at the Cp_2Zr-bent metallocene template (or derivatives thereof) to give nine-membered metallacyclic zirconoxycarbene complexes **4** [1]. This C–C-bond forming reaction sequence is initiated by a non-nucleophilic carbene complex synthesis by reaction of (butadiene)zirconocene (**1**) [2] with a wide variety of $L_nMC{\equiv}O$ reagents to yield **3** [3]. Subsequent ketone insertion into the $Zr–CH_2$(allyl) linkage gives the chiral medium-ring sized carbene complexes **4**, exhibiting an endocyclic *trans*-C=C double bond.

For many examples with $R^1 \neq R^2$, complexes **4** are obtained with high diastereomeric excess under thermodynamic control. Thus, only the ($2R^*$)(4,5,6-pS^*) configurated diastereoisomer **6** was found to be formed upon reaction of **3a** ($L_nM = W(CO)_5$) with pinacolone [1]. This carbene complex, like several analogous species, undergoes rather stereoselective base-induced alkylation at the C-center adjacent to the carbene carbon atom. Starting from **6**, the C6-methylated product **7**, exhibiting a ($2R^*$, $6S^*$)(4,5,6-pS^*) relative configuration, was formed in ca. 80% diastereomeric excess and this represents an example of a remarkably effective 1,5-asymmetric induction [4]. Apparently, the stereochemical information originating from the stereogenic center C2 is very efficiently transferred to the reactive position at C6 via the chiral metallacyclic ring system. We assume that steric interaction of the incoming electrophilic reagent with the hydrogen-substituent at C5 (unfavourable 1,2-rather than 1,3-interaction) determines the overall stereochemical outcome of the asymmetric substitution reaction.







6 7

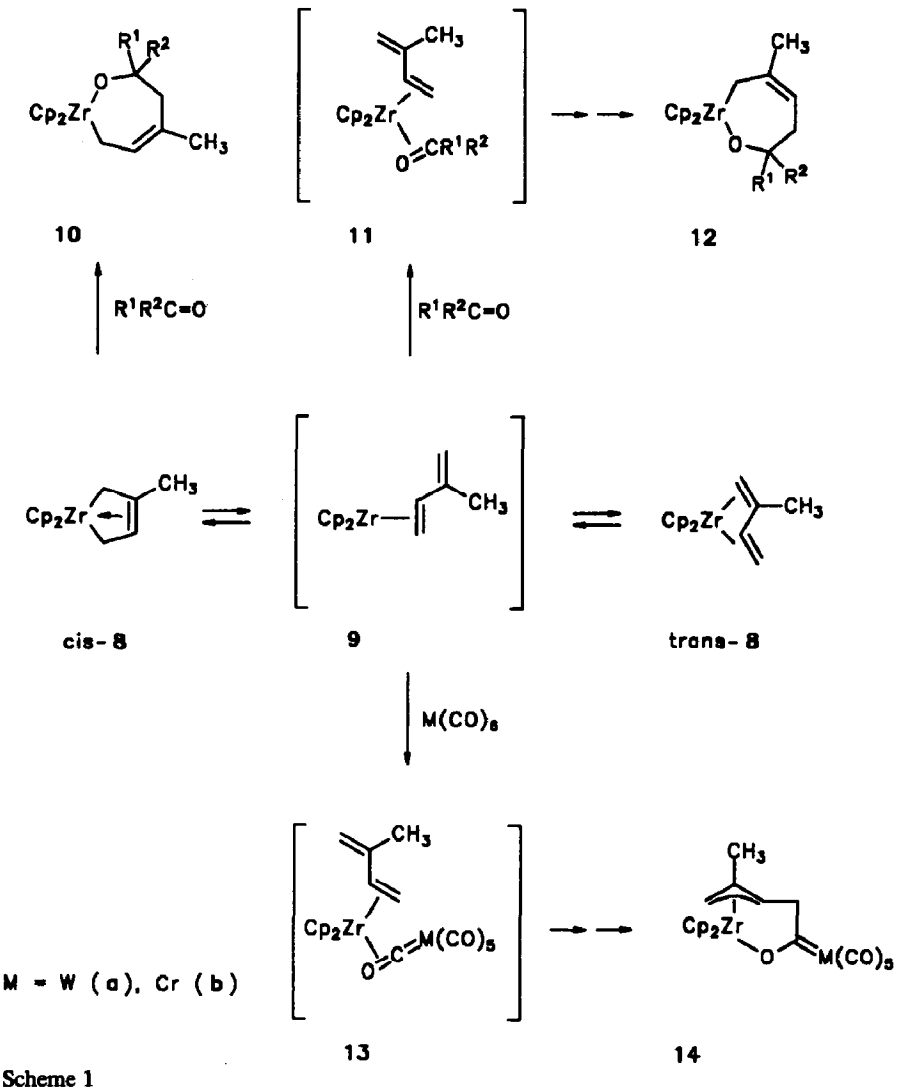
The zirconoxycarbene complexes can readily be converted into various metal-free organic compounds (a typical example is given in eq. 2) [1]. Starting from, e.g. **7**, the stereochemistry at carbon centers C2 and C6 is retained in the products. For application of this overall reaction sequence to the synthesis of many attractive organic target molecules it would be highly desirable to introduce alkyl substituents regioselectively at the sp^2-carbon center C4, especially a methyl group. We have found that the sequential CC-coupling process can be carried out very regioselectively when the (η^4-isoprene)zirconocene reagent is used. This regioselective introduction of the isoprene building block appears to be a straightforward consequence of the reaction mechanism (i.e. CC-coupling taking place by means of an electrocyclic ring-closure reaction [5] rather than a nucleophilic addition process [6]) of the initial step in our carbene complex synthesis. Moreover, the regioselective introduction of a methyl substituent at C4 enabled a further assessment of the factors that control the remarkably selective asymmetric 1,5-induction depicted in eq. 3. A representative example is described in some detail in this paper.

Results and discussion

(Isoprene)zirconocene (**8**) can be readily made by treating zirconocene dichloride with isoprene-magnesium [7]. There are two isolable isomers known: (*s-cis-* and (*s-trans-*η^4-isoprene)$ZrCp_2$ (*cis-***8**; *trans-***8**). Only the (*s-cis-*η^4-diene)metallocene isomer *cis-***8** is observed under equilibrium conditions at ambient temperature, but the *cis-***8** $\rightleftharpoons$ *trans-***8** equilibrium is sufficiently rapid at room temperature to allow reactions via (*s-trans-*η^4-isoprene)zirconocene to take place. At low temperature, *trans-***8** is by far the dominant component in the photostationary equilibrium under Pyrex-filtered UV irradiation [2].

(Isoprene)zirconocene reacts with a variety of ketones to form seven-membered metallacycles [7]. It is well established that the regioselectivity of this CC-coupling process depends on whether the (*s-cis-*) or (*s-trans-*η^4-diene)metallocene isomer is the reacting species; *cis-***8** adds as a carbon-nucleophile to give predominately the product **10**, whereas *trans-***8** gives the regioisomer **12**, probably by means of a non-nucleophilic (i.e. electrocyclic) ring closure reaction via the (η^2-isoprene)$ZrCp_2$ reactive intermediate **9** that has the smallest possible number of substituents at the coordinated C=C double bond [8] (Scheme 1).

The course of the thermally induced addition of (isoprene)zirconocene to hexacarbonyltungsten at 50 °C is analogous to that shown in Scheme 1. A major product is obtained in which CC-coupling has taken place between the carbonyl carbon atom at tungsten and the isoprene C4 methylene terminus which is away from the $=C(CH_3)$-moiety.



Scheme 1

The (π-allyl)zirconoxytungstencarbene complex **14a** in solution shows IR ν(CO) bands at 2055, 1956, and 1901 cm^{-1}. In the $^1H/^{13}C$ NMR spectra (benzene-d_6) it exhibits signals from diastereotopic Cp ligands (δ 5.31, 5.21/110.0, 109.8). The carbene-C resonates at δ 339.4. The methylene hydrogens at the adjacent carbon center C4 are diastereotopic (δ 3.82, 2.98) and each of them is coupled with the hydrogen H(3) at δ 4.42 (^3J (H(3), H(4)) 10.3 Hz, ^3J (H(3), H(4')) 4.4 Hz, ^2J(H(4), H(4')) 18.7 Hz). This clearly shows the methyl-substituent to be on C(2) of the zirconium-bound π-allyl ligand (δ 1.83, 1.48 ($H(1)_{syn}$, $H(1)_{anti}$; ^2J 5.0 Hz)). We observed a second minor isomer of **14a** in solution (ca. 15%); although it was not completely characterized, some very typical ^1H NMR spectral features revealed that a related regioselective coupling between the less substituted isoprene C=C double bond and $W(CO)_6$ had taken place (e.g. H(4), H(4'): δ 4.02, 2.44; ^2J (H(4), H(4')) 17.9 Hz, ^3J(H(3), H(4)) 9.9 Hz, ^3J(H(3), H(4')) 4.9 Hz). (Isoprene)zirconocene also

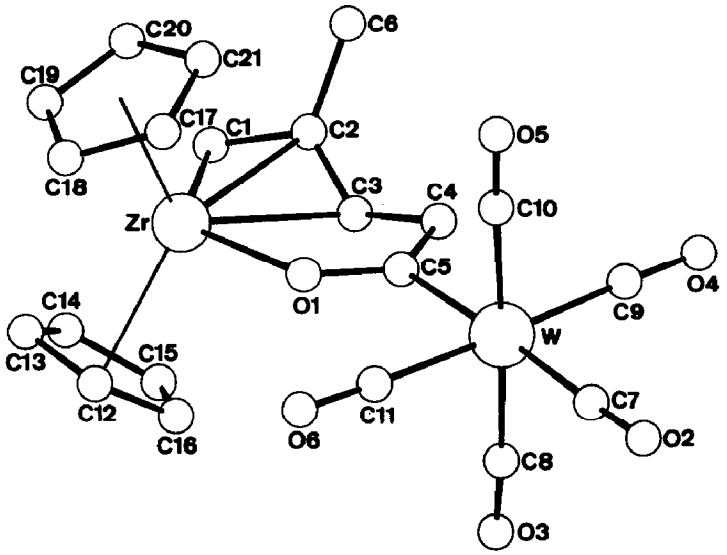


Fig. 1. A view of the molecular structure of the zirconoxycarbene complex **14a**.

couples regioselectively with hexacarbonylchromium to yield **14b**; in this case only one set of typical NMR signals is observed in solution.

The structure of complex **14a** in the solid state was determined by an X-ray diffraction study. The zirconium center in **14a** is pseudotetrahedrally coordinated to the two η^5-cyclopentadienyl ligands, the carbene oxygen atom (O(1)), and a distorted η^3-(2-methylallyl) moiety. Overall, the molecular structure of **14a** is related to that of the (butadiene)zirconocene-derived (π-allyl)zirconoxycarbene complex **3a**, which was described recently [3b]. The W–C(carbene) bond length in **14a** (2.22(1) Å) is similar to that in other heteroatom-stabilized tungsten carbene complexes [9] (**3a**: 2.20(1) Å; $(CO)_5W{=}C(OEt)C_5H_4RuCp$ (**15**): 2.23(2) Å; $(CO)_5W{=}C(OEt)C_5H_8$-$CH{=}CPh_2$ (**16**): 2.18(1) Å; $(CO)_5W{=}C(OCH_3)C_5H_7$ (**17**): 2.09(2) Å). The O(1)–C(carbene) bond length of 1.29(1) Å is only slightly greater than that in **3a** (1.262(11) Å). This indicates a pronounced metal acyl complex character for the zirconoxycarbene complex **14a** (see for a comparison d(O–C(carbene)) 1.35(2) Å in **15**, 1.29(2) Å in **16**, 1.32(2) Å in **17**). The Zr–O(1) bond in **14a** is rather long (2.211(8) Å; **3a**: 2.179(5) Å).

The most interesting structural features are associated with the allyl zirconium moiety of **14a**. The methyl substituent is bonded to carbon atom C(2) of the allylic part of the carbene ligand chain. Thus, carbon–carbon coupling has occurred exclusively between the end of the less substituted carbon–carbon double bond of the former isoprene ligand (i.e. at C(4)) and the carbonyl carbon center at tungsten (C(5)). The resulting 2-methyl-substituted η^3-allyl ligand is unsymmetrically bonded to zirconium, the Zr–C(1) bond (2.42(1) Å) being considerably shorter than the Zr–C(2) (2.56(1) Å) and the Zr–C(3) bond (2.52(1) Å). A σ,π-type of bonding in the (allyl)zirconium unit is also observed for **3a** [3b] and several other compounds of related structure [10], although a careful comparison of bond lengths (**3a**: Zr–C(1) 2.421(14), Zr–C(2) 2.497(12), Zr–C(3) 2.621(15) Å) and torsional angles (θ(C(2), C(3), C(4), C(5)) 111(1)° (**14a**), 102.3° (**3a**)) reveals pronounced differences.

Table 1

Selected bond lengths (Å) and angles (°) in **14a**

W–C(5)	2.22(1)	O(2)–C(7)	1.15(2)
W–C(7)	2.03(1)	O(3)–C(8)	1.19(2)
W–C(8)	1.99(2)	O(4)–C(9)	1.18(1)
W–C(9)	1.98(1)	O(5)–C(10)	1.18(2)
W–C(10)	2.00(2)	O(6)–C(11)	1.16(2)
W–C(11)	2.00(1)	C(1)–C(2)	1.45(2)
Zr–O(1)	2.211(8)	C(2)–C(3)	1.33(2)
Zr–C(1)	2.42(1)	C(2)–C(6)	1.51(2)
Zr–C(2)	2.56(1)	C(3)–C(4)	1.51(2)
Zr–C(3)	2.52(1)	C(4)–C(5)	1.50(1)
O(1)–C(5)	1.29(1)		
C(5)–W–C(7)	177.4(6)	Zr–C(1)–C(2)	78.5(6)
C(5)–W–C(8)	86.5(5)	Zr–C(2)–C(1)	67.9(6)
C(5)–W–C(9)	91.8(4)	Zr–C(2)–C(3)	73.1(6)
C(5)–W–C(10)	90.9(5)	Zr–C(2)–C(6)	127.2(7)
C(5)–W–C(11)	85.7(5)	C(1)–C(2)–C(3)	118(1)
C(7)–W–C(8)	91.3(6)	C(1)–C(2)–C(6)	117(1)
C(7)–W–C(9)	89.7(5)	C(3)–C(2)–C(6)	125(1)
C(7)–W–C(10)	91.3(6)	Zr–C(3)–C(2)	76.7(7)
C(7)–W–C(11)	92.8(6)	Zr–C(3)–C(4)	112.1(6)
C(8)–W–C(9)	92.4(5)	C(2)–C(3)–C(4)	129(1)
C(8)–W–C(10)	177.2(6)	C(3)–C(4)–C(5)	111.3(9)
C(8)–W–C(11)	88.8(6)	W–C(5)–O(1)	121.6(7)
C(9)–W–C(10)	88.5(5)	W–C(5)–C(4)	124.0(8)
C(9)–W–C(11)	177.2(5)	O(1)–C(5)–C(4)	114(1)
C(10)–W–C(11)	90.1(6)	W–C(7)–O(2)	178(1)
O(1)–Zr–C(1)	123.7(3)	W–C(8)–O(3)	175(1)
O(1)–Zr–C(2)	91.5(3)	W–C(9)–O(4)	178(1)
O(1)–Zr–C(3)	66.7(3)	W–C(10)–O(5)	176(1)
C(1)–Zr–C(2)	33.6(4)	W–C(11)–O(6)	178(1)
C(1)–Zr–C(3)	57.5(4)		
C(2)–Zr–C(3)	30.2(4)		
Zr–O(1)–C(5)	131.8(6)		

Attachment of the methyl group at C(2) has apparently resulted in an unfavourable steric CH_3/Cp interaction which has caused the Zr–C(2) bond length to be increased, whereas the adjacent sp^2-hybridized carbon center C(3) is allowed to move closer to the transition metal center than in the unsubstituted analogue **3a**.

Complex **14a** reacted readily with one molar equivalent of acetone at room temperature to give the nine-membered metallacyclic zirconoxycarbene complex **18**. At low temperature complex **18** exhibits NMR spectra that indicate a chiral molecular structure. At 230 K ^{1}H (200 MHz)/^{13}C (50 MHz) NMR signals due to diastereotopic Cp ligands are observed (in $CDCl_3$ solution at δ 6.28, 6.25/113.1, 112.7). In addition, the acetone-derived methyl groups have become inequivalent (δ 1.28, 1.24/33.2, 29.6) as have the methylene hydrogens at C3 (δ 2.12, 1.92; ^2J (H(3), H(3′)) 12.3 Hz) and at C(6) (δ 4.15, 3.51). The latter show strong proton–proton coupling with the olefinic hydrogen H(5) (δ 4.60; ^2J(H(6), H(6′)) 19.4 Hz, ^3J(H(5), H(6)) 10.5 Hz, ^3J (H(5), H(6′)) 4.1 Hz).

Table 2

Atomic coordinates of the non-hydrogen atoms of **14a**

Atom	*x*	*y*	*z*
W	0.44266(7)	0.73463(6)	0.15040(3)
Zr	0.2030(1)	0.3392(1)	0.28885(7)
O(1)	0.3180(9)	0.5124(7)	0.2470(5)
O(2)	0.614(1)	1.0080(9)	0.1330(8)
O(3)	0.090(1)	0.835(1)	0.1501(8)
O(4)	0.357(1)	0.6723(9)	−0.0730(6)
O(5)	0.789(1)	0.619(1)	0.1555(7)
O(6)	0.529(2)	0.783(1)	0.3738(7)
C(1)	0.025(1)	0.170(1)	0.1771(8)
C(2)	0.111(1)	0.233(1)	0.1156(8)
C(3)	0.102(1)	0.358(1)	0.1156(7)
C(4)	0.215(1)	0.454(1)	0.0829(7)
C(5)	0.316(1)	0.547(1)	0.1649(7)
C(6)	0.210(2)	0.153(1)	0.0605(8)
C(7)	0.551(2)	0.910(1)	0.1407(9)
C(8)	0.224(2)	0.804(1)	0.149(1)
C(9)	0.391(1)	0.694(1)	0.0106(8)
C(10)	0.658(2)	0.658(1)	0.1542(8)
C(11)	0.495(2)	0.767(1)	0.2919(9)
C(12)	0.146(2)	0.491(1)	0.4204(9)
C(13)	0.096(2)	0.370(1)	0.4379(9)
C(14)	−0.042(2)	0.324(1)	0.3659(9)
C(15)	−0.076(1)	0.418(1)	0.3054(8)
C(16)	0.039(1)	0.520(1)	0.3397(8)
C(17)	0.518(1)	0.350(1)	0.3481(9)
C(18)	0.445(1)	0.309(1)	0.4189(8)
C(19)	0.362(1)	0.190(1)	0.3853(9)
C(20)	0.373(1)	0.151(1)	0.2930(8)
C(21)	0.472(2)	0.252(1)	0.2683(8)

Complex **14a** exhibits temperature-dependent dynamic NMR spectra. Increase in temperature results in a pairwise coalescence of the afore-mentioned signals of the diastereotopic groups. The limiting high temperature NMR spectra suggest an apparent overall C_s-molecular symmetry for the rapidly equilibrating enantiomeric conformers of the chiral medium-ring sized metaloxycarbene complex **18**. A Gibbs activation energy barrier of $\Delta G^{\neq}_{ent}$ (280 K) of 14.3 ± 0.3 kcal/mol was derived from the coalescence temperature for the ^{1}H NMR Cp singlets. This value is similar to that for the analogous topomerization process of the chiral metallacycles **4** containing a *trans*-C=C bond in the ring (e.g $R^1 = R^2 = CH_3$, $ML_n = W(CO)_5$: $\Delta G^{\neq}_{ent}$(323 K) 16.6 ± 0.4 kcal/mol; $ML_n = Cr(CO)_5$: $\Delta G^{\neq}_{ent}$ (323 K) 16.5 ± 0.4 kcal/mol; $R^1 = R^2 = Ph$, $ML_n = W(CO)_5$: $\Delta G^{\neq}_{ent}$ (350 K) 17.0 ± 0.4 kcal/mol; $R^1 = CH_3$, $R^2 = CH=CH_2$, $ML_n = W(CO)_5$: two diastereoisomers, 60/40 ratio, the rearrangement of major → minor isomer has $\Delta G^{\neq}_{dia}$ (317 K) 16.5 ± 0.4 kcal/mol) [1]. The enantiomerization barrier for the parent hydrocarbon *trans*-cyclononene is only slightly higher, at $\Delta G^{\neq}_{ent}$ (262 K) ≈ 19 kcal/mol [11].

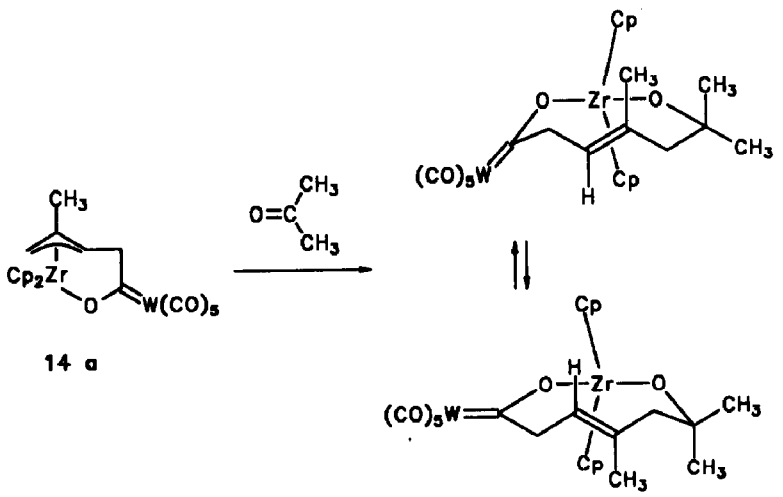
The low temperature NMR spectra and the observed activation barrier for the enantiomerization process indicate that **18** possesses a chiral ring structure analogous to that in the well-investigated analogues **4**, i.e. complex **18** must be assigned

Table 3

Details of the determination of the crystal structure of **14a**

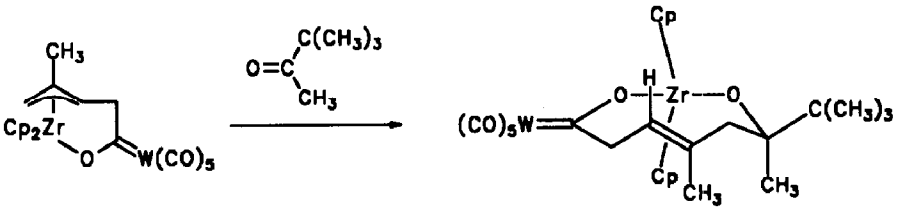
Formula:	$C_{21}H_{18}O_6WZr \times 0.5C_7H_8$
M.W.	687.5
Space group	$P\bar{1}$
a (Å)	8.255(1)
b (Å)	10.573(3)
c (Å)	14.586(4)
α (°)	96.93(2)
β (°)	102.46(2)
γ (°)	94.33(2)
V (Å^3)	1227.2
d_{calc} (g cm^{-3})	1.86
μ(cm^{-1})	52.36
Z	2
λ (Å)	0.71069
Measured reflections	5896($+h, \pm k, \pm l$)
sin θ/λ_{max}	0.65
Empirical abs. corr.(min-max)	0.597–0.999
Independent reflections	5570
Observed reflections	4541
Refined parameters	283
R	0.069
R_w	0.060
ρ (max), eÅ^{-3}	4.4
H atoms calculated, toluene molecule disordered	

an endocyclic *E*-configurated trisubstituted carbon carbon double bond. Similar structures have been proposed for the products of addition of two molar equivalents of ketones or aldehydes to (isoprene)zirconocene or analogous compounds [12].



18

Scheme 2

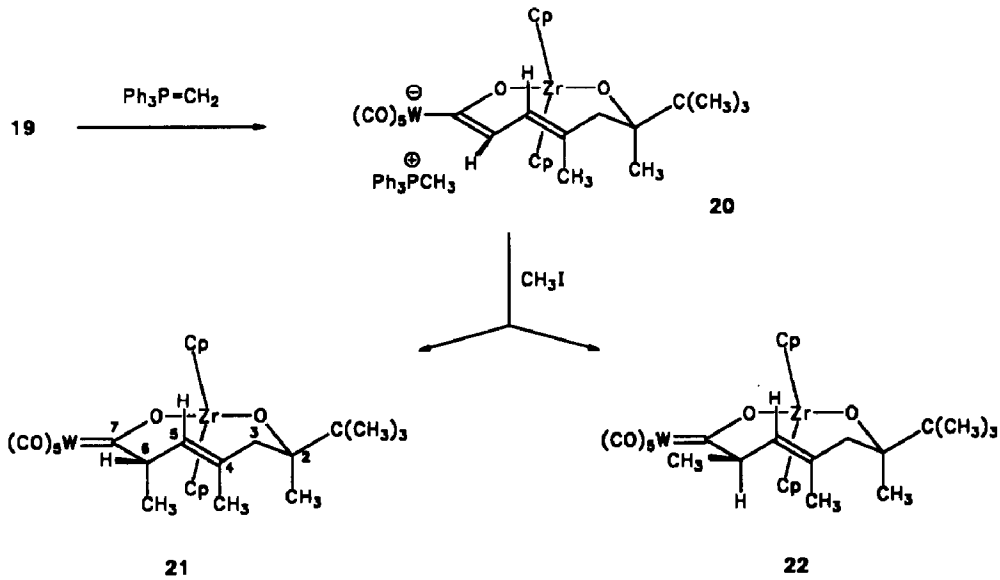


14 a 19

Scheme 3

We subsequently treated the carbene complex **14a** with pinacolone and obtained a single insertion product **19**. The spectroscopic data for **19** are similar to those observed for the chiral nine-membered metallacyclic zirconoxycarbene complexes [1]. In principle, two diastereomeric *E*-configurated conformers of **19** could be formed. However, the observation that the ^1H NMR spectra remain essentially unchanged even at temperatures as low as 230 K indicates that only a single isomer is present under equilibrium conditions. Complex **19** thus appears to exhibit similar stereochemical features as those observed in the analogously-prepared (butadiene)-zirconocene-derived zirconoxycarbene complex **4a** ($R^1 = CH_3$, $R^2 = C(CH_3)_3$, $ML_n = W(CO)_5$). Complex **19**, like **4a**, seems to be characterized by relative configurations (2*R**)(4,5,6-*pS**) of the two elements of chirality present. This would permit a maximum steric separation of bulky substituents attached to the rather rigid medium-sized metallacyclic ring system (Scheme 3).

The zirconoxycarbene complex can readily be deprotonated in the α-position by addition of an appropriate base. Thus treatment with the phosphorus ylide $Ph_3P{=}CH_2$ produces the anion **20**, isolated as its $Ph_3PCH_3^+$ salt as an air-sensitive oil.



Scheme 4

Alkylation of **20** with methyl iodide proceeds cleanly. The NMR spectra of the product mixture indicates that only α-methylation had occurred. This is strictly analogous to the outcome of base-induced α-alkylation of similar zirconoxycarbene complexes such as **6** [1]. However, the α-alkylation reaction of the (butadiene)$ZrCp_2$-derived carbene complex **6** shows some marked differences from the (isoprene)$ZrCp_2$ based system **19** in respect of the stereochemical outcome. The **6** → **7** α-alkylation is rather diastereoselective (ca. 80% de), whereas an almost equimolar mixture of the respective (2*R**, 6*S**)(4,5,6-*pS**) and (2*R**, 6*R**)(4,5,6-*pS**) diastereoisomers **21** and **22** was isolated from the reaction of the carbene complex anion **20** with the alkyl halide at temperatures above 0 °C (Scheme 4).

Conclusions

We have recently shown that α-alkylation of the carbene complex anion derived from **6** proceeds in a highly diastereoselective manner. The product formed is predominantly that derived from electrophilic attack taking place from the *si*-face at C(6). Independent spectroscopic studies with the corresponding carbene complex anion derived from complex **4** with $R^1 = R^2 = CH_3$, $ML_n = W(CO)_5$ have previously revealed that the C(7)–C(6) and C(5)–C(4) carbon–carbon double bonds are probably oriented in perpendicular planes [1]. Therefore, the high diastereoselectivity of the α-alkylation observed in several cases in this series may be the result of shielding of the *re*-side from electrophilic attack by the hydrogen atom bonded to the olefinic carbon center C(5). The stereoselectivity would thus be the consequence of an unfavourable 1,2-interaction between a substituent and the incoming reagent, which approaches C(6) from a direction similar to that of a Bürgi–Dunitz trajectory. The observed dominant *si*-attack on the **6** derived α-anions is not substantially hindered by 1,3-interaction with the hydrogen substituent at C(4).

The situation is different when a methyl group is attached to C(4). The resulting decrease of the ring-inversion activation barrier, as observed for **18** ($\Delta G^{\ddagger}_{ent}$ (280 K) = 14.3 ± 0.3 kcal/mol) relative to **4** ($R^1 = R^2 = CH_3$, $ML_n = W(CO)_5$: $\Delta G^{\ddagger}_{ent}$ (323 K) = 16.6 ± 0.4 kcal/mol), indicates that there is some torsional distortion of the metallacyclic framework of **18** that moves the H(5) substituent closer to the inside and the **4**-CH_3 group further out towards the perimeter of the ring. This effect, along with that of the increased steric bulk of the alkyl substituent at C(4), now generates a serious repulsive 1,3-interaction, making *si*-face electrophilic attack less favourable. Thus, *re*-side addition of a methyl electrophile on **20** giving **22** can now effectively compete with *si*-face attack to give **21**.

A decrease in the stereoselectivity of the α-alkylation process is the price that had to be paid for achieving almost complete regioselective control. The non-nucleophilic nature of the initiating step of our new carbene complex synthesis [3] permits almost exclusive formation of only one regioisomeric isoprene/metal carbonyl coupling product on the early transition metal bent-metallocene template. This regiochemistry is then transferred to the nine-membered metallacycles, and subsequently to organic products such as the analogues of **5** (see eq. 2). Use of this methodology should provide simple routes to regioselective unsymmetrical functionalization of the isoprene building block, to yield organic compounds such as $HOCR^1R^2CH_2C(CH_3)=CHCH_2CO_2H$. We are currently investigating ways of using such reaction sequences in organic synthesis.

Experimental section

All reactions with organometallic compounds were carried out under an inert atmosphere by use of Schlenk-type glassware or in a glove box. Solvents were dried and distilled under argon prior to use. Elemental analyses were carried out by the Institut für Anorganische Chemie der Universität Würzburg. For additional general information, including a list of spectrometers used, see ref. [1]. (Isoprene)zirconocene was prepared as previously described [7].

*Dicyclopentadienyl[μ-[(1,2,3-η : 5-η)-2-methyl-5-oxo-2-pentene-1,5-diyl-O]](pentacarbonyltungsten)zirconium (**14a**)*

A mixture of (isoprene)zirconocene **8** (1.80 g, 6.2 mmol) and hexacarbonyltungsten (2.19 g, 6.2 mmol) in 50 ml of toluene was stirred for 60 h at ambient temperature and then for an additional 22 h at 50 °C. The mixture was allowed to cool, and some residual hexacarbonyltungsten separated. The supernatant solution was decanted and evaporated in vacuo. The residue was washed with four 20 ml portions of petrol and dried in vacuo to yield 2.52 g (64%) of **14a**, m.p. 145 °C (decomp.). Recrystallization of a sample from toluene/heptane (1/1) at −30 °C gave crystals suitable for X-ray diffraction. According to the elemental analysis and the ^{1}H NMR spectrum these contained 0.5 equiv. of toluene. The ^{1}H NMR spectrum of the crude material showed signals of two isomeric compounds in a 85/15 ratio. The ^{1}H NMR spectrum of the recrystallized material revealed the presence of only one isomer (**14a**). Anal. Found: C, 43.19; H, 3.12. $C_{21}H_{18}O_6ZrW \cdot 0.5\ C_7H_8$ (687.5) calcd.: C, 42.80; H, 3.22%. ^{1}H NMR (benzene-d_6, 200 MHz), **14a**: δ 5.31/5.21 (each s, 5H, Cp), 4.42 (1H, H(3)), 3.82 (1H, H(4′)), 2.98 (1H, H(4)), 1.83/1.48 (each 1H, H(1_{syn}), H(1_{anti})), 1.24 (s, 3H, 2-CH_3), H,H-coupling constants (Hz): ^2J 5.0 (H(1_s), H(1_a)), 18.7 (H(4), H(4′)), ^3J 10.3 (H(3), H(4)), 4.4 (H(3), H(4′)); (minor isomer): δ 5.27 (s, 5H, Cp), 4.02 (1H, H(4′)), 2.44 (1H, H(4)), the additional signals of the minor isomer were not located. H,H-coupling constants (Hz): ^2J 17.9 (H(4), H(4′)), ^3J 9.9 (H(3), H(4)), 4.9 (H(3), H(4′)). ^{13}C NMR (benzene-d_6, 50.3 MHz), **14a**: δ 339.4 (C-carbene), 205.9 (CO_{trans}), 200.9 (CO_{cis}), 147.9 (C(2)), 110.0/109.8 (Cp), 102.0 (C(3)), 67.9 (C(4)), 48.4 (C(1)), 22.0 (2-CH_3). IR (KBr): 2964. 2055, 1956, 1901, 1429, 1397, 1343, 1266, 1234, 1099, 1068, 1016, 912, 873, 810, 739, 716, 596, 576 cm^{-1}.

*Dicyclopentadienyl[μ-[(1,2,3-η : 5-η)-2-methyl-5-oxo-2-pentene-1,5-diyl-O]](pentacarbonylchromium)zirconium (**14b**)*

A mixture of 700 mg (2.42 mmol) (isoprene)zirconocene **8** and 530 mg (2.41 mmol) hexacarbonylchromium in 20 ml of toluene was stirred for 20 h at 50 °C, then concentrated to about half its volume to bring about precipitation of residual hexacarbonylchromium. The solution was decanted and evaporated to dryness in vacuo and the oily residue solidified on treatment with 40 ml of petrol. The solvent was removed and the solid residue washed twice with petrol and then dried in vacuo to give 730 mg (59%) of **14b**. A 600 mg sample was recrystallized from toluene/n-heptane (5/2) at −30 °C. Yield: 350 mg (28%), m.p. 130 °C (decomp.). Anal. Found: C, 49.03; H, 3.66. $C_{21}H_{18}O_6CrZr$ (509.6) calcd.: C, 49.50; H, 3.56%. ^{1}H NMR (benzene-d_6, 200 MHz): δ 5.34/5.24 (each s, 5H, Cp), 4.40 (1H, H(3)), 4.01 (1H, H(4′)), 3.23 (1H, H(4)), 1.84/1.47 (each 1H, H(1_{syn}), H(1_{anti})), 1.24 (s, 3H,

2-CH_3), H,H-coupling constants (Hz): ^2J 5.0 (H(1_s), H(1_a)), 18.6 (H(4), H(4′)), ^3J 10.3 (H(3), H(4)), 4.4 (H(3), H(4′)). ^{13}C NMR (THF-d_8, 50.3 MHz): δ 358.7 (C-carbene), 225.6 (CO_{trans}), 220.2 (CO_{cis}), 149.6 (C(2)), 111.2/110.9 (Cp), 100.8 (C(3), ^1J(CH) 148 Hz), 65.1 (C(4), ^1J(CH) 129 Hz), 49.4 (C(1), ^1J(CH) 149 Hz) 22.2 (2-CH_3, ^1J(CH) 128 Hz), IR (KBr): 3113, 2963. 2924, 2904, 2047, 1960(sh), 1902, 1426, 1396, 1384, 1342, 1262, 1234, 1016, 919, 873, 810, 738, 717, 673, 656, 541, 459 cm^{-1}.

E-Dicyclopentadienyl[μ-[(1-η : 7-η)-2,2,4-trimethyl-7-oxo-1-oxa-4-heptene-1,7-diyl-O]](pentacarbonyltungsten)zirconium (18)

To a suspension of 770 mg (1.20 mmol) of **14a** in 30 ml of toluene was added 100 μl of acetone (1.32 mmol). The mixture was stirred for 20 h at room temperature and the small amount of a precipitate removed by filtration. The solvent was evaporated in vacuo and the oily yellow residue washed with pentane. Yield 620 mg (74%) of **18**. Two recrystallizations from toluene/pentane (5/1) gave 590 mg (69%) of analytically pure **18**. Anal. Found: C, 41.40; H, 3.55. $C_{24}H_{24}O_7ZrW$ (699.5) calcd.: C, 41.21; H, 3.46%. ^{1}H NMR ($CDCl_3$, 200 MHz, 230 K): δ 6.28/6.25 (each s, 5H, Cp), 4.60 (1H, H(5)), 4.15 (1H, H(6′)), 3.51 (1H, H(6)), 2.12 (1H, H(3′)), 1.92 (1H, H(3)), 1.46 (s, 3H, 4-CH_3), 1.28/1.24 (each s, 3H, 2-CH_3); coupling constants in Hz: ^2J 12.3 (H(3), H(3′)), ^3J 19.4 (H(6), H(6′)), 10.5 (H(5), H(6)), 4.1 (H(5), H(6′)). ^{13}C NMR ($CDCl_3$, 50.3 MHz, 230 K): δ 331.6 (C-carbene), 205.5 (CO_{trans}), 199.4 (CO_{cis}, ^1J(CW) 127 Hz), 137.1 (C(4)), 122.5 (C(5), ^1J(CH) 151 Hz), 113.1/112.7 (Cp), 83.2 (C(2)), 68.0 (C(6), ^1J(CH) 126 Hz), 54.5 (C(3), ^1J(CH) 121 Hz), 33.2/29.6 (each 2-CH_3, ^1J(CH) 123 Hz), 17.8 (4-CH_3, ^1J(CH) 130 Hz). IR (KBr): 2972, 2060, 1937(sh), 1901, 1878, 1437, 1253, 1162, 1129, 1019, 950, 910, 813, 786, 595, 577 cm^{-1}.

E-Di(cyclopentadienyl[μ-[(1-η : 7-η)-2-t-butyl-2,4-dimethyl-7-oxo-1-oxa-4-heptene-1,7-diyl-O]](pentacarbonyltungsten)zirconium (19)

To a solution of 980 mg (1.53 mmol) **14a** in 60 ml of toluene was added pinacolone, 210 μl (1.68 mmol). The mixture was stirred for 15 h at 40 °C and the resulting solution then filtered at room temperature. The solvent was removed in vacuo and the brown-red residue was solidified at 0 °C by addition of pentane. The resulting yellow product was filtered off and dried in vacuo. Yield 600 mg (53%), m.p. 136 °C (decomp.). Anal. Found: C, 43.61; H, 4.23. $C_{27}H_{30}O_7ZrW$ (741.6) calcd.: C, 43.73; H, 4.08%. ^{1}H NMR ($CDCl_3$): δ 6.34/6.28 (each s, 5H, Cp), 4.73 (1H, H(5)), 3.99 (1H, H(6′)), 3.78 (1H, H(6)), 2.15 (1H, H(3′)), 1.97 (1H, H(3)), 1.54 (s, 3H, 4-CH_3), 1.27 (s, 3H, 2-CH_3), 0.97 (s, 9H, t-Bu). Coupling constants (in Hz): ^2J 12.2 (H(3), H(3′)), 19.7 (H(6), H(6′)), ^3J 10.1 (H(5), (H(6)), 5.1 (H(5), H(6′)). ^{13}C NMR ($CDCl_3$): δ 332.7 (C-carbene), 204.9 (CO_{trans}), 199.7 (CO_{cis}, ^1J(CW) 128 Hz), 136.6 (C(4)), 123.4 (C(5), ^1J(CH) 157 Hz), 113.9/113.1 (Cp), 91.2 (C(2)), 68.3 (C(6), ^1J(CH) 127 Hz), 46.7 (C(3), ^1J(CH) 128 Hz), 39.1 (CMe_3), 26.0 ($C(CH_3)_3$, ^1J(CH) 126 Hz), 23.5 (2-CH_3, ^1J(CH) 125 Hz), 19.1 (4-CH_3, ^1J(CH) 126 Hz). IR (KBr): 3116, 2050, 1961, 1902, 1421, 1393, 1382, 1366, 1251, 1106, 1017, 972, 806, 597, 577 cm^{-1}.

Deprotonation of the zirconoxycarbenetungsten complex 19

To a solution of 580 mg (0.78 mmol) of **19** in 60 ml of toluene at room temperature was added 240 mg (0.86 mmol) of the ylide methylenetri-

phenylphosphorane. The mixture was stirred for 15 min and the product allowed to separate as an orange-brown oil, which was washed twice with toluene and then dried in vacuo. Yield: 460 mg (58%). ^{1}H NMR (THF-d_8): δ 7.90–7.60 (m, 15H, Ph), 6.25/6.19 (each s, 5H, Cp), 5.33/5.12 (each br s, 1H, H(5), H(6)), 2.90 (3H, P-CH_3), 2.33 (1H, H(3')), 1.77 (1H, H(3)), 1.75 (4-CH_3), 1.38 (2-CH_3), 0.99 (t-Bu). Coupling constants (in Hz): ^2J(HH) 11.6 (H(3), H(3')), ^2J(PH) 14.0 (H_3C-P). ^{13}C NMR (THF-d_8): δ 209.4 (CO_{trans}), 206.9 (CO_{cis}), 195.2 (C-carbene), 135.6 (*p*-C(Ph)), 134.1 (*o*-C(Ph), ^2J(PC) 10 Hz), 133.6 (C4), 131.1 (m-C(Ph), ^3J(PC) 12 Hz), 121.6 (C5), 120.5 (*ipso*-C(Ph), ^1J(PC) 89 Hz), 112.7/112.0 (Cp), 105.4 (C(6)), 84.8 (C(2)), 46.1 (C(3)), 40.3 (CMe_3), 26.5 (C(CH_3)$_3$), 25.3 (2-CH_3), 22.6 (4-CH_3), 8.7 (H_3C-PPh_3, ^1J(PC) 58 Hz). ^{31}P NMR (THF-d_8): δ 22.8.

E-Dicyclopentadienyl[μ-[(1-η : 7-η)-2-t-butyl-2,4,6-trimethyl-7-oxo-1-oxa-4-heptene-1,7-diyl-O]](pentacarbonyltungsten)zirconium (21,22)

To a solution of 1.00 g(1.35 mmol) of **19** in 20 ml of toluene at room temperature was added a solution of 410 mg of methylenetriphenylphosphorane (1.48 mmol) in 4.5 ml of toluene. The mixture was stirred for 1 h and the toluene then decanted from the precipitated red-brown oil, which was then dissolved in 20 ml of THF. Methyl-iodide (420 μl, 6.75 mmol) was added at 0 °C and the mixture stirred for 4 h at room temperature. The precipitated methyltriphenylphosphonium iodide was filtered off and the filtrate evaporated to dryness. Washing of the resulting oil at 0 °C with pentane gave the product as an amorphous powder. Yield 590 mg (58%), m.p. 157 °C (decomp.). Anal. Found: C, 44.79; H, 4.33. $C_{28}H_{30}O_7ZrW$ (755.6) calcd.: C, 44.51; H, 4.27%. Mixture of two isomers in a ratio of A/B = 55/45. ^{1}H NMR (benzene-d_6): δ 6.09 (s, 5H, Cp (B)), 6.07 (s, 5H, Cp (A)), 5.89 (s, 5H, Cp (A)), 5.85 (s, 5H, Cp (B)), 4.55 (1H, H(5) (B)), 4.43 (1H, H(5) (A)), 3.94 (1H, H(6) (B)), 3.83 (1H, H(6) (A)), 1.95 (1H, H(3') (A)), 1.93 (1H, H(3') (B)), 1.74 (1H, H(3) (B)), 1.62 (1H, H(3) (A)), 1.53 (3H, 6-CH_3 (A)), 1.48 (3H, 6-CH_3 (B)), 1.29 (s, 3H, 2-CH_3 (A)), 1.27 (s, 3H, 4-CH_3 (B)), 1.01 (s, 3H, 2-CH_3 (B)), 0.94 (s, 3H, 2-CH_3 (A)), 0.79 (s, 9H, t-Bu (B)), 0.78 (s, 9H, t-Bu(A)). Coupling constants ^2J = 12.4 (H(3), H(3') (A)), 14.3 (H(3), H(3') (B)), ^3J 9.01 (H(5), H(6) (A)), 6.50 (H(5), H(6) (B)), 7.54 (H(6), 6-CH_3 (A)), 7.54 (H(6), 6-CH_3 (B)). ^{13}C NMR ($CDCl_3$): δ 340.9 (C(7) A), 339.5 (C(7) B), 204.2 (CO_{trans} A, B), 199.9 (CO_{cis} A, B), 137.2 (C(4) B), 134.1 (C(4) A), 131.4 (C(5) A), 126.7 (C(5) B), 113.9/113.2 (Cp A, B), 91.2 (C(2) A), 90.9 (C(2) B), 67.0 (C(6) A, B), 46.7 (C(3) A), 44.0 (C(3) B), 39.6/39.1 (CMe_3 A, B), 26.0/25.9 (C(CH_3)$_3$ A, B), 23.4 (2-CH_3 A), 21.9 (2-CH_3 B), 19.9 (4-CH_3 A), 19.9 (4-CH_3 B). IR (KBr): 3101, 2057, 1965, 1907, 1439, 1262, 1116, 1094, 1017, 801, 745, 690, 596 cm^{-1}.

Further details of the crystal structure investigation of **14a** are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD54379, the names of the authors, and the journal citation.

Acknowledgement

Financial support from the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

References and notes

1 G. Erker, F. Sosna, R. Zwettler, C. Krüger, Organometallics, 8 (1989) 450; M.G. Humphrey, F. Sosna, G. Erker, R. Zwettler, C. Krüger, in U. Schubert (Ed.), Advances in Metal Carbene Chemistry, Kluwer Academic Publishers, Deventer, 1989, p. 163; G. Erker, F. Sosna, R. Zwettler, C. Krüger, Z. Anorg. Allg. Chem., in press; G. Erker, M. Aulbach, M. Mena, R. Pfaff, F. Sosna, Chemica Scripta, in press; G. Erker, F. Sosna, J.L. Peterson, R. Benn, H. Grondey, submitted; G. Erker, F. Sosna, Organometallics, in press.

2 G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich, C. Krüger, J. Am. Chem. Soc., 102 (1980) 6344; *Review*: G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem., 24 (1985) 1.

3 (a) G. Erker, U. Dorf, R. Benn, R.-D. Reinhardt, J.L. Petersen, J. Am. Chem. Soc., 106 (1984) 7649; G. Erker, U. Dorf, R. Mynott, Y.-H. Tsay, C. Krüger, Angew. Chem., 97 (1985) 572; Angew. Chem. Int. Ed. Engl., 24 (1985) 584; G. Erker, R. Lecht, J. Organomet. Chem., 311 (1986) 45; G. Erker, R. Lecht, R. Schlund, K. Angermund, C. Krüger, Angew. Chem., 99 (1987) 708; Angew. Chem. Int. Ed. Engl., 26 (1987) 666; G. Erker, R. Lecht, J.L. Petersen, H. Bönnemann, Organometallics, 6 (1987) 1962; G. Erker, R. Lecht, C. Krüger, Y.-H. Tsay, H. Bönnemann, J. Organomet. Chem., 326 (1987) C75; G. Erker, R. Lecht, Y.-H. Tsay, C. Krüger, Chem. Ber., 120 (1987) 1763; G. Erker, R. Lecht, F. Sosna, S. Uhl, Y.-H. Tsay, C. Krüger, H. Grondey, R. Benn, Chem. Ber., 121 (1988) 1069; G. Erker, U. Dorf, R. Lecht, M.T. Ashby, M. Aulbach, R. Schlund, C. Krüger, R. Mynott, Organometallics, 8 (1989) 2037; Reviews: G. Erker, in A. de Meijere, H. tom Dieck (Eds.), Organometallics in Organic Synthesis, Springer Verlag, Berlin, Heidelberg, 1987, p. 143; G. Erker, Polyhedron, 7 (1988) 2451; G. Erker, Angew. Chem., 101 (1989) 411; Angew. Chem. Int. Ed. Engl., 28 (1989) 397; G. Erker, F. Sosna, U. Hoffmann, J. Organomet. Chem., 372 (1989) 41; (b) U. Dorf, Dissertation, Univ. Bochum 1985.

4 For other recent examples of remote asymmetric induction see e.g.: E. Vedejs, R.A. Buchanan, Y. Watanabe, J. Am. Chem. Soc., 111 (1989) 8430; M. Uemura, T. Minami, K. Hirotsu, Y. Hayashi, J. Org. Chem., 54 (1989) 469, and ref. therein; S. Stanchev, M. Hesse, Helv. Chim. Acta, 72 (1989) 1052; K. Endo, K. Seya, H. Hikono, J. Chem. Soc., Chem. Commun., (1988) 934.

5 A. Stockis, R. Hoffmann, J. Am. Chem. Soc., 102 (1980) 2952.

6 (a) E.O. Fischer, A. Masböl, Angew. Chem., 76 (1964) 645; Angew. Chem. Int. Ed. Engl., 3 (1964) 580; Chem. Ber., 100 (1967) 2445; Adv. Organomet. Chem., 14 (1976) 1; (b) See also: E.O. Fischer, S. Fontana, J. Organomet. Chem., 40 (1972) 159; H.G. Raubenheimer, E.O. Fischer, J. Organomet. Chem., 91 (1975) C23; W. Petz, ibid., 72 (1974) 369; J. Pebler, W. Petz, Z. Naturforsch. B, 29 (1974) 658; R.S. Threlkel, J.E. Bercaw, J. Am. Chem. Soc., 103 (1981) 2650; P.T. Barger, J.E. Bercaw, Organometallics, 3 (1984) 278; idem, J. Organomet. Chem., 201 (1980) C39; G.S. Ferguson, P.T. Wolczanski, J. Am. Chem. Soc., 108 (1986) 8293; P.T. Wolczanski, R.S. Threlkel, J.E. Bercaw, ibid., 101 (1979) 218; P.T. Barger, B.D. Santarsiero, J. Armantrout, J.E. Bercaw, ibid., 106 (1984) 5178.

7 H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, K. Lee, A. Nakamura, Organometallics, 1 (1982) 388.

8 (a) G. Erker, U. Dorf, Angew. Chem., 95 (1983) 800; Angew. Chem. Int. Ed. Engl., 22 (1983) 777; (b) See for a comparison: G. Erker, K. Engel, J.L. Atwood, W.E. Hunter, Angew. Chem., 95 (1983) 506; Angew. Chem. Int. Ed. Engl., 22 (1983) 494; H. Yasuda, Y. Kajihara, K. Mashima, K. Nagasuna, A. Nakamura, Chem. Lett., (1981) 671; G. Erker, U. Korek, Z. Naturforsch, B., in press.

9 E.O. Fischer, F.J. Gammel, J.O. Besenhard, A. Frank, D. Neugebauer, J. Organomet. Chem., 191 (1980) 261; J.-C. Daran, Y. Jeannin, Acta Cryst., B, 36 (1980) 1392; C.A. Toledano, A. Parlier, H. Rudler, J.-C. Daran, Y. Jeannin, J. Chem. Soc., Chem. Commun., (1984) 576; C.A. Toledano, H. Rudler, J.-C. Daran, Y. Jeannin, ibid., (1984) 574.

10 G. Erker, K. Engel, U. Dorf, J.L. Atwood, W.E. Hunter, Angew. Chem., 94 (1982) 915; Angew. Chem. Int. Ed. Engl., 21 (1982) 914; Y. Kai, N. Kanehisa, K. Miki, N. Kasai, K. Mashima, K. Nagasuna, H. Yasuda, A. Nakamura, Chem. Lett., (1982) 1979; G. Erker, K. Berg, C. Krüger, G. Müller, K. Angermund, R. Benn, G. Schroth, Angew. Chem., 96 (1984) 445; Angew. Chem. Int. Ed. Engl., 23 (1984) 455; G. Erker, K. Berg, K. Angermund, C. Krüger, Organometallics, 6 (1987) 2620, and ref. therein, see also: E.J. Larson, P.C.V. Dort, J.R. Lakanen, D.W. O'Neill, L.M. Pederson, J.J. McCandless, M.E. Silver, S.O. Russo, J.C. Huffman, Organometallics, 7 (1988) 1183.

11 A.C. Cope, K. Banhölzer, H. Keller, B.A. Pawson, J.J. Wang, H.J.S. Winkler, J. Am. Chem. Soc., 87 (1965) 3644.

12 H. Yasuda, A. Nakamura, Angew. Chem., 99 (1987) 745; Angew. Chem. Int. Ed. Engl., 26 (1987) 723; H. Yasuda, T. Okamoto, Y. Matsuoka, A. Nakamura, Y. Kai, N. Kanehisa, N. Kasai, Organometallics, 8 (1989) 1139.