mmol) was dissolved in 4 mL of hexane. An 8.0-μL aliquot of thiophene (0.10 mmol) and 12.0 μL of 2,5-dimethylthiophene (0.10 mmol) were added to this solution via syringe. The reaction solution was stirred in a glass ampule fitted with a Teflon stopcock for 20 h at 60 °C. The solvent was removed and the product was dissolved in 0.5 mL of C_6D_6. The products observed were **2** (67%) and **3** (33%) by ^1H NMR spectroscopy.

Reaction of 2 with DMAD. A solution of **2** (10 mg, 0.025 mmol) in C_6D_6 (0.5 mL) was treated with DMAD (5 μL, 0.041 mmol) at 25 °C. Complete reaction occurred over 24 h, giving a mixture of four products. These species were characterized by ^1H NMR, ^{31}P NMR, and mass spectroscopies, but could not be easily separated. In addition to thiophene (40%) (^1H NMR: δ 6.920 (d, J = 4.6 Hz, 2 H), 6.815 (d, J = 4.6 Hz, 2 H)), the major organometallic product (60%) was assigned structure **5**. For **5**, ^1H NMR (C_6D_6): δ 1.636 (s, 15 H), 1.224 (d, J = 10.5 Hz, 9 H), 3.498 (s, 3 H), 3.485 (s, 3 H), 3.531 (t, J = 8 Hz, 1 H_b), 4.355 (dd, J = 7.7, 1.4 Hz, 1 H_a), 5.872 (dd, J = 9.8, 8.7 Hz, 1 H_c), 6.104 (d, J = 9.9 Hz, 1 H_d). Homonuclear decoupling indicates connectivity $Rh—CH_a—CH_b=CH_c—CH_d—S$. MS (75 eV) m/e 464 (M^+), 463 ($M^+ - H$), 269 ($[(C_5Me_5)Rh(S)]^+ - H$). The remaining two products were assigned structures **6** and **7**, formed in 25% and 20% yields, respectively. **6** can be independently synthesized by the reaction of DMAD with $(C_5Me_5)Rh(PMe_3)(\eta^2$-phenanthrene).[22] For $(C_5Me_5)Rh(PMe_3)[C_4(COOMe)_4]$ (**6**), ^1H NMR (C_6D_6): δ 1.853 (d, J = 2.5 Hz, 15 H), 0.947 (d, J = 9.0 Hz, 9 H), 3.46 (s, 6 H), 3.39 (s, 6 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −1.06 (d, J = 188 Hz). MS (75 eV): 598 (M^+), 522 ($M^+ - PMe_3$). For $(PMe_3)_4Rh[C_5Me_5C_2(COOMe)_2]$ (**7**), ^1H NMR (C_6D_6): δ 1.224 (virtual q, J = 10.4 Hz, 36 H), 1.345 (s, 6 H), 1.557 (s, 6 H), 1.866 (s, 3 H), 3.641 (s, 3 H), 3.661 (s, 3 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.08 (d, J = 145 Hz). Upon heating to 80 °C for 40 h, compounds **5** and **6** were observed to go away and dimethyl phthalate was formed (^1H NMR: δ 6.876 (dd, J = 5.6, 3.3 Hz, 2 H), 7.512 (dd, J = 5.6, 3.3 Hz, 2 H), 3.499 (s, 6 H); 60% based on **2**). This product was confirmed by GC-MS comparison with an authentic sample. In addition, formation of $S=PMe_3$ (^{31}P NMR: δ 30.45 (br s)) was evident and **7** was the only significant organometallic complex remaining.

X-ray Structural Characterization of 3. Well-formed dark red crystals of the compound were prepared by slow evaporation of a hexane solution. The lattice constants were obtained from 25 centered reflections with values of χ between 5 and 70°. Cell reduction with the program TRACER revealed only a primitive triclinic crystal system. Data were collected on the crystal at −75 °C in accord with the parameters in Table II. The space group was assigned as the centric choice $P\bar{1}$ on the basis of N(z) statistics and Z_{calc}. The correctness of this choice was confirmed by successful solution of the Patterson map, showing a rhodium atom in a general position. The structure was expanded by using the DIRDIF program supplied by the Molecular Structure Corp., whose programs were used for further refinement of the structure.[42] Following full isotropic refinement of the structure containing the non-hydrogen atoms, an absorption correction was applied with the DIFABS absorption correction program. Full least-squares anisotropic refinement of the structure with hydrogens placed in idealized positions based upon a difference Fourier map converged with R_1 = 0.0457 and R_2 = 0.0583.

Acknowledgment. We thank the U.S. Department of Energy (DE-FG02-86ER13569) for their partial support of the studies leading up to this work.

Supplementary Material Available: Tables (S-I–S-V) of bond distances and angles, anisotropic thermal parameters, and coordinates of hydrogen atoms (7 pages); listings of calculated and observed structure factors (20 pages). Ordering information is given on any current masthead page.

(42) $R_1 = (\sum||F_o| - |F_c||)/(\sum|F_o|)$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}(\sum wF_o^2)$, where $w = [\sigma^2(F_o) + (\rho F_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Stereoselective α-Alkylation of Metallacyclic Zirconoxycarbene Complexes—A Case of Asymmetric 1,5-Induction

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Contribution from the Institut für Organische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG, and Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a. d. Ruhr, FRG. *Received January 22, 1990*

Abstract: Coupling of $W(CO)_6$, butadiene, and pinacolone or acetone at the Cp_2Zr template yields the chiral nine-membered metallacyclic zirconoxycarbene complexes $Cp_2ZrOC[=W(CO)_5]CH_2CH=CHCH_2CR^1R^2O$ (**3a**) (R^1 = CH_3, R^2 = $C(CH_3)_3$) and (**3b**) (R^1 = R^2 = CH_3), respectively, exhibiting a trans C=C double bond in the ring. Complex **3b** is deprotonated by the ylide $Ph_3P=CH_2$ at the α-position to the carbene carbon center to yield the chiral unconjugated metallacyclic carbene complex anion **5b**. Ylide deprotonation of **3a** gives the carbanion **5a** which is stereoselectively alkylated at C6 to yield predominately the (2*R**,6*S**)(4,5,6-p*S**) configurated carbene complexes $Cp_2ZrOC[=W(CO)_5]CR^3R^4CH=CHCH_2CR^1R^2O$ (e.g., **6a**, R^3 = H, R^4 = CH_3, 70% de). Repetition of the deprotonation/alkylation reaction sequence stereoselectively yields doubly α-alkylated carbene complexes (e.g., **10**, R^3 = CH_3, R^4 = CD_3, 86% de or **15**, R^3 = C_2H_5, R^4 = $CH_2CH=CH_2$, >96% de). The stereo- and regiochemical assignments are based on X-ray crystal structure analyses of the representative complexes **6a** and **9**. Complex **6a** crystallizes in the space group $P\bar{1}$ with cell parameters a = 11.036 (2) Å, b = 12.998 (3) Å, c = 13.259 (3) Å, α = 97.59 (1)°, β = 103.88 (1)°, γ = 107.59 (1), Z = 2, R = 0.058, R_w = 0.058. Complex **9** crystallizes in the space group $Pna2_1$ with cell parameters a = 15.779 (2) Å, b = 13.736 (3) Å, and c = 13.311 (3) Å, Z = 4, R = 0.050, R_w = 0.027. Hydrolysis of the α-methylated zirconoxycarbene complex **6a** in the presence of diazomethane gives the enol ether $HOC(CH_3)(CMe_3)$-$CH_2CH=CHCH(CH_3)C(OCH_3)=CH_2$ with conservation of the stereochemistry introduced at the metallacyclic starting material. Similarly, treatment of **6a** with water/pyridine *N*-oxide produces (2*R**,6*S**)-*trans*-6-hydroxy-2,6,7,7-tetramethyl-3-octenoic acid (**19**).

Introduction

We have recently introduced a novel method for converting metal carbonyls to transition-metal carbene complexes.[1] The key step of this procedure is the addition of the very reactive (η^2-olefin) group 4 metallocene type reagents to the M—C≡O moiety, followed by a (probably concerted) ring closure reaction to yield, e.g., metallacyclic zirconoxycarbene complexes. Starting from the readily available (butadiene)zirconocene reagent (**1**) one

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(1) (a) Erker, G. Carbene Complex Synthesis with Group 4 Metallocene Reagents. In Organometallics *in Organic Synthesis*; de Meijere, A., tom Dieck, H., Eds.; Springer Verlag: Berlin, 1988. (b) Erker, G. *Angew. Chem.* **1989**, *101*, 411; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397.

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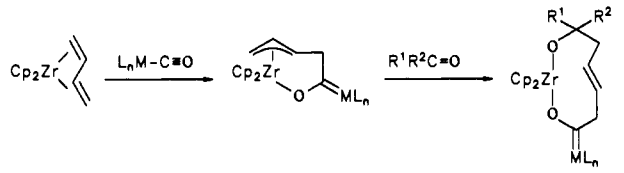
Table I. A Comparison of Selected ^1H, ^{13}C NMR, and IR Data of the Zirconoxycarbene Complexes **3–5**

counterion	**3a** (−)	**4a** (Li^+)	**5a** ($Ph_3PCH_3^+$)	**3b** (−)	**5b** ($Ph_3PCH_3^+$)
^1H NMR[a] in	$CDCl_3$	THF-d_8	THF-d_8	$CDCl_3$	THF-d_8
3-H	1.95	1.83	1.90	1.83	2.11
3-H′	2.10	2.26	2.37	2.19	
4-H	5.17	5.41	5.52	5.11	5.49–5.24 (m)
5-H	4.89	5.17	5.39	4.88	
6-H	3.16			3.04	
6-H′	4.46	4.99	5.28	4.55	5.16
2-CH_3	1.20	1.26	1.32	1.25/1.20	1.22
2-*t*Bu	0.96	0.92	1.02		
Cp	6.33/6.26	6.19/6.34	6.34/6.30	6.31/6.25	6.23
^3J(4-H,5-H)	15.2	15.4	14.9	14.9	*b*
^{13}C NMR[a] in	$CDCl_3$	THF-d_8	THF-d_8	$CDCl_3$	THF-d_8
C3	40.9	40.3	40.3	48.7	47.7
C4	133.2	129.8[c]	130.1[c]	132.1	129.3[c]
C5	127.6	123.1	123.3	127.8	122.7
C6	71.9	128.7[c]	129.7[c]	72.0	128.8[c]
C7	332.2	195.6	196.2	332.5	195.7
IR[d] in	KBr	THF	THF	KBr	THF
	2057	2047	2036	2059	2036
	1964	1949	1932	1968	1942
	1911	1906	1893	1913	1897
			1851		

[a] $^1H/^{13}C$ NMR chemical shifts relative TMS, δ scale. [b] Not determined. [c] Tentative relative assignment. [d] ν(CO) in cm^{-1}.

Scheme I

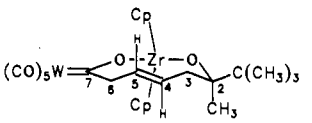


1 2 3

obtains (π-allyl)zirconoxycarbene complexes (**2**)[2] which undergo ring expansion when treated with organic carbonyl compounds to yield nine-membered metallacyclic carbene complexes **3**.[3] The overall reaction sequence is similar to the coupling of a conjugated diene with two ketone equivalents at the group 4 bent metallocene unit to give metalladioxa-*trans*-cyclononene systems, as recently described by H. Yasuda et al.[4]

The trans configurated nine-ring systems **3** exhibit a persistent chiral conformation of the metallaheterocyclic ring system. Barriers of the thermally induced enantiomerization of the chiral ring system of $\Delta G^{\ddagger}_{ent} \approx 16$–17 kcal/mol have been measured for several examples of **3**,[3] being very similar to the racemization activation barrier of the structurally related chiral hydrocarbon *trans*-cyclononene.[5]

Complexes **3** with $R^1 \neq R^2$ should form two diastereoisomers of relative configurations (2*R**)(4,5,6-*pR**) and (2*R**)(4,5,6-*pS**), respectively. There is evidence that both isomers can be formed. However, for many R^1,R^2 substituent combinations, it has been established that the (2*R**)(4,5,6-*pS**) isomer is much preferred at equilibrium conditions. A typical example is the pinacolone addition product **3a** ($R^1 = CH_3$, $R^2 = C(CH_3)_3$), where the (2*R**)(4,5,6-*pS**) diastereoisomer is exclusively observed in solution.[6]



3o (2R*)(4,5,6-pS*)

Ordinary Fischer carbene complexes $L_nM{=}C(OR)CH_2R$ readily undergo base-induced alkylation reactions at the carbon atom adjacent to the carbene carbon center.[7] Starting from metallacyclic zirconoxycarbene complexes **3** the analogous reaction sequence introduces a new chiral center at C6 (or C4, if conjugate electrophilic addition were preferred). We thought that due to the highly rigid framework that is characteristic of complexes **3** there might be a good chance of remote stereocontrol of the alkylation reaction. Ideally, the stereochemical information at the chiral carbon center C2 would be transferred by means of the chiral ring conformation and eventually determine the preferred configuration at the newly formed stereogenic center at C6. This would constitute a rare example of an asymmetric 1,5-induction in a carbon–carbon bond-forming reaction.[8] We have indeed observed that this type of a conformationally controlled remote stereocontrol can be very effective in the base-induced α-alkylation of the chiral metallacyclic zirconoxycarbene complexes **3**. Details of this type of a diastereoselective 1,5-induction process are reported in this paper for selected examples.

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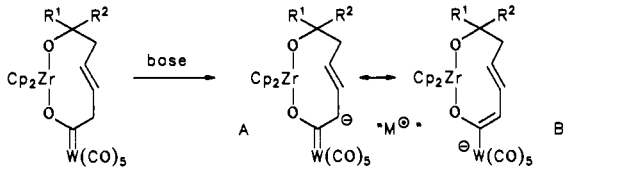
Scheme II



3a (R^1=Me, R^2=tBu) 4a ($^{\oplus}M^{\ominus}$=Li$^{\oplus}$) 5a ($^{\oplus}M^{\ominus}$=$Ph_3\overset{\oplus}{P}CH_3$)

3b (R^1=R^2=Me) 5b

Results and Discussion

Carbanion Formation. The metallacyclic zirconoxycarbene complexes **3a** (ML_n = $W(CO)_5$, R^1 = CH_3, R^2 = $C(CH_3)_3$) and **3b** (ML_n = $W(CO)_5$, R^1 = R^2 = CH_3) were used as starting materials for α-deprotonation reactions. These complexes were prepared as described previously by reacting the (*s-cis-/s-trans*-η^4-butadiene)zirconocene equilibrium mixture with $W(CO)_6$ to give **2a** (ML_n = $W(CO)_5$), followed by treatment with pinacolone or acetone, respectively.[3]

Complex **3a** was reacted with 1 equiv of *n*-butyllithium in ether at 0 °C to give **4a**. The NMR and IR spectra indicated that a clean α-deprotonation was achieved (see Table I). Noteworthy are the shifts of the IR ν(CO) bands to lower wave numbers[9] and the drastic chemical shift changes of some of the ^{13}C NMR resonances attributed with the formation of the carbanionic system. Thus the signal of the "carbene carbon atom" (C7) has featured an upfield shift of >130 ppm upon converting **3a** into **4a**, whereas the C6 resonance has been decreased by some 50 ppm. The ^3J(H4,H5) coupling constant of 15.4 Hz indicates the presence of an intact trans C=C double bond in the ring. The lithiated complex **3a** turned out to be rather sensitive. It was difficult to handle at higher concentrations for prolonged times without some decomposition taking place. Therefore, we have prepared the analogous carbanionic system by using a different counterion.

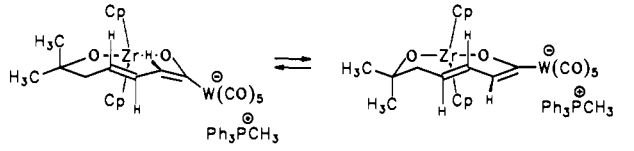
This was achieved by using the phosphorus ylide methylenetriphenylphosphorane in benzene solution as a base. Reaction of **3a** with 1 molar equiv of $Ph_3P{=}CH_2$ thus yielded the phosphonium salt **5a** as an orange-colored oil. Again, clean α-deprotonation has occurred as evidenced by the very characteristic ^1H, ^{13}C NMR, and IR spectra (see Table I). Similar ^1H and ^{13}C NMR shift differences as for the **3a** → **4a** transformation are observed for the **3a** → **5a** interconversion, whereas **5a** exhibits even lower ν(CO) values as compared to the corresponding α-lithio compound **4a**.

Both **4a** and **5a** contain a chiral center at C2. Therefore, the $^1H/^{13}C$ NMR signals of diastereotopic Cp ligands are observed for each complex at all temperatures. Only using a substrate lacking this inherent stereochemical information has enabled us to gain insight into the symmetry properties of the preferred ring conformation of the anionic systems. We therefore have reacted the acetone-derived nine-membered metallacyclic zirconoxycarbene complex **3b** with $Ph_3P{=}CH_2$ as a base and obtained the phosphonium salt **5b**.

Complex **5b** shows the typical IR and NMR features characteristic of anion formation (see Table I). Moreover, at ambient temperature it features only one Cp resonance each in the ^1H (δ 6.23) and ^{13}C (δ 112.2) NMR spectra. Similarly only one set of CH_3 resonances is observed. However, variable-temperature ^1H NMR spectroscopy has revealed that complex **5b** possesses a lower overall molecular symmetry than C_s in solution.

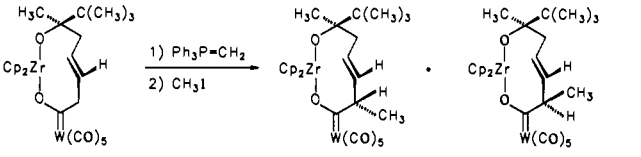
Decreasing the monitoring temperature results in broadening of the NMR signals. Below the coalescence temperature T_c = 225 K (at 4.7 T) the ^1H NMR methyl group resonance splits into two different signals ($\Delta\delta$ = 30.6 Hz at 203 K). Similar splitting of the cyclopentadienyl ^1H NMR resonance into two singlets of equal intensity is observed at low temperature. Apparently, the anionic metallacyclic complex **5b** has retained a chiral overall ring conformation similar to that of its precursor system **3**. This means that the trans C=C bond between carbon atom C4 and C5 is being retained upon carbanion formation. The variable-temperature NMR spectra of **5b** indicate that there is no efficient delocalization between the C4/C5 and C6/C7 double bond systems (resonance form B) in the ground state of the deprotonated metallacyclic zirconoxycarbene complexes. However, the barrier of enantiomerization of **5b** is markedly lower than that of the neutral system **3b** [**5b**: $\Delta G^{\ddagger}_{ent}$(225 K) = 11.1 ± 0.4 kcal/mol as estimated from the coalescence of the resonances of the diastereotopic CH_3 substituents at C2; **3b**: $\Delta G^{\ddagger}_{ent}$(323 K) = 16.6 ± 0.4 kcal/mol]. This indicates that C7,C6,C5,C4-π-conjugation may be of some importance for lowering the energy content of the transition state of the ring topomerization process.

Scheme III



5b: $\Delta G^{\ddagger}_{ent}$(225K) = 11.1 ± 0.4 kcal/mol (THF-d_8)

Scheme IV



3a (2R*)(4,5,6-pS*) 6a (2R*,6S*)(4,5,6-pS*) 7a (2R*,6R*)(4,5,6-pS*)

Alkylation Reactions. The α-lithiated zirconoxycarbene complex **4a** does not react cleanly with electrophilic alkylation reagents such as methyl iodide or benzyl bromide. In contrast, the phosphonium salt **5a** is more reactive. It can cleanly be alkylated under mild conditions. If one adds 1 equiv of methyl iodide to a solution of the phosphonium salt **5a** in tetrahydrofuran at 0 °C and then allows the mixture to slowly warm up to room temperature, one observes precipitation of methyltriphenylphosphonium iodide and the formation of a monoalkylated zirconoxycarbene complex. The organometallic product was isolated in ca. 60% yield. The spectroscopic data reveal that exclusively α-alkylation was achieved. Moreover, this α-alkylation process is rather stereoselective. In principle, four different stereoisomers exhibiting trans C4,C5 double bonds could have been formed, characterized by relative configurations (2*R**,6*S**)(4,5,6-*pS**), (2*R**,6*R**)(4,5,6-*pS**), (2*R**,6*S**)(4,5,6-*pR**), and (2*R**,6*R**)(4,5,6-*pR**), respectively. Out of these, only two are observed, in a ratio of ca. 85:15. Both, the major and the minor reaction products exhibit a trans-configured C=C double bond between carbon centers C4 and C5 [^3J(H4,H5) = 15.2 Hz (**6a**, 85%); 15.3 Hz (**7a**, 15% component)]. A comparison of selected characteristic ^1H NMR data of **3a**, **6a**, and **7a** reveals that the ylide-base induced α-alkylation of **3a** has resulted in a predominant substitution of the hydrogen atom H6 at δ 3.16 ppm by a methyl group to give **6a**, whereas exchange of H6′ at δ 4.46 of **3a** has yielded the minor reaction product **7a**. From these observations it is indicated that the products formed are only distinguished by exhibiting opposite configurations at C6 and hence are of relative configurations (2*R**,6*S**)(4,5,6-*pS**) and (2*R**,6*R**)(4,5,6-*pS**). This overall stereochemical assignment was confirmed by an X-ray crystal structure determination of the major stereoisomer formed. Complex **6a** was found to be correctly described by a (2*R**,6*S**)(4,5,6-*pS**) relative stereochemistry.

In the solid state, complex **6a** shows interesting bonding parameters around the Cp_2Zr unit. The Cp(centroid)-Zr-Cp(centroid) angle (126.1°) is as typically found for many group 4 bent metallocene complexes.[10] However, the σ-bond angle at

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Table II. A Comparison of Selected ^{1}H NMR Data of Complexes **3a**, **6a**, **7a**, and **9**

	3a	**6a**	**7a**	**9**
3-H	1.95	1.72	*b*	1.73
3-H′	2.10	1.97	*b*	1.94
4-H	5.17	5.04	*b*	5.05
5-H	4.89	4.85	4.62	4.80
6-H	3.16		3.05	
6-H′	4.46	4.27		
2-CH_3	1.20	0.94	*b*	0.93
6-CH_3		1.17	1.62	1.56/1.12
2-*t*Bu	0.96	0.84	0.83	0.84
Cp	6.33/6.26	6.09/6.00	6.17/5.97	6.08/6.06
^3J (4-H,5-H)	15.2	15.2	15.3	15.6

[a] 200 MHz, **3a** in $CDCl_3$; **6a** and **7a** in $C_6D_6/CDCl_3$ 1:1 TMS. [b] Not localized.

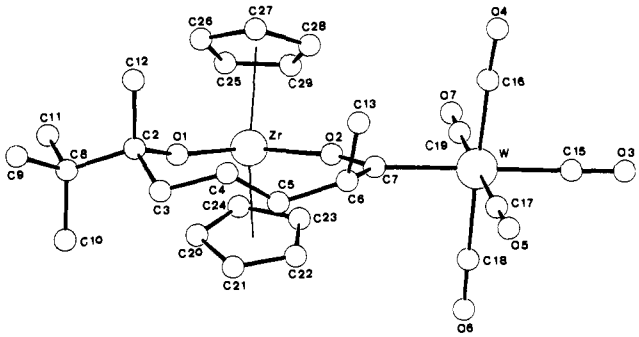


Figure 1. A projection of the molecular structure of **6a** in the crystal.

the early transition-metal center (O1–Zr–O2: 106.3 (2)°) is very large for a four-coordinate pseudotetrahedral Cp_2ZrL_2 moiety. It is indicative for a pronounced metal oxygen π-interaction with both chalcogen termini of the σ-ligand chain. This is substantiated by the pertinent bonding parameters around both oxygen centers featuring very large bonding angles and short metal oxygen bond distances [Zr–O1, 1.941 (5) Å; Zr–O1–C2, 164.8 (5)°; Zr–O2, 2.092 (5) Å; Zr–O2–C7, 168.0 (5)°].[11,12] The C7–O2 distance is short at 1.26 (1) Å as is very typical for many zirconoxycarbene complexes.[2,13] Compound **6a** exhibits a high metal acyl-type character. In the crystal an eclipsed conformation of the [Zr]-OC(R)···$W(CO)_5$ unit is observed, in contrast to the staggered arrangement found for the majority of the conventional Fischer-type carbene complexes.[14]

The bonding features around the rigid coplanar -O1-[Zr]-O2-C7 structural unit forces the metallacycle into a rather flat crown-shaped arrangement. This leads to a clear differentiation of pseudo-axial and -equatorial substituents at the sp^3-hybridized ring carbon atoms C2, C3, and C6. In **6a**, the bulky *tert*-butyl group at C2 is oriented pseudoequatorially, i.e., almost parallel

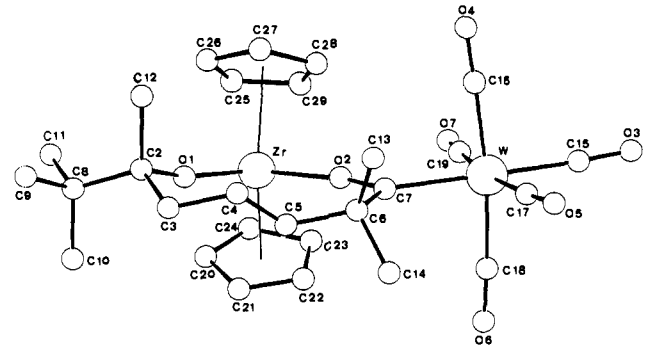
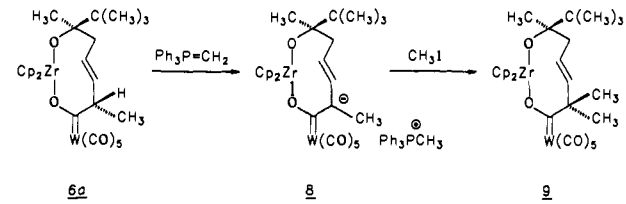
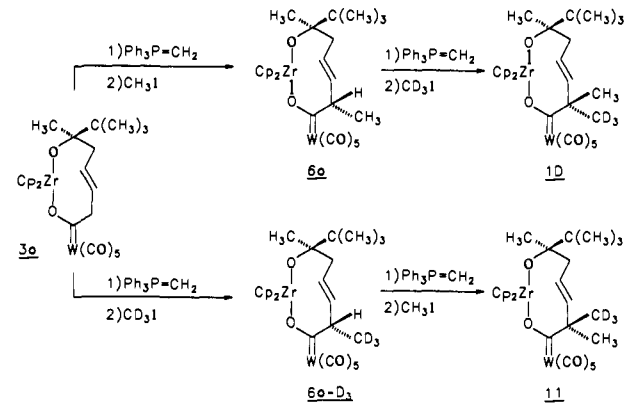


Figure 2. A view of the molecular structure of **9** in the crystal.

Scheme V



Scheme VI



to the mean ring plane, whereas the methyl substituent at C2 is staged pseudoaxially, i.e., the C2–C12 vector being almost normal (85.7°) to the mean plane going through Zr,O1,O2,C2,C7.

In the X-ray diffraction analysis of **6a** the position of the C3C6 unit containing the C=C double bond between C4 and C5 was localized without the disorder problems which have often been encountered with many other metallacyclic zirconoxycarbene complexes of similar structural types.[3,6] The plane of the C4–C5 double bond is inclined with an angle of 107° to the ring plane of the metallacycle featuring the hydrogen at C4 cis to the methyl substituent at C2, whereas the hydrogen at the sp^2 carbon atom C5 is positioned trans to C12. Thus the stereochemical descriptor of the chirality elements of the basic metallacyclic system is (2*R**)(4,5,6-*pS**).

The α-alkylation reaction has led to a methyl group becoming attached at C6 in a pseudo-axial position. This newly introduced alkyl substituent is found to be in a cis relationship with the smaller substituent at the chiral carbon center at C2 (relative configuration 6*S**). The C13 methyl carbon is cis oriented to the hydrogen atom at C4, and it is trans oriented to the hydrogen atom at the adjacent sp^2 carbon center C5 at the nine-membered metallacyclic ring system.

Complex **6a** is cleanly deprotonated at C6 by using the ylide $Ph_3P{=}CH_2$ as a base as well, yielding the zirconoxycarbene phosphonium salt **8**. Subsequent treatment of **8** with methyl iodide gives a single alkylation product **9**. According to its spectroscopic data (see Table II) and the results of an X-ray crystal structure analysis, the second alkylation process is again highly regioselective. Base-induced alkylation is exclusively observed to take place at the carbon center C6 adjacent to the sp^2-hybridized

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Table III. Selected Bonding Parameters of the Zirconoxycarbene Tungsten Complexes **6a** and **9**

	6a	9		6a	9
W–C(7)	2.193 (8)	2.212 (7)	Zr–C(28)	2.56 (1)	2.550 (9)
W–C(15)	2.02 (1)	1.999 (9)	Zr–C(29)	2.57 (1)	2.53 (1)
W–C(16)	2.00 (1)	2.00 (1)	O(1)–C(2)	1.424 (9)	1.418 (9)
W–C(17)	2.044 (9)	2.014 (9)	O(2)–C(7)	1.26 (1)	1.269 (9)
W–C(18)	2.05 (1)	2.04 (1)	C(2)–C(3)	1.54 (1)	1.55 (1)
W–C(19)	2.05 (1)	2.017 (9)	C(2)–C(8)	1.55 (1)	1.52 (1)
Zr–O(1)	1.941 (5)	1.918 (5)	C(2)–C(12)	1.52 (1)	1.58 (1)
Zr–O(2)	2.092 (5)	2.091 (5)	C(3)–C(4)	1.49 (1)	1.49 (1)
Zr–C(20)	2.50 (1)	2.50 (1)	C(4)–C(5)	1.32 (1)	1.31 (1)
Zr–C(21)	2.54 (1)	2.557 (9)	C(5)–C(6)	1.52 (1)	1.50 (1)
Zr–C(22)	2.54 (1)	2.56 (1)	C(6)–C(7)	1.55 (1)	1.56 (1)
Zr–C(23)	2.53 (1)	2.54 (1)	C(6)–C(13)	1.53 (1)	1.53 (1)
Zr–C(24)	2.51 (1)	2.514 (9)	C(6)–C(14)		1.54 (1)
Zr–C(25)	2.50 (1)	2.52 (1)	C(8)–C(9)	1.52 (1)	1.51 (1)
Zr–C(26)	2.53 (1)	2.527 (9)	C(8)–C(10)	1.51 (1)	1.54 (1)
Zr–C(27)	2.53 (1)	2.535 (9)	C(8)–C(11)	1.52 (1)	1.52 (1)
C(2)–O(1)–Zr	164.8 (5)	163.9 (5)	C(6)–C(5)–C(4)	127.7 (8)	129.9 (8)
C(7)–O(2)–Zr	168.0 (5)	169.5 (5)	C(14)–C(6)–C(13)		110.0 (7)
C(12)–C(2)–C(8)	111.3 (7)	109.7 (6)	C(14)–C(6)–C(7)		109.3 (7)
C(12)–C(2)–C(3)	109.4 (7)	107.0 (7)	C(14)–C(6)–C(5)		106.8 (7)
C(12)–C(2)–O(1)	110.2 (7)	108.3 (6)	C(13)–C(6)–C(7)	108.3 (7)	106.8 (6)
C(8)–C(2)–C(3)	111.2 (7)	112.6 (7)	C(13)–C(6)–C(5)	114.3 (7)	112.8 (7)
C(8)–C(2)–O(1)	108.2 (6)	111.2 (7)	C(7)–C(6)–C(5)	111.2 (7)	111.2 (7)
C(3)–C(2)–O(1)	106.4 (6)	107.8 (5)	C(6)–C(7)–O(2)	111.9 (7)	111.8 (6)
C(4)–C(3)–C(2)	111.0 (7)	112.6 (7)	C(6)–C(7)–W	122.7 (5)	128.0 (5)
C(5)–C(4)–C(3)	123.3 (9)	124.1 (8)	O(2)–C(7)–W	125.4 (6)	120.2 (5)

Table IV. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Standard Deviations in Parentheses of **6a**[a]

atom	x	y	z	U_{eq}
W	0.4446 (1)	0.8969 (1)	0.7839 (1)	0.044 (1)
Zr	−0.0577 (1)	0.7496 (1)	0.6711 (1)	0.036 (1)
O(1)	−0.1632 (5)	0.7270 (4)	0.5248 (4)	0.040 (4)
O(2)	0.1413 (5)	0.8010 (4)	0.6715 (4)	0.046 (4)
O(3)	0.7219 (6)	0.9728 (7)	0.9608 (5)	0.091 (7)
O(4)	0.4917 (8)	0.6735 (6)	0.7178 (7)	0.102 (8)
O(5)	0.6000 (7)	1.0127 (6)	0.6347 (6)	0.086 (7)
O(6)	0.4068 (8)	1.1240 (6)	0.8666 (6)	0.094 (8)
O(7)	0.2989 (7)	0.7884 (6)	0.9413 (5)	0.094 (7)
C(2)	−0.2168 (8)	0.6963 (6)	0.4118 (6)	0.044 (6)
C(3)	−0.1251 (8)	0.7820 (8)	0.3680 (6)	0.057 (7)
C(4)	0.0145 (9)	0.7842 (8)	0.4036 (7)	0.058 (7)
C(5)	0.1072 (8)	0.8579 (7)	0.4860 (6)	0.049 (6)
C(6)	0.2429 (7)	0.8551 (7)	0.5425 (6)	0.046 (6)
C(7)	0.2535 (7)	0.8442 (6)	0.6591 (6)	0.040 (6)
C(8)	−0.3603 (8)	0.7000 (7)	0.3819 (6)	0.048 (6)
C(9)	−0.4323 (9)	0.6528 (8)	0.2637 (8)	0.074 (8)
C(10)	−0.3605 (9)	0.8160 (8)	0.4100 (7)	0.063 (8)
C(11)	−0.4419 (8)	0.6307 (8)	0.4427 (8)	0.071 (8)
C(12)	−0.2163 (9)	0.5818 (8)	0.3704 (7)	0.062 (7)
C(13)	0.2796 (9)	0.7630 (9)	0.4879 (7)	0.072 (9)
C(15)	0.6210 (9)	0.9463 (8)	0.8982 (7)	0.062 (8)
C(16)	0.4707 (9)	0.7540 (8)	0.7396 (8)	0.065 (8)
C(17)	0.5438 (8)	0.9712 (7)	0.6863 (7)	0.054 (7)
C(18)	0.4201 (9)	1.0424 (8)	0.8373 (7)	0.062 (8)
C(19)	0.3485 (9)	0.8262 (8)	0.8853 (7)	0.062 (8)
C(20)	−0.1832 (9)	0.8700 (8)	0.7204 (8)	0.064 (8)
C(21)	−0.077 (1)	0.9408 (7)	0.6915 (8)	0.066 (9)
C(22)	0.037 (1)	0.9514 (8)	0.768 (1)	0.09 (1)
C(23)	0.004 (1)	0.891 (1)	0.8423 (8)	0.08 (1)
C(24)	−0.130 (1)	0.8424 (8)	0.8123 (8)	0.07 (1)
C(25)	−0.167 (1)	0.5952 (9)	0.749 (1)	0.09 (1)
C(26)	−0.183 (1)	0.5443 (8)	0.641 (1)	0.076 (9)
C(27)	−0.054 (1)	0.5548 (7)	0.6396 (8)	0.067 (9)
C(28)	0.033 (1)	0.6062 (8)	0.7436 (9)	0.072 (9)
C(29)	−0.037 (1)	0.6302 (9)	0.8092 (8)	0.08 (1)
C(31)	0.8596	0.7585	0.0621	0.090
C(32)	0.7434	0.6770	0.0251	0.090
C(33)	0.7337	0.5720	0.0238	0.090
C(34)	0.8474	0.5464	0.0619	0.090
C(35)	0.9686	0.6271	0.1005	0.090
C(36)	0.9751	0.7357	0.1008	0.090

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

Table V. Atomic Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å²) with Standard Deviations in Parentheses of **9**[a]

atom	x	y	z	U_{eq}
W	0.0244 (1)	0.2030 (1)	0.0000	0.047 (1)
Zr	0.0679 (1)	0.3448 (1)	−0.3409 (1)	0.036 (1)
O(1)	0.1196 (3)	0.2780 (3)	−0.4515 (3)	0.039 (3)
O(2)	0.0707 (4)	0.2514 (4)	−0.2170 (4)	0.044 (3)
O(3)	−0.0676 (5)	0.2302 (5)	0.2086 (5)	0.095 (6)
O(4)	−0.1359 (5)	0.1024 (6)	−0.0966 (7)	0.108 (7)
O(5)	0.0848 (5)	0.0056 (5)	0.1007 (5)	0.082 (5)
O(6)	0.1923 (5)	0.3156 (6)	0.0619 (6)	0.115 (7)
O(7)	−0.0557 (5)	0.4051 (4)	−0.0608 (5)	0.076 (5)
C(2)	0.1433 (5)	0.2071 (6)	−0.5235 (5)	0.050 (6)
C(3)	0.2028 (5)	0.1332 (5)	−0.4712 (5)	0.048 (5)
C(4)	0.1665 (5)	0.0941 (6)	−0.3761 (7)	0.051 (6)
C(5)	0.1820 (6)	0.1301 (6)	−0.2872 (7)	0.049 (6)
C(6)	0.1439 (5)	0.1051 (6)	−0.1874 (6)	0.043 (5)
C(7)	0.0846 (5)	0.1885 (6)	−0.1492 (6)	0.040 (5)
C(8)	0.1836 (7)	0.2539 (7)	−0.6150 (6)	0.054 (6)
C(9)	0.2034 (8)	0.1824 (8)	−0.6976 (7)	0.09 (1)
C(10)	0.2660 (6)	0.3046 (8)	−0.5832 (7)	0.080 (7)
C(11)	0.1277 (7)	0.3327 (8)	−0.6593 (7)	0.069 (7)
C(12)	0.0613 (6)	0.1494 (6)	−0.5561 (7)	0.068 (7)
C(13)	0.0904 (6)	0.0123 (6)	−0.1905 (7)	0.060 (6)
C(14)	0.2177 (6)	0.0923 (7)	−0.1134 (7)	0.069 (7)
C(15)	−0.0318 (8)	0.2202 (6)	0.1333 (7)	0.068 (7)
C(16)	−0.0775 (6)	0.1385 (7)	−0.0601 (7)	0.061 (7)
C(17)	0.0652 (6)	0.0768 (7)	0.0599 (6)	0.056 (6)
C(18)	0.1310 (7)	0.2753 (7)	0.0433 (7)	0.072 (8)
C(19)	−0.0267 (6)	0.3309 (6)	−0.0431 (6)	0.056 (5)
C(20)	0.1692 (8)	0.4812 (8)	−0.3731 (7)	0.077 (8)
C(21)	0.2150 (6)	0.4179 (7)	−0.314 (1)	0.073 (8)
C(22)	0.1775 (9)	0.4172 (8)	−0.2207 (9)	0.079 (9)
C(23)	0.1095 (8)	0.480 (1)	−0.221 (1)	0.09 (1)
C(24)	0.1059 (8)	0.5209 (6)	−0.317 (1)	0.080 (9)
C(25)	−0.0609 (6)	0.4304 (8)	−0.4088 (8)	0.067 (7)
C(26)	−0.0573 (6)	0.3434 (9)	−0.4590 (7)	0.069 (7)
C(27)	−0.0734 (5)	0.2706 (6)	−0.3885 (7)	0.056 (6)
C(28)	−0.0867 (5)	0.3160 (7)	−0.2948 (7)	0.058 (7)
C(29)	−0.0782 (6)	0.4130 (7)	−0.3060 (7)	0.064 (7)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\cdot\bar{a}_j$.

carbene carbon atom C7. In the solid state only one diastereoisomer **9** is found which is again characterized by a (2*R**)-(4,5,6-*pS**) relative stereochemical configuration (see Figure 2 and Tables II and V).

Table VI. Crystal Structure Determination of **6a** and **9**

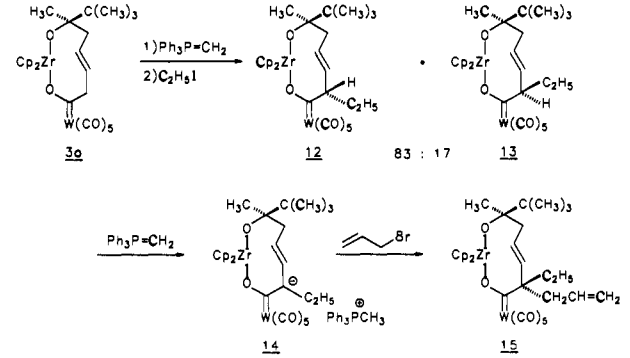
	6a	**9**
formula	$C_{27}H_{30}O_7WZr \times C_7H_8$	$C_{28}H_{32}O_7WZr$
mw	833.7	755.6
space group	$P\bar{1}$	$Pna2_1$
a (Å)	11.036 (2)	15.799 (2)
b (Å)	12.998 (3)	13.736 (3)
c (Å)	13.259 (3)	13.311 (3)
α (deg)	97.59 (1)	90.
β (deg)	103.88 (1)	90.
γ (deg)	107.59 (1)	90.
V (Å^3)	1717	2888.8
d_{calc} (g cm^{-3})	1.61	1.74
μ (cm^{-1})	37.60	44.59
Z	2	4
λ (Å)	0.71069	0.71069
measd reflcns	11898 ($\pm h,\pm k,+l$)	8988 ($\pm h,+k,+l$)
sin θ/λ_{max}	0.75	0.83
empirical abs. corr (min–max)	0.884–0.999	0.948–0.999
independent reflcns	11898	8380
obsd reflcns	8538	4846
refined parameters	325	333
R	0.058	0.50
R_w	0.058	0.27
ρ (max), e/Å^3	1.86	2.15

Starting from **3a**, the stereochemical result of the 2-fold alkylation process at C6 is thus dependent on the order of the alkylation reagents applied. This was demonstrated experimentally by using CH_3I and CD_3I, respectively, as the alkylating electrophiles. Treatment of **3a** with a base ($Ph_3P{=}CH_2$) followed by CH_3I addition yielded **6a** predominantly, as was described above. The resulting **6a**/**7a** mixture (85:15) was then α-deprotonated by using methylenetriphenylphosphorane, and CD_3I was added to give a 93:7 mixture of the epimeric zirconoxycarbene complexes **10** and **11**. We then reacted the carbene complex **3a** with $Ph_3P{=}CH_2$ and subsequently with CD_3I to give **6a**-d_3 [(2*R**,6*S**)(4,5,6-*pS**)] as the main product. In turn, this was α-deprotonated and then reacted with CH_3I to yield the (2*R**,6*R**) configurated geminally dialkylated complex **11** as the major product [**10**:**11** = 9:91]. The diastereoselectivity of the second alkylation step is >80% de, which represents an even more effective 1,5-asymmetric induction than observed for the first α-alkylation step starting from **3a**.

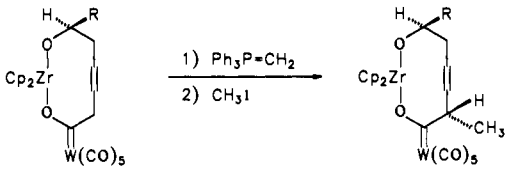
Orientating experiments have revealed that highly regio- and stereoselective alkylation reactions can be carried out with systems **3** carrying various other substituents or using other electrophilic alkylating reagents as well. This shall be illustrated by the following representative examples. Ylide deprotonation of **3a** followed by alkylation with ethyl iodide gave a 83:17 mixture of **12** and **13**. Again, the major stereoisomer was identified to have a (2*R**,6*S**)(4,5,6-*pS**) relative configuration by comparison of typical spectroscopic data. Subsequent α-deprotonation with $Ph_3P{=}CH_2$ and alkylation with allyl bromide proceeded with predominant overall stereochemical inversion at the ring carbon C6 to give only a single dialkylation product (**15a**) within the limits of the accuracy of the ^1H NMR analysis.

It appears that the α-alkylation of aldehyde-derived nine-membered metallacyclic zirconoxycarbene complexes (e.g., **3c**, **3d**) proceeds with effective stereochemical 1,5-induction as well. At room temperature complex **3c** is obtained as a mixture of cis and trans C=C double bond isomers [*cis*-/*trans*-**3c** = 45:55].[3b] Deprotonation with $Ph_3P{=}CH_2$ followed by alkylation with methyl iodide yields a mixture of two major isomers (*cis*-**6c**, *trans*-**6c** ca. 35:45 ratio) which is probably formed by addition of the methyl electrophile at C6 by an orientation cis to the small pseudo-axial hydrogen substituent at the inducing stereogenic center C2. Two minor components (probably *cis*- and *trans*-**7c**) can in addition be observed by ^1H NMR spectroscopy (each ca. 10%). Similarly, the deprotonation/alkylation reaction sequence starting from **3d** (cis/trans ratio 60:40)[3b] yields a 60:40 mixture of monoalkylation products which we assign the structures *cis*- and *trans*-**6d** (for details see Experimental Section).

Scheme VII



Scheme VIII



cis-/trans-**3c** (R = C_2H_5) cis-/trans-**6c**

cis-/trans-**3d** (R = $CH{=}CH_2$) cis-/trans-**6d**

Formation of Metal-Free Organic Products. Any application of a stereoselective CC-coupling reaction sequence as described above in organic synthesis must be supported by an easy means of removing the transition-metal complex template (here Zr) and functional group (here $W(CO)_5$). Since the zirconoxycarbene moiety is far less reactive than ordinary Fischer carbene complexes, the early transition-metal center has first to be removed from the complex to achieve a situation which may allow us to take advantage of the broad reaction spectrum of the conventional heteroatom-stabilized carbene complex functionality.[15] We have shown recently that controlled hydrolysis of zirconoxycarbene complexes **3** yields the hydroxycarbene tungsten species $HOCR^1R^2CH_2CH{=}CHCH_2C[{=}W(CO)_5]OH$[16] which are very unstable with regard to rapidly losing $W(CO)_6$. However, the hydroxycarbene complexes can very efficiently be transformed into simple organic products without elimination of hexacarbonyltungsten if generated in the presence of sufficiently reactive trapping reagents such as excess diazomethane[17] or pyridine *N*-oxide.[18]

We have, therefore, reacted the 85:15 mixture of the α-methylated zirconoxycarbene complexes **6a** and **7a** with H_2O in tetrahydrofuran to which we added an ethereal solution of diazomethane.[19] A mixture of three metal free organic products was isolated in a combined yield of 88%. The mixture consisted of the enol ethers **16**, **17**, and **18** in a 70:10:20 ratio. According to their spectroscopic features compounds **16** and **17** appear to have retained the stereochemical information characteristics of their precursors **6a** and **7a**, whereas formation of the conjugated diene system in the minor product **18** has eliminated the stereogenic center formed in the α-alkylation process starting from **3a**.

In a similar degradation process, the **6a**/**7a** mixture was hydrolyzed in tetrahydrofuran in the presence of pyridine *N*-oxide.

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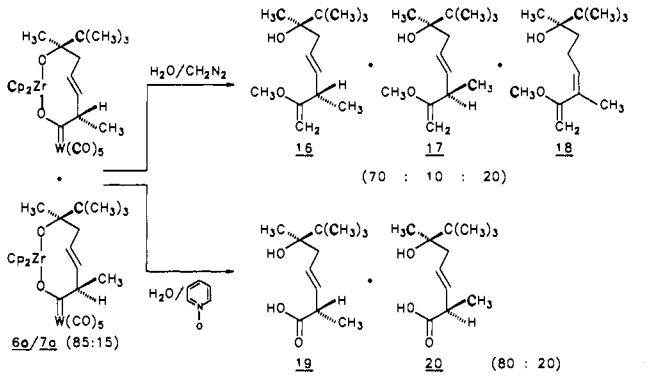
(17) (a) Casey, C. P.; Bertz, S. H.; Burkhardt, T. J. *Tetrahedron Lett.* **1973**, *16*, 1421. (b) See also ref 9b.

(18) Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 2672. Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 3552. Lukehart, C. M.; Zeile, J. V. *J. Organomet. Chem.* **1975**, *97*, 421.

(19) The zirconoxycarbene complexes were shown to be not reactive enough for producing zirconium enolates when treated with diazomethane. We have noted, however, that complex **9** was converted into a zirconium enolate in a slow reaction when treated with an excess of the ylide $Ph_3P{=}CH_2$.

Scheme IX



We have isolated a mixture of the substituted unconjugated 6-hydroxyoctenoic acids **19** and **20** in a 80:20 ratio. Again, it appears that the stereochemical information present in the organometallic system has almost completely been retained during formation of the final organic reaction product.

Conclusion

We have shown that a metal carbonyl, butadiene, and an organic carbonyl compound can be assembled at the Cp_2Zr template and coupled with carbon–carbon bond formation to yield chiral nine-membered metallacyclic systems **3**. Thermodynamically controlled diastereoselection (the $\Delta G^{\ddagger}_{ent}$ barrier of the metalladioxa-*trans*-cyclononene system is usually about 16–17 kcal/mol) can lead to one diastereoisomer predominantly if a suitable controlling stereogenic center is introduced at carbon atom C2. Complexes **3** can subsequently undergo base-induced alkylation reactions with a significant 1,5-asymmetric induction. It is, of course, not the direct steric influence of the asymmetric carbon center at C2 that determines the re/si discrimination at the newly formed stereogenic center C6. The stereochemical information is rather transferred across such a large distance by means of the rigid chiral conformation of the nine-membered metallacyclic ring system.

A key feature of this process is the observation that the anionic intermediate **5**, formed by deprotonation of **3**, has clearly retained the chiral ring conformation. There is no indication of a planarization of the ring system in the ground state of **5**, which would lead to a conjugation of the C7–C6 and C5–C4 π-systems. Only the transition state of the thermally induced nine-membered ring inversion process seems to be influenced by some noticeable C7–C4 π-conjugation; this lowers the $\Delta G^{\ddagger}_{ent}$ barrier of the anionic system by some 5–6 kcal/mol relative to the neutral parent system. Our detailed structural investigation of the alkylation process has revealed that the incoming electrophile becomes attached at C6 predominantly from the si face, i.e., the alkyl substituent at C6 is becoming cis oriented to the smaller axially positioned substituent at the stereogenic center C2 which controls the overall stereochemical outcome of this reaction. We assume that this way of a cis addition is preferred over the trans attack to avoid an unfavorable interaction between the incoming electrophile and the hydrogen substituent at C5.

We have shown that both metal centers can be cleaved conveniently from the final organometallic product with conservation of the stereochemistry at the stereogenic carbon centers. This should make this stereocontrolled CC-coupling process proceeding with remote asymmetric induction an interesting method for the construction of organic target molecules. Incorporation of chiral bent metallocene units, some of which have become readily available enantiomerically pure,[20] should allow for enantioselective variations of this type of stereocontrolled CC-coupling reactions by using rigid organometallic systems.

Experimental Section

Reactions with organometallic compounds were carried out in an argon atmosphere with Schlenk type glassware. Solvents were freshly distilled from potassium/benzophenone (THF, benzene), sodium/benzophenone (toluene), aluminium hydride (diethyl ether, *n*-hexane, petroleum ether 30–50), or P_4O_{10} (methylene chloride) prior to use. Benzene-d_6 and THF-d_8 were dried over sodium/potassium alloy and $CDCl_3$ over P_4O_{10} (Sicapent, Merck) and subsequently distilled. Methyl iodide and methyl iodide-d_3 were distilled over CaH_2, and ethyl iodide was distilled over sodium[21] prior to use. Allyl bromide was distilled. Pyridine *N*-oxide was sublimed in vacuo. Stock solutions of $Ph_3P{=}CH_2$ and pyridine *N*-oxide with known concentrations were prepared and used in the reactions. The following spectrometers were used: NMR Bruker WP 200 SY (^{1}H 200.1 MHz, ^{13}C 50.3 MHz), ^{1}H chemical shifts are given with multiplicity, integral, and assignment in parentheses; ^{13}C NMR data give ^1J(C,H) coupling constants in parentheses; IR Nicolet 5DXC FT IR spectrometer; MS Varian MAT CH7 and Finnigan 8200 MAT (exact mass). Elemental analyses were carried out at the Institut für Anorganische Chemie der Universität Würzburg. Melting points are uncorrected. Complexes **1**,[22] **2** ($ML_n = W(CO)_5$),[2a] **3a**,[6] **3b**,[3a] **3c**,[3b] **3d**,[3b] and $Ph_3P{=}CH_2$[23] were prepared according to literature procedures. We thank Prof. Dr. H. Quast for a gift of methyl iodide-d_3.

Reaction of 3a with *n*-Butyllithium. To a solution of **3a** (140 mg, 0.19 mmol) in 3 mL of diethyl ether was added 0.14 mL of a 1.41 M ethereal *n*-butyllithium solution (0.20 mmol) dropwise at 0 °C, on which the reaction mixture turned to orange. The mixture was stirred for 5 min. The solvent was evaporated, and the residue was dried in vacuo to give 170 mg of **4a** as a very air-sensitive orange-brown powder, which turned dark above 200 °C. ^{1}H NMR spectroscopy showed the coordination of 2 equiv of diethyl ether: ^{1}H NMR (THF-d_8) δ 6.19/6.15 (each: s, 5 H, H-Cp), 5.41 (dddd, 1 H, H4), 5.17 (ddd, 1 H, H5), 4.99 (m, 1 H, H6), 2.26 (br t, 1 H, H3′), 1.83 (ddt, 1 H, H3), 1.26 (s, 3 H, 2-CH_3), 0.92 (s, 9 H, $-C(CH_3)_3$), coupling constants (Hz), ^2J = 11.5 (H3, H3′), ^3J = 3.8 (H3, H4), 10.0 (H3′, H4), 15.4 (H4, H5), 2.7 (H5, H6), ^4J = 1.4 (H3, H5), 0.9 (H4, H6), ^5J = 1.7 (H3, H6); ^{13}C NMR (THF-d_8) δ 208.9 ($C\text{-}CO_{trans}$), 206.2 ($C\text{-}CO_{cis}$), 195.6 (C7), 129.8 (C4), 128.7 (C6), 123.1 (C5), 112.6/111.9 (C-Cp), 84.5 (C2), 40.3 (C3), 39.5 ($-C(CH_3)_3$), 26.4 ($-C(CH_3)_3$), 23.6 (2-CH_3); IR (THF) 2047, 1949, 1906 cm^{-1}.

Reaction of 3a with Methylenetriphenylphosphorane. A solution of $Ph_3P{=}CH_2$ (190 mg, 0.34 mmol) in 2 mL of benzene was added to a solution of **3a** in 2 mL of benzene. The reaction mixture was stirred for 5 min, and then an orange oil was allowed to settle. The upper benzene phase was removed, and the residual oil of compound **5a** was washed once with 2 mL of benzene and characterized spectroscopically: ^{1}H NMR (THF-d_8) δ 7.90–7.54 (m, 15 H, H-Ph), 6.34/6.30 (each: s, 5 H, H-Cp), 5.59 (ddd, 1 H, H4), 5.34 (br d, 1 H, H5), 5.28 (br s, 1 H, H6), 2.79 (d, 3 H, H_3C-P, ^2J(P, H) = 13.8 Hz), 2.37 (br t, 1 H, H3′), 1.90 (br dd, 1 H, H3), 1.32 (s, 3 H, 2-CH_3), 1.02 (s, 9 H, $C(CH_3)_3$), coupling constants (Hz), ^2J = 12.2 (H3, H3′), ^3J = 10.2 (H3, H4), 4.2 (H3′, H4), 14.9 (H4, H5); ^{13}C NMR (THF-d_8) δ 209.1 ($C\text{-}CO_{trans}$), 206.3 ($C\text{-}CO_{cis}$), ^1J(W, C) = 127 Hz), 196.2 (C7, ^2J(C7, H6) = 11 Hz, ^3J(C7, H5) = 5 Hz), 135.8 (*p*-C-Ph), 133.9 (*o*-C-Ph, ^2J(P, C) = 11.0 Hz), 131.0 (*m*-C-Ph, ^3J(P, C) = 11.9 Hz), 130.1 (C4, 152), 129.7 (C6, the C6,H6-coupling constant could not be determined due to overlap with benzene signals), 123.3 (C5, 158), 120.2 (ipso-C-Ph, ^1J(P, C) = 90.3 Hz), 112.7/112.0 (C-Cp), 84.7 (C2), 40.3 (C3, 125), 39.5 ($-C(CH_3)_3$), 26.4 ($-C(CH_3)_3$, 124), 23.7 (2-CH_3, 124), 8.6 (CH_3-P, 135, ^1J(P, C) = 57.7 Hz); ^{31}P NMR (THF-d_8) δ 22.3; IR (THF) 2036, 1932, 1893, 1851 cm^{-1}.

Reaction of 3b with Methylenetriphenylphosphorane. To a solution of 100 mg (0.15 mmol) of **3b** in 0.6 mL of benzene-d_6 was added 44 mg (0.16 mmol) of $Ph_3P{=}CH_2$ in 0.55 mL of benzene-d_6. The mixture was stirred for 5 min, and then a red oil was allowed to settle. The upper benzene-d_6 phase was removed, and the residual oil of compound **5b** was washed once with 0.5 mL of benzene-d_6, then redissolved in THF-d_8, and characterized spectroscopically: ^{1}H NMR (THF-d_8) δ 7.92–7.59 (m, 15 H, H-Ph), 6.23 (s, 10 H, H-Cp), 5.49–5.24 (m, 2 H, H4 and H5), 5.16 (d, 1 H, H6), 2.89 (d, 3 H, H_3C-P, ^2J(P, C) = 13.9 Hz), 2.11 (d, 2 H,

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H3 and H3′), 1.22 (s, 6 H, CH_3), coupling constants (Hz), ^3J = 4.8 (H3 and H3′, H4), 2.0 (H5, H6); for the enantiomerization process ΔG^*_{ent} = 11.1 + 0.4 kcal/mol (T_c = 225 K, $\Delta\nu$ (CH_3, 203 K) = 30.6 Hz) was determined by dynamic NMR spectroscopy; ^{13}C NMR (THF-d_8) δ 209.0 (C-CO_{trans}), 206.2 (C-CO_{cis}, ^1J (W, C) = 127 Hz), 195.7 (C7, ^2J(C7, H6) = 12 Hz), 135.9 (*p*-C-Ph), 134.0 (*o*-C-Ph, ^2J(P, C) = 10.7 Hz), 131.1 (*m*-C-Ph, ^3J(P, C) = 13.1 Hz), 129.3 (C4, 145), 128.8 (C6, 151), 122.7 (C5, 155), 120.3 (ipso-C-Ph, ^1J(P, C) = 88.9 Hz), 112.2 (C-Cp), 77.7 (C2), 47.7 (C3, 122), 31.9 (both 2-CH_3, 128), 8.7 (CH_3-P, 135, ^1J(P, C) = 57.5 Hz); IR (THF) 2036, 1942 (sh on solvent band), 1897 cm^{-1}.

(2*R,6*S**)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-2,6-dimethyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 6a and (2*R**,6*R**)(4,5,6-*pS**)-7a.** To a solution of **3a** (2.25 g, 3.09 mmol) in 40 mL of toluene was added 8.32 mL of a toluene solution containing 940 mg (3.40 mmol) of $Ph_3P{=}CH_2$ over a 10-min period at 0 °C. The mixture was stirred for 10 min, and then the oily phosphonium salt was allowed to settle. The upper toluene phase was removed, and the lower oily residue was redissolved in 50 mL of THF. To 40 mL of this solution was added 0.80 mL (12.9 mmol) of methyl iodide at 0 °C, and the reaction mixture was stirred at ambient temperature for 3.5 h during which time $Ph_3PCH_3{}^+I^-$ precipitated. The mixture was filtered, and the solvent was evaporated. The residue was washed once with 40 mL of *n*-hexane and dried in vacuo (2 h) to give 1.32 g (58%) of **6a**/**7a** as a yellow microcrystalline material, mp 146 °C. The ^{1}H NMR spectrum revealed a 85:15 mixture of **6a** and **7a**. A sample was recrystallized from toluene/*n*-hexane (2:1) at −30 °C to yield crystals, which were suitable for X-ray diffraction. The ^{1}H NMR spectrum of this material showed only the signals of **6a**: ^{1}H NMR (C_6D_6/$CDCl_3$ 1:1, TMS) **6a**, δ 6.09/6.00 (each: s, 5 H, H-Cp), 5.09 (dddd, 1 H, H4), 4.85 (ddd, 1 H, H5), 4.27 (br q, 1 H, H6), 1.97 (dd, 1 H, H3′), 1.72 (br t, 1 H, H3), 1.17 (d, 3 H, 6-CH_3), 0.94 (s, 3 H, 2-CH_3), 0.84 (s, 9 H, $C(CH_3)_3$), coupling constants (Hz), ^2J = 10.4 (H3, H3′), ^3J = 10.3 (H3, H4), 4.3 (H3′, H4), 15.2 (H4, H5), 3.5 (H5, H6), 7.3 (H6, C6-CH_3), ^4J = 1.2 (H3′, H5), 1.4 (H4, H6), ^5J = 1.2 (H3′, H6); **7a**, δ 6.17/5.97 (each: s, H-Cp), 4.62 (dd, H5), 3.05 (m, H6), 1.62 (d, 6-CH_3), 0.83 (s, $C(CH_3)_3$), the other signals of **7a** are probably hidden under the signals of **6a** or were too weak to be localized, coupling constants (Hz), ^3J = 15.3 (H4, H5), 9.4 (H5, H6), 7.6 (H6, C6-CH_3); ^{13}C NMR ($CDCl_3$), **6a**, δ 338.0 (C-carbene), 204.2 (C-CO_{trans}), 199.6 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 132.7 (C4), 127.5 (C5), 113.7/112.9 (C-Cp), 91.4 (C2), 68.9 (C6), 40.8 (C3), 38.6 (−$C(CH_3)_3$), 26.0 (−C-$(CH_3)_3$), 21.6 (2-CH_3), 13.6 (6-CH_3); **7a**, δ 341.2 (C-carbene), 199.8 (C-CO_{cis}), 70.7 (C6), 25.3 (−$C(CH_3)_3$), 21.9 (2-CH_3)*, the remaining signals of **7a** were not localized, * = assignment uncertain; IR ($CDCl_3$), mixture of isomers 2059, 1967, 1920 cm^{-1}. Anal. Calcd for $C_{27}H_{30}O_7WZr$ (741.6): C, 43.73; H, 4.08. Found: C, 43.58; H, 4.16.

(2*R,6*S**)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-2-methyl-6-[$^2H_3$]methyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium 6a-d_3 and (2*R**,6*R**)(4,5,6-*pS**)-7a-d_3.** To a solution of 2.36 g (3.24 mmol) of **3a** in 40 mL of toluene was added dropwise 994 mg (3.60 mmol) of $Ph_3P{=}CH_2$ in 8.8 mL of toluene at 0 °C. The reaction mixture was stirred for 5 min, and then an orange oil was allowed to settle. The upper toluene phase was removed, and the oily phosphonium salt was redissolved in 50 mL of THF. Deuteriated methyl iodide (1.03 mL, 16.2 mmol) was added, and the mixture was stirred overnight at ambient temperature. A precipitate ($Ph_3PCH_3{}^+I^-$) was allowed to settle. The solution was decanted and evaporated to dryness. The residue was washed with 20 mL of petroleum ether and dried in vacuo to give 1.96 g (81%) of **6a**-d_3/**7a**-d_3 as a yellow powder, mp 156 °C dec. The ^{1}H NMR spectrum revealed a 82:18 mixture of **6a**-d_3 and **7a**-d_3 isomers. ^{1}H NMR (C_6D_6/$CDCl_3$ 1:1, TMS), **6a**-d_3, δ 6.09/6.01 (each: s, 5 H, H-Cp), 5.08 (dddd, 1 H, H4), 4.85 (ddd, 1 H, H5), 4.26 (m, 1 H, H6), 1.97 (ddt, 1 H, H3′), 1.72 (br t, 1 H, H3), 0.94 (s, 3 H, 2-CH_3), 0.84 (s, 9 H, $C(CH_3)_3$), coupling constants (Hz), ^2J = 12.0 (H3, H3′), ^3J = 10.3 (H3, H4), 4.3 (H3′, H4), 15.5 (H4, H5), 3.6 (H5, H6), ^4J = 1.1 (H3′, H5), 1.4 (H4, H6), ^5J = 1.1 (H3′, H6); **7a**-d_3, δ 6.17/5.97 (each: s, H-Cp), 4.88 (dd, H5), 3.12 (br d, H6), 0.83 (s, $C(CH_3)_3$), the remaining signals of **7a**-d_3 were not localized, coupling constants (Hz), ^3J = 15.1 (H4, H5), 9.0 (H5, H6); ^{13}C NMR (C_6D_6/$CDCl_3$ 1:1, TMS), **6a**-d_3, δ 338.1 (C-carbene), 204.3 (C-CO_{trans}), 199.9 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 132.9 (C4), 127.4 (C5, coincides with solvent signal), 113.7/112.9 (C-Cp), 91.3 (C2), 68.9 (C6), 40.8 (C3), 38.5 (−$C(CH_3)_3$), 26.0 (−$C(CH_3)_3$), 21.5 (2-CH_3); **7a**-d_3, δ 113.8/113.2 (C-Cp), 70.7 (C6), 21.9 (2-CH_3), the remaining signals of **7a**-d_3 were not localized; IR ($CDCl_3$), mixture of isomers 2059, 1966, 1920 cm^{-1}. Anal. Calcd for $C_{27}H_{27}D_3O_7WZr$ (744.6): C, 43.55; H, 4.06. Found: C, 43.70; H, 4.09.

Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-ethyl-6-methyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 6c. As described above, the phosphonium salt of **3c** was prepared from 1.07 g (1.56 mmol) of **3c** and 431 mg (1.56 mmol) of $Ph_3P{=}CH_2$ in toluene solution at 0 °C. The oily salt was isolated and redissolved in 50 mL of THF. Methyl iodide (0.5 mL, 8.03 mmol) was added at 0 °C, and the reaction mixture was stirred for 4 h at ambient temperature. A precipitate ($Ph_3PCH_3{}^+I^-$) was allowed to settle. The solution was decanted and evaporated to dryness. The sticky residue was stirred for 1 h with 20 mL of petroleum ether to solidify. The solvent was removed, and the residue was redissolved in 20 mL of toluene. The solution was filtered, then evaporated. The residue was washed with 10 mL of petroleum ether and dried in vacuo to give 750 mg (69%) of **6c** as a yellow powder, mp 98 °C. The ^{1}H NMR spectrum showed four pairs of cyclopentadienyl resonances in the ratio A:B:C:D = 45:35:10:10 and furthermore a small amount (ca. 15%) of starting complex **3c**: ^{1}H NMR ($CDCl_3$), mixture of isomers, δ 6.30/6.18 (each: s, H-Cp(A)), 6.28/6.26 (each: s, H-Cp(B)), 6.27, 6.26*, 6.25, 6.24 (H-Cp of C and D, * = shoulder on Cp signal of B), 5.55–4.90 (m, H4 and H5), 4.26 (br q, H6), 3.92–3.60 (m, H6 and H2), 2.43–2.11, 2.05–1.71, and 1.63–1.28 (each: m, H3 and −CH_2CH_3), 1.54 (d, 6-CH_3(B), ^3J(H6, 6-CH_3) = 6.8 Hz), 1.23 (d, 6-CH_3(A), ^3J(H6, 6-CH_3) = 7.4 Hz), 0.92 (t, −CH_2CH_3(A), ^3J(−CH_2CH_3) = 7.3 Hz), 0.90 (t, −CH_2CH_3(B), ^3J(−CH_2CH_3) = 7.4 Hz), both methyl resonances of isomers C and D could not be localized; ^{13}C NMR ($CDCl_3$) mixture of isomers, δ 347.3, 337.2 (C-carbene(A, B)), 204.8, 204.5 (C-CO_{trans}), 199.7 (C-CO_{cis}), 132.4, 128.5, 127.8, 126.8 (C4 and C5 of A and B), 113.6, 113.5, 112.8, 112.4 (C-Cp), 86.8, 85.9 (C2(A, B)), 68.9, 64.9 (C6(A, B)), 42.3, 41.6, 36.4, 36.2 (C3), 31.4 (−CH_2CH_3, double intensity), 21.9, 13.6 (6-CH_3(A, B)), 10.7, 10.5 (−CH_2CH_3(A,B)), the remaining signals were not localized; IR ($CDCl_3$), mixture of isomers 2059, 1971, 1922 cm^{-1}. Anal. Calcd for $C_{24}H_{24}O_7WZr$ (699.5): C, 41.21; H, 3.46. Found: C, 41.31; H, 3.47.

Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-ethenyl-6-methyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 6d. As described above, the phosphonium salt of **3d** was prepared from 970 mg (1.42 mmol) **3d** and 392 mg (1.42 mmol) $Ph_3P{=}CH_2$ in toluene solution at 0 °C. The oily salt was isolated and redissolved in 40 mL of THF. Methyl iodide (0.5 mL, 8.03 mmol) was added at 0 °C, and the reaction mixture was stirred for 3 h at ambient temperature. A $Ph_3PCH_3{}^+I^-$ precipitate was allowed to settle. The solution was decanted and evaporated to dryness. The sticky residue was stirred for 1.5 h with 80 mL of petroleum ether at −78 °C to solidify. The solvent was evaporated at ambient temperature, and the residue was dried in vacuo to give 790 mg (80%) of a yellow powder, which could not be recrystallized by using different solvent mixtures. The remaining amount of **6d** was finally dissolved in 10 mL of methylene chloride and filtered through Florisil (degassed in vacuo and stored under argon). The column was washed with an additional 10 mL of methylene chloride. The combined solutions were evaporated, and the residue was washed once with 3 mL of *n*-hexane and dried in vacuo to give 220 mg (22%) of **6d** as a yellow powder, mp 136 °C dec. The ^{1}H NMR spectrum showed two major isomers in a ratio of A:C = 60:40 and a small amount of starting complex **3d**: ^{1}H NMR ($CDCl_3$), mixture of isomers, δ 6.31/6.30 (each: s, H-Cp(A)), 6.35/6.20 (each: s, H-Cp(B)), 6.33, 6.32, 6.28, 6.27, 6.25 (s, H-Cp), 5.93–5.72 (m, −$CH{=}CH_2$), 5.60–4.94 (m, H4, H5, H6 and −CH=CH_2), 4.45–4.17 (m, H2), 2.49–2.19 and 2.12–1.80 (each: m, H3′ and H3), 1.56 (d, 6-CH_3(A), ^3J(H6, 6-CH_3) = 6.8 Hz), 1.28 (d, 6-CH_3(B), ^3J(H6, 6-CH_3) = 7.4 Hz), no further methyl doublets were localized; ^{13}C NMR ($CDCl_3$) mixture of isomers, δ 347.8, 338.8, 337.7 (C-carbene), 204.6, 204.3 (C-CO_{trans}), 202.4, 199.6, 197.2 (C-CO_{cis}), 141.7, 141.4 (−$CH{=}CH_2$), 133.2, 129.2, 127.1, 126.2, 122.5 (C4, C5 and −CH=CH_2), 113.7, 113.6, 113.3, 112.9, 112.7, 112.5 (C-Cp), 85.5, 85.3, 85.0 (C2), 72.0, 69.0, 65.9, 64.9 (C6), 42.7, 40.5, 37.0, 31.5 (C3), 22.6, 21.9, 14.1, 13.9 (6-CH_3); IR ($CDCl_3$), mixture of isomers: 2059, 1977 [W-$(CO)_6$], 1924 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_7WZr$ (697.5): C, 41.33; H, 3.18. Found: C, 40.99; H, 3.14.

Reaction of 6a/7a with Methylenetriphenylphosphorane. To a solution of 100 mg (0.14 mmol) of **6a**/**7a** in 1 mL of benzene-d_6 was added 41 mg (0.15 mmol) of $Ph_3P{=}CH_2$ in 0.55 mL of benzene-d_6 at ambient temperature. The mixture was stirred for 5 min, and then a brown oil was allowed to settle. The upper benzene-d_6 phase was decanted, the oily residue was redissolved in THF-d_8, and the compound **8** was characterized spectroscopically: ^{1}H NMR (THF-d_8) δ 7.93–7.62 (m, 15 H, H-Ph), 6.21 (s, 10 H, H-Cp), 5.43 (m, 2 H, H4 and H5), 2.91 (d, 3 H, H_3C-P, ^2J(P, C) = 14.0 Hz), 2.31 (br t, 1 H, H3′), 1.93 (s, 3 H, C6-CH_3), 1.9 (dd, 1 H, H3, under the signal of 6-CH_3), 1.30 (s, 3 H, 2-CH_3), 0.98 (s, 9 H, $C(CH_3)_3$).

(2*R)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-2,6,6-trimethyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 9.** To a sample of 690 mg (0.93 mmol) of **6a**/**7a** in 30 mL of toluene was added 309 mg (1.12 mmol) of $Ph_3P{=}CH_2$ in 3.2 mL of toluene at 0 °C. The mixture was stirred for 5 min, and a red

brown oil was allowed to settle. The toluene phase was removed, and the residue was redissolved in 40 mL of THF. Methyl iodide was added, and the mixture was stirred for 3.5 h at ambient temperature, during which time $Ph_3PCH_3^+I^-$ precipitated. The mixture was filtered, and the solvent was evaporated. The yellow residue was extracted three times with a total of 250 mL of *n*-hexane. The combined hexane phases were evaporated, and the residue was dried in vacuo to give 210 mg (30%) of **9** as a yellow microcrystalline material, mp 168 °C dec: ^{1}H NMR (C_6D_6/$CDCl_3$ 1:1, TMS) δ 6.08/6.06 (each: s, 5 H, H-Cp), 5.05 (ddd, 1 H, H4), 4.80 (d, 1 H, H5), 1.94 (dd, 1 H, H3′), 1.73 (br t, 1 H, H3), 1.56 (s, 3 H, 6-CH_3′), 1.12 (s, 3 H, 6-CH_3), 0.93 (s, 3 H, 2-CH_3), 0.84 (s, 9 H, C$(CH_3)_3$), coupling constants (Hz), ^2J = 11.5 (H3, H3′), ^3J = 10.0 (H3, H4), 4.7 (H3′, H4), 15.6 (H4, H5); ^{13}C NMR (C_6D_6/$CDCl_3$ 1:1, TMS) δ 345.1 (C-carbene), 203.6 (C-CO_{trans}), 200.5 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 140.0 (C4, 151), 124.9 (C5, 164), 113.9/113.1 (C-Cp), 91.2 (C2), 64.4 (C6), 40.6 (C3, 126), 38.5 (-$C(CH_3)_3$), 28.7 (6-CH_3′, 116), 26.0 (-C(CH_3)$_3$, 125), 21.8, 21.6 (2-CH_3 and 6-CH_3, each: 125); IR (*n*-hexane) 2058, 1962, 1934, 1909 cm^{-1}; ($CDCl_3$) 2057, 1963, 1925 (sh), 1913 cm^{-1}. Anal. Calcd for $C_{28}H_{32}O_7WZr$ (755.6): C, 44.51; H, 4.27. Found: C, 44.54; H, 4.43.

(2*R,6*S**)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-2,6-dimethyl-6-[$^2H_3$]methyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 10.** As described above, the phosphonium salt **8** was prepared by adding a toluene solution containing 265 mg (0.96 mmol) of $Ph_3P{=}CH_2$ to 710 mg (0.96 mmol) of **6a**/**7a** in 30 mL of toluene at 0 °C. The oily phosphonium salt was isolated and redissolved in 40 mL of THF. Methyl iodide-d_3 (303 μL, 4.79 mmol) was added at 0 °C, and the mixture was stirred overnight at ambient temperature. A $Ph_3PCH_3^+I^-$ precipitate was allowed to settle. The upper solution was decanted, and the solvent was removed in vacuo. The residue was extracted five times with 80-mL portions of *n*-hexane. The combined extracts were evaporated to dryness, and the residue was dried in vacuo to give 440 mg (61%) of **10** as a yellow powder, which turned dark above 180 °C but did not melt below 220 °C. The ^{1}H NMR spectrum shows two signals for the nondeuteriated methyl group at C6 at 1.56 and 1.12 ppm in the ratio **10**:**11** = 93:7. The complete data of isomer **11** are given below. ^{1}H NMR (C_6D_6/$CDCl_3$ 1:1, TMS), **10**, δ 6.08/6.05 (each: s, 5 H, H-Cp), 5.04 (ddd, 1 H, H4), 4.79 (d, 1 H, H5), 1.93 (dd, 1 H, H3′), 1.72 (br t, 1 H, H3), 1.56 (s, 3 H, 6-CH_3), 0.92 (s, 3 H, 2-CH_3), 0.83 (s, 9 H, C$(CH_3)_3$), coupling constants (Hz), ^2J = 11.7 (H3, H3′), ^3J = 10.1 (H3, H4), 4.7 (H3′, H4), 15.6 (H4, H5); **11**, δ 1.12 (s, 6-CH_3); ^{13}C NMR (C_6D_6/$CDCl_3$ 1:1, TMS), **10**, δ 345.2 (C-carbene), 203.5 (C-CO_{trans}), 200.5 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 140.0 (C4), 124.9 (C5), 113.9/113.1 (C-Cp), 91.2 (C2), 64.2 (C6), 40.6 (C3), 38.5 (-$C(CH_3)_3$), 28.6 (6-CH_3), 26.0 (-C(CH_3)$_3$), 21.6 (2-Ch_3); IR (*n*-hexane) 2058, 1962, 1934, 1909 cm^{-1}. Anal. Calcd for $C_{28}H_{29}D_3O_7WZr$ (758.7): C, 44.33; H, 4.25. Found: C, 44.00; H, 4.32.

(2*R,6*R**)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-2,6-dimethyl-6-[$^2H_3$]methyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 11.** To a solution of 990 mg (1.33 mmol) of **6a**-d_3/**7a**-d_3 in 40 mL of toluene was added dropwise 3.42 mL of a toluene solution containing 404 mg (1.46 mmol) of $Ph_3P{=}CH_2$ at 0 °C. The mixture was stirred for 5 min, and then an orange oil was allowed to settle. The toluene phase was removed, and the oil was redissolved in 40 mL of THF. Methyl iodide (420 μL, 6.78 mmol) was added, and the mixture was stirred overnight at ambient temperature. The mixture was filtered, and the filtrate was evaporated to dryness. The residue was extracted four times with 80-mL portions of *n*-hexane. The hexane solution was evaporated to give 650 mg (64%) of **11** as a yellow microcrystalline material, which turned dark above 180 °C but did not melt below 220 °C. The ^{1}H NMR spectrum showed two signals for the nondeuteriated methyl group at C6 at 1.56 and 1.12 ppm in the ratio **10**:**11** = 9:91. The ^{1}H and ^{13}C NMR data of isomer **10** are given above. ^{1}H NMR (C_6D_6/$CDCl_3$ 1:1, TMS), **11**, δ 6.08/6.06 (each: s, 5 H, H-Cp), 5.05 (ddd, 1 H, H4), 4.79 (d, 1 H, H5), 1.93 (dd, 1 H, H3′), 1.73 (br t, 1 H, H3), 1.12 (s, 3 H, 6-CH_3), 0.93 (s, 3 H, 2-CH_3), 0.84 (s, 9 H, C$(CH_3)_3$), coupling constants (Hz), ^2J = 11.7 (H3, H3′), ^3J = 10.1 (H3, H4), 4.7 (H3′, H4), 15.8 (H4, H5); **10**, δ 1.56 (s, 6-CH_3); ^{13}C NMR (C_6D_6/$CDCl_3$ 1:1, TMS, 50.3 MHz), **11**, δ 345.2 (C-carbene), 203.5 (C-CO_{trans}), 200.5 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 140.0 (C4), 124.9 (C5), 113.9/113.1 (C-Cp), 91.2 (C2), 64.2 (C6), 40.6 (C3), 38.5 (-$C(CH_3)_3$), 26.0 (-C(CH_3)$_3$), 21.6 (2-CH_3 and 6-CH_3, signal with a shoulder); **10**, δ 28.7 (6-CH_3); IR (*n*-hexane) 2058, 1962, 1934, 1909 cm^{-1}. Anal. Calcd for $C_{28}H_{29}D_3O_7WZr$ (758.7): C, 44.33; H, 4.25. Found: C, 44.09; H, 4.33.

(2*R,6*S**)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-6-ethyl-2-methyl-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 12 and (2*R**,6*R**)(4,5,6-*pS**)-13.** To a solution of 1.78 g (2.45 mmol) of **3a** in 30 mL of toluene was added dropwise 714 mg (2.58 mmol) of $Ph_3P{=}CH_2$ in 6.5 mL of toluene at 0 °C. The mixture was stirred for 5 min, and an orange oil was allowed to settle. The upper toluene phase was decanted, and the residual oil was redissolved in 40 mL of THF. Ethyl iodide (1.5 mL, 18.8 mmol) was added, and the mixture was stirred overnight at ambient temperature. A precipitate of $Ph_3PCH_3^+I^-$ was allowed to settle. The solution was decanted and evaporated. The residue was dried in vacuo to give 1.57 g (85%) of **12**/**13** as a yellow powder. A sample of 620 mg was washed twice with 10-mL portions of *n*-hexane and dried in vacuo to give 320 mg of **12**/**13** as a yellow powder, mp 164 °C dec. The ^{1}H NMR revealed a 85:15 mixture of **12** and **13**. ^{1}H NMR ($CDCl_3$), **12a**, δ 6.32/6.26 (each: s, 5 H, H-Cp), 5.26 (dddd, 1 H, H4), 4.93 (dd, 1 H, H5), 4.10 (br d, 1 H, H6), 2.19 (br dd, ^{1}H, H3′), 1.92 (br t, 1 H, H3), 1.44–1.22 (m, 2 H, 6-CH_2CH$_3$), 1.19 (s, 3 H, 2-CH_3), 1.11 (t, 3 H, 6-CH$_2$CH_3), 0.98 (s, 9 H, C$(CH_3)_3$), coupling constants (Hz), ^2J = 12.1 (H3, H3′), ^3J = 10.6 (H3, H4), 4.3 (H3′, H4), 15.8 (H4, H5), 4.1 (H5, H6), 7.2 (-CH_2CH_3), ^4J = 1.3 (H4, H6); **13**, δ 6.39/6.24 (each: s, H-Cp), 4.82 (dd, H5), 2.97 (m, H6), 2.30 (m, 6-CH_2CH$_3$), 1.05 (t, 6-CH$_2$CH_3), the remaining signals of **13** were not localized, coupling constants (Hz), ^3J = 15.5 (H4, H5), 9.2 (H5, H6), 7.4 (-CH_2CH_3); ^{13}C NMR (C_6D_6/$CDCl_3$ 1:1, TMS), **12**, δ 338.1 (C-carbene), 204.2 (C-CO_{trans}), 199.7 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 130.0 (C4), 128.0 (C5), 113.7/113.0 (C-Cp), 91.4 (C2), 76.9 (C6, δ = 77.3 ppm in benzene-d_6), 41.1 (C3), 38.7 (-$C(CH_3)_3$), 26.0 (-C(CH_3)$_3$), 21.7 (2-CH_3), 21.2 (6-CH_2CH_3), 12.9 (6-CH_2CH_3); **13**, δ 199.9 (C-CO_{cis}), 134.8 (C4), 130.6 (C5), 113.9/113.2 (C-Cp), 78.2 (C6), 40.8 (C3), 28.3 (6-CH_2CH_3), 21.9 (2-CH_3), the remaining signals of **13** were not localized; IR ($CDCl_3$), mixture of isomers 2058, 1967, 1920 cm^{-1}. Anal. Calcd for $C_{28}H_{32}O_7WZr$ (755.6): C, 44.51; H, 4.27. Found: C, 44.66; H, 4.36.

(2*R,6*S**)(4,5,6-*pS**)-*trans*-Bis(cyclopentadienyl)[μ-[(1-η:7-η)-2-*tert*-butyl-6-ethyl-2-methyl-6-(2-propenyl)-7-oxo-1-oxa-4-heptene-1,7-diyl-*O*]](pentacarbonyltungsten)zirconium, 15.** To a sample of **12**/**13** (950 mg, 1.26 mmol) in 20 mL of toluene was added dropwise $Ph_3P{=}CH_2$ (83 mg, 1.23 mmol) in 4.4 mL of toluene at 0 °C. The mixture was stirred for 5 min, then an orange oil was allowed to settle. The upper toluene phase was decanted, and the oil was redissolved in 40 mL of THF. Allyl bromide (1.0 mL, 11.6 mmol) was added, and the mixture was stirred overnight at ambient temperature. A precipitate ($Ph_3PCH_3^+I^-$) was allowed to settle. The solution was decanted and evaporated to dryness. The residue was extracted with 40-mL portions of *n*-hexane until the solvent remained colorless (nine times). The combined extracts were evaporated to dryness. The residue was washed once with 20 mL of *n*-hexane to remove some grease, and the residue was dried in vacuo to give 620 mg (62%) of **15** as a yellow powder, mp 132 °C dec. The ^{1}H NMR spectrum showed only one diastereomer. ^{1}H NMR (C_6D_6) δ 6.03/5.94 (each: s, 5 H, H-Cp), 5.69 (m, 1 H, -$CH_2CH{=}CH_2$), 5.32–4.98 (m, 3 H, H4 and -$CH_2CH{=}CH_2$), 4.72 (d, 1 H, H5), 2.85 and 2.68 (each dd, 1 H, -$CH_2CH{=}CH_2$), 2.37 and 1.99 (each dq, 1 H, -CH_2CH_3), 1.84 (dd, 1 H, H3′), 1.61 (br t, 1 H, H3), 0.93 (t, 3 H, -CH_2CH_3), 0.76 (s, 12 H, -C(CH_3)$_3$ and C2-CH_3); in $CDCl_3$ the signals of H4, H5, -$CH_2CH{=}CH_2$, *cis*- and *trans*-$CH_2CH{=}CH_2$, -C(CH_3)$_3$, and 2-CH_3 are separated; ($CDCl_3$) δ 6.34/6.31 (each: s, 5 H, H-Cp), 5.61 (m, 1 H, -$CH_2CH{=}CH_2$), 5.41 (ddd, 1 H, H4), 5.17 (dd, 1 H, *trans*-$CH_2CH{=}CH_2$), 5.09 (dd, 1 H, *cis*-$CH_2CH{=}CH_2$), 4.87 (d, 1 H, H5), 2.69 (br d, 2 H, -$CH_2CH{=}CH_2$), 2.17 (m, 2 H, -CH_2CH_3), 1.89 (m, 2 H, H3 and H3′), 1.23 (s, 3 H, 2-CH_3), 0.98 (s, 9 H, C$(CH_3)_3$), 0.94 (t, 3 H, -CH_2CH_3, partially overlapping with the C$(CH_3)_3$ resonance), coupling constants (Hz), ^2J = 11.9 (H3, H3′), 14.3 (-CH_2CH_3), 15.3 (-$CH_2CH{=}CH_2$), 1.7 (-$CH_2CH{=}CH_2$), ^3J = 10.0 (H3, H4), 5.0 (H3′, H4), 15.8 (H4, H5), 7.4 (-CH_2CH_3), 8.0 (-C(*H*)(H′)C$H{=}CH_2$), 5.1 (-C(H)(*H*′)C$H{=}CH_2$), 10.2 (-$CH_2CH{=}C(H_{cis})$(H)), 17.2 (-$CH_2CH{=}C(H)(H_{trans})$); ^{13}C NMR ($CDCl_3$) δ 349.8 (C-carbene), 202.8 (C-CO_{trans}), 199.8 (C-CO_{cis}, ^1J(W, C) = 127 Hz), 136.2, 134.9 (C4 and -$CH_2CH{=}CH_2$), 127.6 (C5), 117.1 (-$CH_2CH{=}CH_2$), 113.9/113.2 (C-Cp), 91.6 (C2), 70.3 (C6), 40.9 (C3), 38.5 (-$C(CH_3)_3$ and -$CH_2CH{=}CH_2$), 33.4 (-CH_2CH_3), 26.0 (-C(CH_3)$_3$), 21.6 (2-CH_3), 9.7 (-CH_2CH_3); IR (*n*-hexane) 2059, 1963, 1935, 1910 cm^{-1}. Anal. Calcd for $C_{31}H_{36}O_7WZr$ (795.7): C, 46.79; H, 4.56. Found: C, 46.89; H, 4.78.

(3*R,7*S**)-*trans*-8-Methoxy-2,2,3,7-tetramethylnona-5,8-dien-3-ol, 16 and (3*R**,7*R**)-17.** A solution of 2.88 g (3.88 mmol) of **6a**/**7a** in 40 mL of THF was cooled to 0 °C. Water (0.16 mL, 8.9 mmol) and 23 mL of a 0.35 *M* ethereal diazomethane solution (8.05 mmol) were added dropwise over a 10-min period with slow stirring of the reaction mixture, during which time the color changed to orange and some gas was evolved. The mixture was allowed to stand for 2 h without stirring. Air was bubbled through the solution (5 min), and the mixture was allowed to stand overnight. The mixture was filtered, and the filtrate was evaporated to dryness. The oily residue was redissolved in 10 mL of methanol and filtered through a column (o.d. = 1 cm) filled with alumina (neutral, activity grade III). The column was washed with 20 mL of methanol, and the combined eluate was evaporated to dryness. The residue was

extracted three times with a total of 4 mL of *n*-hexane. The combined extracts were filtered and evaporated to dryness. The residue was dried in vacuo to give 770 mg (88%) as a brownish oil. The ^{1}H NMR spectrum revealed a mixture of three isomers in the ratio **16**:**17**:**18** = 70:10:20: ^{1}H NMR (C_6D_6), **16**, δ 5.69-5.55 (m, 2 H, H5 and H6), 3.99 (d, 1 H, $H9_{cis}$), 3.81 (d, 1 H, $H9_{trans}$), 3.21 (s, 3 H, $-OCH_3$), 2.96 (m, 1 H, H7), 2.25 (m, 1 H, H4'), 2.01 (m, 1 H, H4), 1.23 (d, 3 H, 7-CH_3), 1.20 (br, -OH, partially coincide with 7-CH_3), 1.02 (d, 3 H, 3-CH_3), 0.93 (s, 9 H, H1), coupling constants (Hz), ^2J = 2.1 ($H9_{cis}$, $H9_{trans}$), ^3J = 7.0 (H7, 7-CH_3), ^4J = 0.8 (H4 or H4', 3-CH_3); **17**, δ 3.20 (s, $-OCH_3$), 1.25 (d, 7-CH_3, ^3J(H7, 7-CH_3) = 7.0 Hz); **18**, δ 4.01 (d, $H9_{cis}$), 3.87 (d, $H9_{trans}$), 3.09 (s, $-OCH_3$), 1.71-1.54 (m, H4 and H5, assignment not certain), 1.30 (br, -OH), 1.04 (d, 3-CH_3), 0.94 (s, H1), coupling constants (Hz), ^2J = 1.9 ($H9_{cis}$, $H9_{trans}$), ^4J = 0.8 (H4 or H4', 3-CH_3), the remaining signals of **17** and **18** were not localized; ^{13}C NMR (C_6D_6), **16**, δ 167.6 (C8), 136.8 (C5, 154), 126.4 (C6, 159), 79.5 (C9, 157), 75.5 (C3), 54.5 ($-OCH_3$, 143), 42.6 (C7, 127), 40.0 (C4, 125), 37.9 (C2), 25.7 (C1, 129), 22.0 (3-CH_3, 125), 19.0 (7-CH_3, 127); **17** and **18**, δ 166.6 (C8), 137.0, 136.9 (C5), 126.6 (C6), 79.9 (C9, 157), the remaining signals of **17** and **18** were not localized; IR (NaCl), mixture of isomers, 3499, 1653, 1605, 976 cm^{-1}; MS (EI) 226 ($M^{\bullet+}$, 0.1) 101 (100); exact mass (CI) calcd for $C_{14}H_{26}O_2$ 227.2011 ($M + H^+$), found 227.2014.

(2*R,6*S**)-*trans*-6-Hydroxy-2,6,7,7-tetramethyl-3-octenoic Acid, 19 and (2*R**,6*R**)-20.** To a solution of 1.19 g (1.36 mmol) of **6a**/**7a** in 40 mL of THF were added 187 mg (1.96 mmol) of pyridine *N*-oxide in 6.8 mL of THF and 75 μL (4.16 mmol) of water. The mixture was stirred for 2 h. The solvent was removed in vacuo. To the orange, viscous residue was added 20 mL of diethyl ether and 20 mL of water. The mixture was acidified with 2 M hydrochloric acid (pH 3). The organic phase was separated, and the water phase was extracted three times with 30-mL portions of diethyl ether. The combined organic phases were washed once with brine, filtered through alumina (neutral, activity grade III), and extracted three times with 30-mL portions of 2/3 saturated sodium carbonate solution. The combined extracts were washed once with diethyl ether and acidified with 5 M hydrochloric acid to pH 3. The cloudy water phase was extracted five times with 30-mL portions of diethyl ether. The combined organic phases were washed with half concentrated brine, dried over sodium sulfate, filtered, and evaporated to dryness. The residue was redissolved in a small amount of acetone to remove grease. The acetone solution was evaporated in vacuo to give 70 mg (20%) of **19**/**20** as a yellowish oil: ^{1}H NMR (C_6D_6), **19**, δ 6.8 (br, 2 H, -OH and $-CO_2H$), 5.78-5.42 (m, 2 H, H3 and H4), 3.07 (quintet, 1 H, H2), 2.24 (br dd, 1 H, H5'), 1.93 (dd, 1 H, H5), 1.18 (d, 3 H, 2-CH_3), 1.00 (s, 3 H, 6-CH_3), 0.89 (s, 9 H, H8), coupling constants (Hz), ^2J = 13.9 (H5, H5'), ^3J = 7.0 (H2, H3), 7.0 (H2, 2-CH_3), 7.3 (H4, H5), 6.0 (H4, H5'); **20**, δ 3.06 (quintet, H2), 0.90 (s, H8), the remaining signals of **20** were not localized; ^{13}C NMR (C_6D_6), **19**, δ 180.7 (C1), 132.3 (C4, 158), 129.1 (C3, 150), 76.5 (C6), 43.0 (C2, 131), 39.7 (C5, 127), 37.9 (C7), 25.5 (C8, 125), 21.6 (6-CH_3, 125), 17.2 (2-CH_3, 129); **20**, δ 180.6 (C1), 132.5 (C4), 43.2 (C2), 39.6 (C5), 17.3 (2-CH_3), the remaining signals of **20** were not localized; IR (NaCl), mixture of isomers, 3428, 3301, 1711, 974 cm^{-1}; MS (EI), 101 (100).

Acknowledgment. Financial support from the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged. F.S. thanks the Volkswagen-Stiftung and the Verband der Chemischen Industrie for a Kekulé-Stipendium.

Registry No. 3a, 124535-63-3; **3b**, 129174-02-3; **3c**, 129261-21-8; **3d**, 129261-83-2; **4a**, 129150-46-5; **5a**, 129261-20-7; **5b**, 129150-45-4; **6a**, 129214-75-1; **6a**-d_3, 129213-54-3; *cis*-**6c**, 129150-56-7; *trans*-**6c**, 129261-82-1; *cis*-**6d**, 129261-22-9; *trans*-**6d**, 129150-55-6; **7a**, 129150-47-6; **7a**-d_3, 129150-53-4; **8**, 129150-49-8; **9**, 129150-50-1; **10**, 129150-51-2; **11**, 129213-52-1; **12**, 129150-52-3; **13**, 129213-53-2; **15**, 129150-54-5; **16**, 129150-39-6; **17**, 129150-40-9; **18**, 129150-41-0; **19**, 129150-42-1; **20**, 129150-43-2.

Supplementary Material Available: Tables of bond distances and angles for **6a** and **9** (16 pages); listings of observed and calculated structure factors for **6a** and **9** (63 pages). Ordering information is given on any current masthead page.

Regio- and Stereocontrolled Functionalization of Acyclic Molybdenum-η^3-Allyl Complexes

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Received June 1, 1990

Abstract: Chemical transformation of the ester $CpMo(CO)_2$(*syn*-η^3-1-C_3H_4COOMe) to its η^3-allyl alcohol, acid, acid chloride, and amide has been achieved. Treatment of $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4CHR(OH)$) (R = H (**2f**), CH_3 (**2g**)) with $(CF_3SO_2)_2O$ in ether at -78 °C stereoselectively generates, the air-stable *s-trans*-η^4-diene cations, which have been characterized by appropriate physical methods. The ionization process proceeds via an intramolecular S_N2 mode. The *s-trans*-η^4-*cis*-pentadiene cation reacts with water, alcohol, thiol, and amine to give η^3-allyl derivatives, which retain the same configuration as that of **2g**. The enolate $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COCH_2Li$) condenses with aldehyde at -78 °C to yield the aldol products $CpMo(CO)_2$(*syn*-η^3-1-$C_3H_4COCH_2CHR(OH)$) (R = Ph (**6a**), CH_3 (**6b**), $(CH_3)_2CH$ (**6c**)) with good diastereoselectivity. The major diastereomer has been isolated and characterized by X-ray diffraction. Further reduction of this diastereomer with $NaBH_4$ produces the corresponding 1,3-diol as a single diastereomer. Utilization of **2g** and **6e** in synthesis of acyclic 1,3-diol and 1,3,5-triol has been achieved, with excellent stereoselectivity; a mechanism is been proposed.

Introduction

The chemical transformation of an organic functional group adjacent to an organometallic unit has been an area of considerable interest.[1-3] In the course of functionalization, the organometallic unit commonly serves as a chiral auxiliary; thus, a highly diastereoselective and stereospecific reaction pattern is followed. The complexes of the type $CpMo(CO)_2(\eta^3$-allyl) represent one case in which the organic moiety has exhibited interesting chemical

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0002-7863/91/1513-573$02.50/0