Journal of Organometallic Chemistry, 363 (1989) 61–76
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09390

Regio- and stereochemistry in the sequential insertion of carbonyl compounds into zirconium-diene complexes

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(Received July 28th, 1988)

Abstract

Group 4 metal-diene complexes of the type Zr(η-C_5H_5)$_2$(s-*cis*-diene) and Zr(η-C_5H_5)$_2$(s-*trans*-diene) (diene = butadiene, isoprene, pentadiene and their derivatives) were found to undergo regioselective 1/1 addition with a variety of aldehydes, ketones, esters and acid amides at the sterically more crowded terminal carbon of the ligated diene to give the (Z)-oxazirconacyclo-4-heptenes. Further addition of carbonyl compounds to the resulting oxametallacycle leads to 1/2 adducts of (E)-1,3-dioxazircona-6-nonene structure when the precursor oxazirconacycloheptene has a less bulky hydrogen group at the C(5) position. Highly selective, three-component, sequential addition was first realized by treatment of a ketone or an aldehyde with Zr(C_5H_5)$_2$(diene)/ester, Zr(C_5H_5)$_2$(diene)/alkene and Zr(C_5H_5)$_2$(diene)/alkyne adducts.

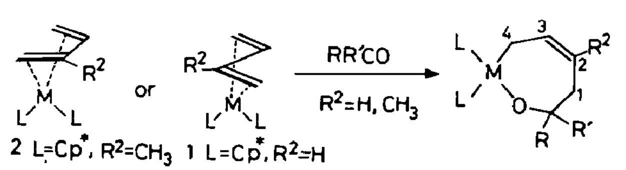
Introduction

Zirconium-diene complexes are known to react readily with saturated or unsaturated aldehydes, ketones, nitriles, and esters [1,2]. Up to now such high oxophilicity has not been observed for alkylzirconium compounds like $ZrCp_2Cl(R)$ (Cp = C_5H_5) and conventional late transition metal-diene complexes. More recently we have found that aldehydes, ketones and acid amides can undergo the double carbometalation (1/2 addition) under appropriate conditions, although esters generally undergo only the 1/1 addition reaction. Here we describe (1) the effect of alkyl substitution on the ligated diene in Zr(C_5R_5)$_2$(s-*cis*-diene) and Zr(C_5R_5)$_2$(s-*trans*-diene) on the regio- and stereochemistry in the carbometalation, (2) the essential factor(s) that determine the course the reaction takes (1/1 and 1/2 insertion), (3) the characteristic chemical behavior of the ester- and acid amide-inserted zirconium compounds, and (4) the selective sequential carbometalation realized by treatment of carbonyl compounds with $ZrCp_2$(diene)/1-alkene and $ZrCp_2$(diene)/alkyne (1/1) adducts.

Results and discussion

Mechanisms of the carbometalation of aldehydes and ketones with zirconium-diene complexes

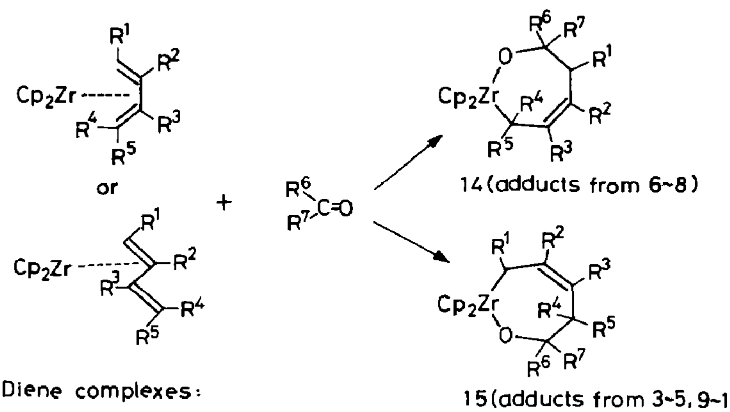
$Zr(C_5R_5)_2$(s-*trans*-butadiene) ($R = CH_3$ (**1**) or $R = H$ (**3**)) and $Zr(C_5R_5)_2$(s-*cis*-isoprene) ($R = CH_3$ (**2**) or $R = H$ (**6**)) readily promote the 1/1 addition reaction with acyclic ketones and aldehydes, which proceeds cleanly, to give the products in excellent yields, with selectivities of > 99%, under optimum conditions [3–7]. The X-ray and NMR analyses confirmed the (*Z*)-oxametallacyclo-4-heptene structure for all of these products, which involves σ-bonding at the M–C(4) and M–O parts and a (*Z*)-olefin bond at the C(2)–C(3) moiety (eq. 1) [3,4]. Similarly, group 4A hafnium- or titanium-diene complexes (e.g. $HfCp_2$(isoprene) [8], $TiCp^*Cl$(isoprene) [9,10] and group 5A niobium- or tantalum-diene complexes (e.g. $NbCpCl_2$(butadiene) [11], TaCp(2,3-dimethylbutadiene)$_2$ [12]) also afford the same type of (*Z*)-oxametallacycloheptenes by the thermal reaction with carbonyl compounds. Thus the bulkiness of the ligated dienes and carbonyl compounds as well as the geometry



(1)

(s-*cis* or s-*trans*) of the dienes (see Table 2) and the identity of the group 4A and 5A transition metals do not alter the reaction pattern, although the photo-induced reaction of isoprene complex **6** with ketone is known to yield an additional regioisomer [7].

During this study, we have found that $ZrCp_2$(butadiene) (**3**) is able to undergo the double insertion (1/2 addition) under mild conditions (0–30 °C), while $ZrCp_2$(isoprene) (**6**) does not induce the double insertion even when the reaction was carried out under vigorous conditions (80–100 °C) in the presence of excess acetone or 2,4-dimethyl-3-pentanone. To gain further information about the effect of methyl substitution at the diene ligand on the regio- and stereo-chemistry of the final products, and about mechanisms (1/1 and 1/2 addition), the carbometalation of carbonyl compounds with a series of pentadiene-zirconium complexes [13] was explored using 2-methylpropanal as a typical electrophile. On the addition of one equiv. of 2-methylpropanal at −20 °C, the complexes of 1,3-pentadiene (**9**), 1,3-hexadiene (**10**), 2-methyl-1,3-pentadiene (**11**), and 2,4-dimethyl-1,3-pentadiene (**12**) readily undergo 1/1 addition selectively at the sterically more-crowded C(4) carbon of the ligated diene to give **15** ($R^3 = H$, $R^5 = CH_3$, C_2H_5) (Table 1). Especially noteworthy is the fact that the regiochemistry observed for complexes **11** and **12** is strikingly different than that for isoprene complex **6** which gives rise to **14** ($R^2 = CH_3$, $R^5 = H$) selectively in spite of the presence of a common carbon skeleton among these complexes (a methyl group lies at the C(2) position). This marked difference indicates that the methyl substitution at C(1) and/or C(4) position(s) exerts a more pronounced electronic (inductive) effect on the terminal carbon of the ligated diene than the substitution at the C(2) and/or C(3) position(s). Hence, the pentadiene complex and its higher homologs generally attack the electrophile at the sterically more congested C(4) atom reflecting the higher electro-



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Diene complexes:

3 $R^{1-5}=H$
4 $R^1=R^5=CH_3$, $R^{2-4}=H$
5 $R^1=R^5=C_6H_5$, $R^{2-4}=H$
6 $R^2=CH_3$, $R^1=R^{3-5}=H$
7 $R^{2-3}=CH_3$, $R^1=R^{4-5}=H$
8 $R^{1-2}=CH_3$, $R^{3-5}=H$
9 $R^5=CH_3$, $R^{1-4}=H$
10 $R^5=C_2H_5$, $R^{1-4}=H$
11 $R^2=R^5=CH_3$, $R^1=R^{3-4}=H$
12 $R^2=R^{4-5}=CH_3$, $R^1=R^3=H$
13 $R^1=SiMe_3$, $R^5=CH_3$, $R^{2-4}=H$

negativity of that carbon, while the isoprene complexes **2** and **6** react at C(1) selectively (> 98%) since the methyl group at C(2) gives rise to a higher electron density at C(1) than at C(4) carbon. Complex **8** is exceptional as it affords a mixture of **14** and **15**.

More remarkable is that complexes **6**–**8** ligated by either isoprene, 2,3-dimethylbutadiene or 3-methyl-1,3-pentadiene yield only the 1/1 adduct even when an excess of carbonyl compound is added under vigorous conditions (100 °C), while

Table 1

Dependence of alkyl substitution of diene ligands on the relative ratio of geometrical isomers, **14** and **15** [a]

	Diene complex					Carbonyl compound	Relative ratio, % [b]	
	R^1	R^2	R^3	R^4	R^5		**14**	**15**
6	H	CH_3	H	H	H	$(CH_3)_2CO$	92	8
						$(i\text{-}C_3H_7)_2CO$	100	0
						$i\text{-}C_3H_7CHO$	99	1
8	CH_3	CH_3	H	H	H	$(i\text{-}C_3H_7)_2CO$	62	38
						$i\text{-}C_3H_7CHO$	59	41
9	H	H	H	H	CH_3	$(i\text{-}C_3H_7)_2CO$	4	96
						$i\text{-}C_3H_7CHO$	5	95
10	H	H	H	H	C_2H_5	$(i\text{-}C_3H_7)_2CO$	5	95
						$i\text{-}C_3H_7CHO$	4	96
11	H	CH_3	H	H	CH_3	$(i\text{-}C_3H_7)_2CO$	2	98
						$i\text{-}C_3H_7CHO$	4	96
12	H	CH_3	H	CH_3	CH_3	$(i\text{-}C_3H_7)_2CO$	3	97
						$i\text{-}C_3H_7CHO$	1	99
13	CH_3	H	H	H	$SiMe_3$	$(i\text{-}C_3H_7)_2CO$	5	95

[a] Reactions were carried out at 0 °C for 5h using 2 equiv. of the relevant carbonyl compound. The relative ratio was determined by gas chromatography. See eq. 2 for numbering system. [b] Optimum total yields are 85–99% by gas chromatography.

Table 2

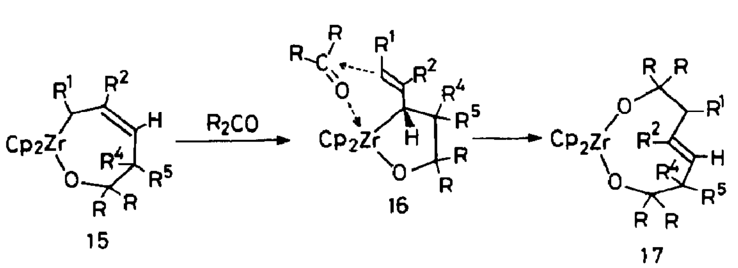
Effect of the alkyl substitution on the diene ligand to the relative ratio between 1/1 adduct **14** and 1/2 adduct **17** [a]

Complex	*s-trans*/*s-cis* ratio	Relative ratio, % [b]	
		1/1 adduct	1/2 adduct
1	100/0	100	0
2	0/100	100	0
3	33/67	5	95
4	65/35	0	100
6	0/100	100	0
7	0/100	100	0
8	0/100	97	3
9	58/42	0	100
10	61/39	1	99
11	0/100	2	98
12	0/100	5	95

[a] 2-Methylpropanal (2 equiv.) was treated with the complex in benzene at 30 °C for 3 h and the relative ratio was determined by gas chromatography after hydrolysis of the product. [b] Total yields are 85–99% by gas chromatography.

other complexes **3–5** and **9–12** readily undergo the 1/2 addition even under mild conditions (0 °C) to yield the 1,3-dioxazirconacyclo-6-nonene derivatives quantitatively. As a typical example, the relative ratio of the 1/1 to the 1/2 adducts derived from 2-methylpropanal (2 equiv.) is listed in Table 2. Thus the oxametallacycles **14** (products from **6–8**) containing a methyl group at the γ-position ($R^2 = CH_3$) always give only the 1/1 adduct, while complexes **15** (products from diene complexes **3–5** and pentadiene complexes **9–12**) possessing a less bulky hydrogen group at that position ($R^3 = H$) allow the double insertion of the aldehyde. Complexes bearing a bulky Cp* ligand are less reactive and always give only the 1/1 adduct even at high temperatures (60–80 °C).

Of significant importance is the (E)-geometry of the resulting 1/2 adduct **17**. For example, a nine-membered 1,3-dioxazirconacyclo-6-nonene derived from $ZrCp_2(C_4H_6)$/acetone (1/2) shows the coupling constant of 15.0 Hz for the olefinic part. Its EIMS spectrum confirms the 9-membered ring structure (monomeric nature). If the double insertion occurs by direct attack of the ketone on the initially formed (Z)-oxametallacyclic species (**15**), it should give the corresponding dioxametallacycle of (Z)-geometry in place of **17** of (E)-geometry. A reaction pathway (eq. 3) via intermediate **16** is thereby proposed to account for the geometrical change during the double insertion. The chair-shaped six-membered transition state seems most likely for **16**, as a similar intermediate has been considered for the *threo*-selective addition of crotylmetal compounds to aldehydes [14]. Significantly, the transitory complex **16** exhibits a secondary carbon at its α-position, while the transtion state **18** expected for **14** must have a sterically unfavorable tertiary carbon at that position (eq. 4). As a consequence, steric repulsion between the Cp groups and the methyl group on the tertiary carbon may hamper the transformation of **14** into **18**. By taking advantage of the above reactions, the successive incorporations of a ketone and then an aldehyde in **3** was achieved. The product yields the expected unsymmetrical diol upon hydrolysis (see Experimental).



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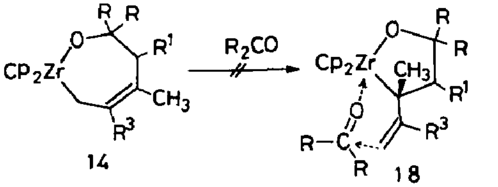

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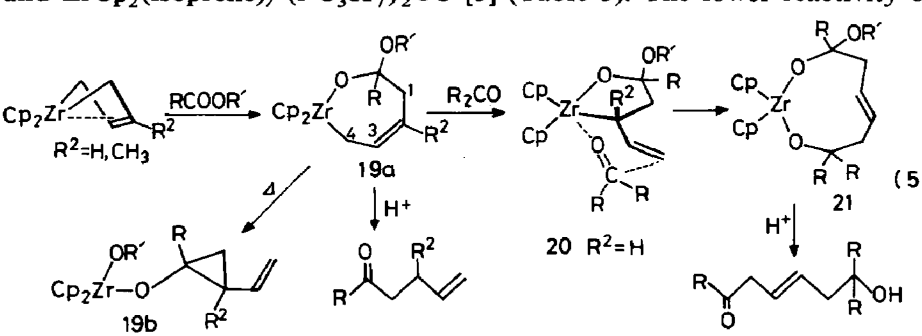
Carbometallation of esters with zirconium-diene complexes

Saturated and unsaturated esters have long been known to undergo the double carbometallation with allylzirconium compounds and main group alkylmetal compounds (e.g. RMgX, AlR_3) to afford tertiary-alkoxymetal derivatives [14]. By contrast, zirconium-diene complexes react with esters to give only the 1/1 adduct at 5–15°C as briefly reported previously [3,15]. Both, $ZrCp_2$(s-*cis*-butadiene) (**3**) and $ZrCp_2$(s-*cis*-isoprene) (**6**) react readily with ethyl acetate, t-butyl acetate and methyl benzoate to provide solely the seven-membered oxametallacycle (**19a**) (1/1 adduct) containing an OR group at its β-position in 80–92% yields. These adducts give the corresponding acetyl or benzoyl derivatives upon hydrolysis (eq. 5). An EIMS spectrum of $ZrCp_2$(s-*cis*-butadiene)/ethyl acetate reveals its monomeric nature. The ^{1}H NMR spectrum clearly indicates the (Z)-oxazirconacyclo-4-heptene structure since their NMR parameters compare very closely with those for crystallographically well-characterized, ketone-inserted complexes, $ZrCp_2$(butadiene)/$(i\text{-}C_3H_7)_2CO$ and $ZrCp_2$(isoprene)/$(i\text{-}C_3H_7)_2CO$ [3] (Table 3). The lower reactivity of esters as



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compared with aldehydes and ketones precludes its double insertion even when highly reactive $ZrCp_2$ complexes (**3**, **4**, **9**) involving butadiene, 2,4-hexadiene or 1,3-pentadiene were subjected to the reaction in the presence of an excess of ester. The ester-inserted products are typified by their significant thermal instability. For example, the ethyl acetate adduct of **3** decomposes at 30°C in solution with half-life of 3 h and the corresponding benzoyl acetate adduct with half-life of ca. 1.2 h. This is due to the migration of OR group (a good leaving group) at the β-position onto

Table 3

^1H NMR chemical shifts (δ, ppm) and coupling constants (Hz) for the 1/1 adducts of $ZrL_2(CH_2CR^2CR^3CH_2)$ with carbonyl compounds, assuming a metallacyclo-4-heptene structure [a]

L		Diene complex		Carbonyl compound		Chemical shifts and coupling constants of products				
		R^2	R^3	R^6	R^7	ν_4, $\nu_{5(4')}$	ν_3	ν_2	ν_1, $\nu_{1'}$	ν_L
C_5H_5	**3**	H	H	i-C_3H_7	i-C_3H_7	1.72(d, $J_{3,4}$ 8.4)	6.28(dt, $J_{2,3}$ 10.0)	5.09(dt)	1.78(d, $J_{1,2}$ 8.6)	5.73
	3	H	H	CH_3	OC_2H_5	1.77(d, $J_{3,4}$ 8.2)	6.25(dt, $J_{2,3}$ 11.6)	5.18(dt)	2.04(d, $J_{1,2}$ 8.0	5.68, 5.74
	3	H	H	C_6H_5	NH_2	1.80(d, $J_{3,4}$ 8.2)	6.12(dt, $J_{2,3}$ 11.0)	5.24(dt)	2.02(d, $J_{1,2}$ 8.1)	5.84
	3	H	H	H	NH_2	1.82(d, $J_{3,4}$ 8.0)	6.31(dt, $J_{2,3}$ 10.3)	5.20(dt)	2.01(d, $J_{1,2}$ 8.5)	5.65, 5.77
	6	CH_3	H	CH_3	CH_3	1.65(d, $J_{3,4}$ 8.3)	6.05(t)		1.74(bs)	5.77
	6	CH_3	H	i-C_3H_7	i-C_3H_7	1.71(d, $J_{3,4}$ 8.5)	6.04(t)		1.87(bs)	5.78
	6	CH_3	H	CH_3	H	1.72(d, $J_{3,4}$ 8.5)	6.04(t)		1.43(m, $J_{1,2}$ 8.3) 1.54(m)	5.74
	6	CH_3	H	i-C_3H_7	H	1.69(d, $J_{3,4}$ 8.6)	6.05(t)		1.38(m, $J_{1,2}$ 8.4) 1.48(m)	5.71, 5.79
	6	CH_3	H	CH_3	OC_2H_5	1.63(d, $J_{3,4}$ 8.2)	6.02(t)		1.87(bs)	5.77, 5.83
	6	CH_3	H	C_6H_5	NH_2	1.88(d, $J_{3,4}$ 8.0)	6.07(t)		2.05(bs)	5.86
	6	CH_3	H	C_6H_5	$NH(C_6H_5)$	1.63(d, $J_{3,4}$ 8.4)	6.18(t)		2.12(bs)	5.56, 5.84
C_5Me_5	**1**	H	H	i-C_3H_7	i-C_3H_7	1.40(d, $J_{3,4}$ 8.3)	6.65(dt, $J_{2,3}$ 11.0)	5.15(dt)	2.09(d, $J_{1,2}$ 8.5)	1.91
	1	H	H	H	$NH(C_6H_5)$	2.07(d, $J_{3,4}$ 8.4)	5.79(dt, $J_{2,3}$ 10.5)	5.01(dt)	2.16(d, $J_{1,2}$ 8.2)	1.87
	1	H	H	H	$N(CH_3)_2$	1.48(d, $J_{3,4}$ 8.4)	6.55(dt, $J_{2,3}$ 10.7)	5.08(dt)	2.24(d, $J_{1,2}$ 8.6)	1.90
	2	CH_3	H	i-C_3H_7	i-C_3H_7	1.81(d, $J_{3,4}$ 8.6)	6.61(t)		2.09(bs)	1.91

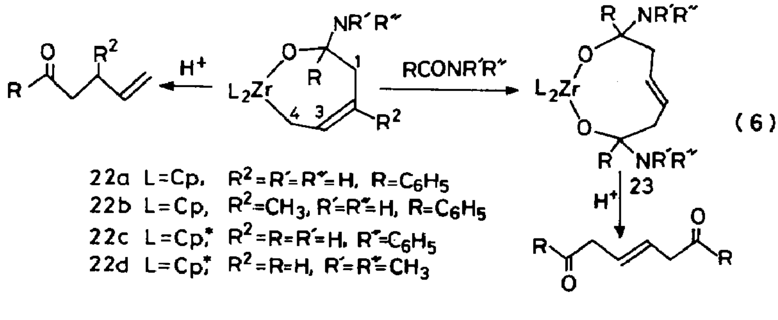
[a] Data were collected at 100 MHz in C_6D_6 at 30 °C after the products were isolated as pure crystals. Numbering system follows those given in eqs. 2 (**14**), 5 and 6.

the metal to give **19b** (see Experimental for details). This type of migration is reinforced when $(C_2H_5O)_2CO$ was treated with **3** or **6**, i.e. this reaction sequence provides only a dibutenyl ketone derivative upon hydrolysis as a result of the intermolecular 1/2 addition reaction [6]. All the esters tested here are completely inert to $ZrCp^{\star}_2$(s-*trans*-butadiene) (**1**) and $ZrCp^{\star}_2$(s-*cis*-isoprene) (**2**) bearing bulky ancillary ligands even under the vigorous conditions (80–110 °C). The steric crowding around the metal probably inhibits access by such a weak donor.

In view of the relative reactivity (basicity) of carbonyl compounds mentioned above, the successive incorporations of an ester and then a ketone was for the first time realized, and the expected 1,3-dioxazirconacyclo-6-nonene derivative (**21**) was obtained with high regioselectivity (> 98%) in 75–85% yields. This insertion may proceed via the transition state **20** similar to **16** because **19a** has a (*Z*)-olefinic unit while the product **21** assumes the (*E*)-geometry. However, if these electrophiles are added in reversed order, i.e. the addition of 2-methylpropanal or 2,4-dimethyl-3-pentanone before addition of ethyl acetate, benzoyl acetate or ethyl benzoate the double insertion reaction does not initiate. The 1/1 addition of the aldehyde or the ketone took place only and the added esters were recovered unchanged.

Carbometallation of acid amides with zirconium-diene complexes

The reaction of acid amides with a series of zirconium-diene complexes was examined to find its unique chemical behavior. The addition of acid amides (*N,N*-dimethylformamide, *N*-phenylformamide, benzamide, benzanilide, etc.) to $ZrCp_2$(s-*cis*-isoprene) (**6**) or to $ZrCp^{\star}_2$(s-*trans*-butadiene) (**1**) provides again (*Z*)-oxametallacycles, in 95% yield, while keeping nearly the same regio- and stereochemistry as reported for the insertion of ketones (see Table 3). These adducts are thermally much more stable as compared with the ester-inserted products and upon hydrolysis give the formyl or benzoyl derivatives, identical with those derived from ester-inserted compounds. Note that the NH or NH_2 group in the acid amides does not cleave the Zr–diene bond while these groups readily cleave the M–R bond of organoaluminum and organomagnesium compounds with evolution of RH [16]. Especially noteworthy is the fact that acid amides can conduct the double insertion into the $ZrCp_2$(diene) bearing the less bulky ancillary ligand, whereas the esters cannot undergo the double insertion. For example, *N,N*-dimethylformamide and acetamide react with $ZrCp_2$(s-*cis*-butadiene) (**3**) at 45 °C to give the nine-membered 1,3-dioxametallacycles (**23**) in good yields (70–85%). Hydrolysis of the product yielded the (*E*)-3-hexen-1,6-dione derivatives. This reaction sequence could find useful application in organic syntheses. The use of the more bulky diene complexes **1** and **2** ligated by Cp* is ineffective in performing the double carbometallation, since it gives only the 1/1 adduct between 50–100 °C.



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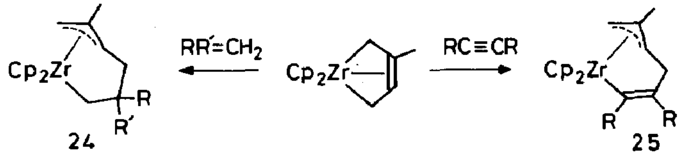
Carbometallation with alkene- and alkyne-inserted zirconium-diene complexes

The s-*cis*- and s-*trans*-butadiene, isoprene- and pentadiene-zirconium complexes of the formula $ZrCp_2$(diene) readily undergo the additions with various 1-alkenes and alkynes to give the 1/1 adduct, σ,*syn*-η^3-allylmetal (**24**, **25** in eq. 7) [17]. Since this class of complexes, like **24** and **25**, has two reactive metal–carbon bonds in the molecule, further reaction with various electrophiles is expected. Thus, sequential three-component addition reactions (e.g. alkene-diene-aldehyde, alkyne-diene-nitrile) have been achieved successfully utilizing this fruitful function with an extremely



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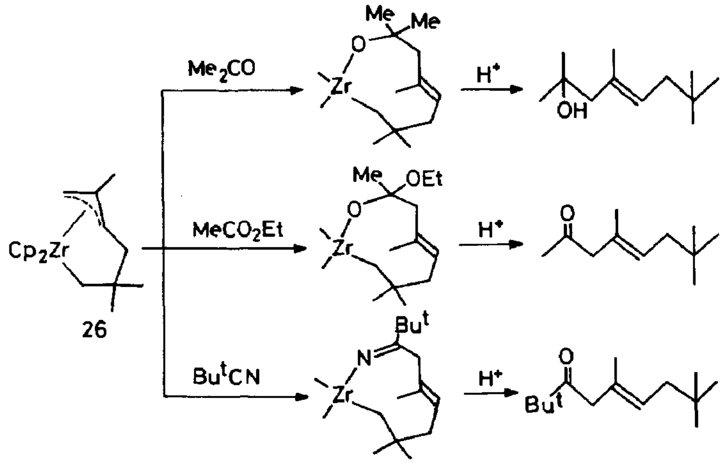
high regioselectivity (> 90%). Typical examples are shown in eqs. 8–10. Thus, the above-noted electrophiles always react with terminal carbon on the allyl side. The insertion into the other end, the σ-bonded Zr–C bond, is negligible in every case.



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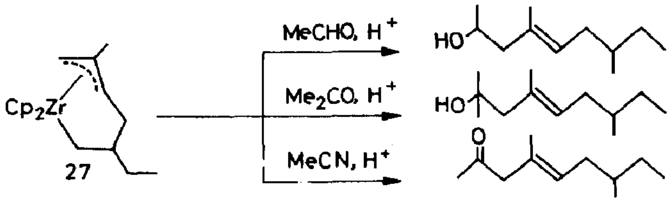

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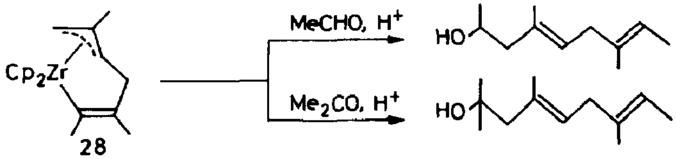

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The mass and ^1H NMR spectral data reveal that the resulting three-component addition products are in the monomeric form and have (E)-geometry. Thus a variety of remarkable macrocyclic metal compounds are now accessible by utilizing the sequences shown in eqs. 8–10. The preferential formation of the (E)-isomer may be correlated directly to the *syn*-allyl structure of the precursor complexes.

Concluding remarks

A series of substituted or unsubstituted zirconium-diene and zirconium-pentadiene complexes was found to undergo regio- and stereo-selective 1/1 addition with ketones, aldehydes, esters, and acid amides to give (Z)-oxametallacycles irrespective of the geometry of the ligated dienes (s-*cis* or s-*trans*) or the bulkiness of the auxiliary ligands (Cp or Cp*), whereas corresponding reactions with heterocumulenes (isocyanates, ketenes, CO_2, etc.) were found usually to give rise to the (E)-isomer (σ,*syn*-η^3-allyl bonded metal compounds) [18*]. This marked difference may be ascribed to the difference in hybridization of the β-carbon connected to the oxygen atom in the final seven-membered products, i.e. the former is an sp^3 whereas the latter is an sp^2 carbon. Zirconium-diene complexes also undergo the unique double carbometallation of carbonyl compounds when the intermediate 1/1 adducts have a sterically less-congested hydrogen substituent at the γ-position, although alkyl substitution at that position always precludes the formation of the 1/2 adducts. Since these products readily yield mono- or di-alcohols or ketones in high selectivity upon hydrolysis, the present chemistry can be applied to many reactions relevant to organic synthesis.

Experimental

All manipulations were conducted under dry argon by standard Schlenk techniques. Hydrocarbon solvents were dried over Na/K alloy and thoroughly purged of air by bulb-to-bulb distillation. Pure samples of zirconium-diene complexes were prepared by the procedures described previously [13,19]. ^1H NMR spectra were recorded on a JEOL Model GX-500 or a Varian XL-100 instrument and analyzed by computer simulation with a Varian spin simulation program. Mass spectra (EI) were recorded on a JEOL DX-300 spectrometer. Elemental analysis, gas chromatographic work and melting point measurements were conducted as described previously [3,5].

Preparation of the 1/1 adducts of $Zr(C_5R_5)_2$(diene) with ketones and aldehydes

The 1/1 addition compounds of zirconium-diene complexes **1**–**7** were allowed to react with the ketones or aldehydes by essentially the same procedure as described previously [3]. A typical example is as follows. To a hexane solution (30 ml) of $ZrCp_2(C_4H_6)$ (**3**) (2.0 mmol) was added 2,4-dimethyl-3-pentanone (0.2 g, 2.0 mmol) in hexane (2 ml) at −70 °C. The mixture was allowed to warm to room temperature (ca. 25 °C) and kept there for 2 h with magnetic stirring. The color of the solution turned from red-brown to pale-yellow. Concentration of the solution to 2 ml

* Reference number with asterisk indicates a note in the list of references.

followed by cooling to $-20\,^{\circ}C$ gave colorless crystals of the 1/1 adduct, $ZrCp_2(C_4H_6)/C_7H_{14}O$, in 90% yield. m.p. 142°C (sealed capillary); EIMS (70 eV, rel. intensity): m/z 392(M^+; ^{94}Zr, 6.3), 390(M^+; ^{92}Zr, 6.2), 389(M^+; ^{91}Zr, 5.9), 388(M^+; ^{90}Zr, 15.8), 220($ZrCp_2$; ^{90}Zr, 100), 171(CpZrO; ^{90}Zr, 73.8). ^{13}C NMR (C_6D_6, J(CH) in Hz): δ 33.0 (t, 131, 1-CH_2), 138.1(d, 158, 2-CH), 114.8(d, 160, 3-CH), 40.9(t, 136, 4-CH_2), 94.2(s, 5-C), 35.7(d,135,C-6), 19.1, 19.8(q,126,C-7), 109.6(d,172, Cp). Anal. Found: C, 64.68; H, 7.51. $C_{21}H_{30}OZr$ calcd.: C, 64.37; H, 7.76%. Acid(acetic acid) cleavage of the adduct gave 2-methyl-3-isopropyl-6-hepten-3-ol in 98% yield. ^1H NMR ($CDCl_3$): δ 0.94(d, 6H, J 7.5 Hz, CH_3), 0.97(d, 6H, J 7.5 Hz, CH_3), 1.56(dt, 1H, J 4.0 Hz, CHH′), 1.60(dt, 1H, J 5.8 Hz, CHH'), 1.84(s, 1H, OH), 1.94(m, 2H, CH(CH_3)$_2$), 2.07(d, 1H, =CHCHH′), 2.17(d, 1H, =CHCHH'), 4.94(dd, 1H, J 10.1 Hz, CHH′=), 5.02(dd, 1H, J 16.8 Hz, CHH'=).

The ^1H NMR spectral data for the 1/1 adduct of ketones and related compounds are listed in Table 1 and those for the typical hydrolysis products are given below:

2-Methyl-6-hepten-3-ol (product from **3**/i-C_3H_7CHO). δ 0.90(d, 6H, J 7.0 Hz, CH_3), 1.48, 1.68(m, 2H, J 4.5 and 6.2 Hz, 4-CH_2), 1.70 (m, 1H, 2-CH), 1.75(s, 1H, OH), 2.28, 2.35(m, 2H, 5-CH_2), 5.08, 5.12(dd, 2H, J 10.1 and 16.2 Hz, CH_2=), 5.75(m, 1H, CH=). Yield (GC) 98%.

2,5-Dimethyl-6-hepten-3-ol (product from **6**/i-C_3H_7CHO). δ 0.90(d, 6H, J 6.8 Hz, CH_3), 1.06(d, 3H, J 6.5 Hz, 5-CH_3), 1.20, 1.40(dd, J 4.5 and 9.8 Hz, 4-CH_2), 1.68(m, 1H, 2-CH), 1.75(s, 1H, OH), 2.32(m, 1H,5-CH), 3.35(m, 1H, $J_{2,3}$ 6.8 Hz, 3-CH), 4.96, 5.03(dd, 2H, J 9.9 and 16.8 Hz, CH_2=), 5.68(ddd, J 6.7 Hz, 6-CH). Yield (GC) 93%.

2,4,5-Trimethyl-5-hexen-2-ol (product from **7**/acetone). δ 1.05(d, 3H, J 6.7 Hz, 4-CH_3), 1.18(s, 6H, CH_3), 1.72, 1.80(dd, 2H, J 6.0 and 8.0 Hz, 3-CH_2), 1.94(s, 3H, 5-CH_3), 2.18(m, 1H, 4-CH), 4.82, 4.97(d, 2H,CH_2=).

Reaction of $ZrCp_2$(pentadiene) and its derivatives (8–13)

Synthesis of the 1/1 adduct was carried out similarly. ^1H NMR data ($CDCl_3$) for the hydrolysis product of the 1/1 adduct of 2-methylpropanal are given below (Product yields (GC) 92–99%):

2,4,5-Trimethyl-6-hepten-3-ol (product from **8**). δ 0.92, 0.98(d, 6H, J 7.2 Hz, CH_3), 1.02(d, 3H, 4-CH_3), 1.08(d, 3H, 5-CH_3), 1.48(m, 1H, 4-CH), 1.71(m, 1H, 2-CH), 1.70(s, 1H, OH), 2.20(dq, 1H, J 7.8 Hz, 5-CH), 3.25(m, 1H, 3-CH), 4.95, 5.09(dd, 2H, CH_2=), 5.74(m, 1H, 6-CH).

2,4-Dimethyl-6-hepten-3-ol (product from **9**). δ 0.91, 0.98(d, 6H, CH_3), 0.97(d, 3H, 4-CH_3), 1.65(m, 1H, 2-CH), 1.84, 1.90(dd, 2H, $J_{4,5}$ 4.0 Hz, $J_{4,5'}$ 6.5 Hz, 5-CH_2), 1.86(s, 1H, OH), 4.94, 4.97(m, 2H, CH_2=), 5.69(m, 1H, CH_2).

2-Methyl-4-ethyl-6-hepten-3-ol (product from **10**). δ 0.92, 0.98(d, 6H, CH_3), 0.87(d, 3H, CH_2CH_3), 0.99(m, 2H, CH_2CH_3), 1.67(m, 1H, 2-CH), 2.01(d, J 7.8 Hz, 5-CH_2), 1.80(s, 1H, OH), 3.08(m, 1H, 3-CH), 5.00, 5.08(dd, 2H, CH_2=), 5.64(m, 1H, CH=).

2,4,6-Trimethyl-6-hepten-3-ol (product from **11**). δ 0.90, 0.93(d, 6H, CH_3), 0.87(d, 3H, 4-CH_3), 1.40(m, 1H, $J_{4,5}$ 7.8 Hz, 4-CH), 1.65(m, 1H, 2-CH), 1.68 (s, 1H, OH), 1.72(s, 3H, 6-CH_3), 2.01(d, 2H, CH_2), 3.08(dd, 1H, 3-CH), 4.72, 4.79(dd, 2H, CH_2=).

2,4,4,6-Tetramethyl-6-hepten-3-ol (product from **12**). δ 0.91, 0.99(d, 6H, CH_3), 0.97(s, 6H, 4-CH_3), 1.66(m, 1H, 2-CH), 1.79(s, 3H, 6-CH_3), 1.85(s, 1H, OH), 2.12(s, 2H, 5-CH_2), 3.22(m, 1H, 3-CH), 4.91, 5.05(d, 2H, CH_2=).

7-(Trimethyl)silyl-2,4-dimethyl-6-hepten-3-ol (product from **13**). δ 0.1 (s, 9H, $SiMe_3$), 0.81(d, 3H, 3-CH_3), 0.90, 0.99(d, 6H, CH_3), 1.48(m, 1H, 4-CH), 1.65(s, 1H, OH), 2.30(m, 2H, 5-CH_2), 3.25(m, 1H, 3-CH), 5.58(d, 1H, J 17.5 Hz, 7-CH), 5.74(m, 2H, CH=CH).

*Preparation of the ester adduct (**19a** and **19b**)*

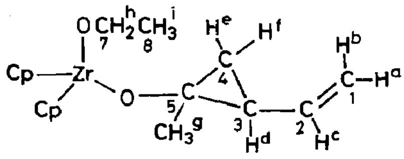
A mixture of $ZrCp_2(C_4H_6)$ (**3**) (2.0 mmol) and ethyl acetate (0.2 ml, 2.0 mmol) in hexane (5 ml) was stirred at 20 °C for 10 h. Then the solution was concentrated and cooled to −20 °C, and pale yellow crystals of the 1/1 adduct **19a** separated in ca. 60% yield; m.p. 58 °C(dec). EIMS (rel. intensity): m/z 366(M^+; ^{94}Zr, 10.5), 364(M^+; ^{92}Zr, 15.8), 363(M^+; ^{91}Zr, 16.4), 362(M^+; ^{90}Zr, 30.6), 317($M^+ - OC_2H_5$; ^{90}Zr, 20.3), 297(M^+ − Cp; ^{90}Zr, 8.3), 220(Cp_2Zr; ^{90}Zr, 100). ^{13}C NMR (C_6D_6, J(CH) in Hz): δ 39.8(t, 130, $ZrCH_2$), 138.1(d, 155, $ZrCH_2$*C*H), 114.6(d, 162, $ZrCH_2$CH*C*H), 40.9(t, 136, CH_2), 110.5(s, t-C), 55.9(t, OCH_2), 16.4(q, CH_3), 25.1(q, CH_3), 110.0, 109.1(s, Cp). Anal. Found: C, 59.05; H, 6.60. $C_{18}H_{24}O_2Zr$ calcd.: C, 59.46; H, 6.65%. Hydrolysis of the adduct gave 4-hexen-2-one in 92% yield. ^{1}H NMR ($CDCl_3$): δ 2.16(s, 3H, CH_3), 1.35(d, 3H, CH_3), 3.19(d, 2H, J 6.2 Hz, CH_2), 5.59, 5.65(m, 2H, CH=CH); IR(NaCl) 1715 cm^{-1} (C=O); EIMS 98(M^+).

The 1/1 adducts of **9** and **12** with ethyl acetate were obtained similarly in 75–82% yield and gave acetyl compounds upon hydrolysis.

3-Methyl-4-hexen-2-one (hydrolysis product from **9**). ^{1}H NMR ($CDCl_3$): δ 1.71 (d, 3H, J 6.8 Hz, CH_3), 1.09(d, 3H, CH_3C=), 2.11(s, 3H, CH_3CO), 3.44(m, 1H, 3-CH), 5.30, 5.40(m, 2H, CH=CH); IR(KBr), 1725 cm^{-1}.

3,3,5-Trimethyl-5-hexen-2-one (hydrolysis product from **12**). ^{1}H NMR ($CDCl_3$): δ 1.16(s, 6H, CH_3), 1.65(s, 3H, CH_3), 2.16(s, 3H, CH_3CO), 2.30(s, 2H, CH_2), 4.60, 4.79(d, 2H, CH_2=); IR (KBr) 1720 cm^{-1}.

Heating of **19a** in benzene to 45 °C for 10 h resulted in the migration of CH_3CH_2O group to give **19b** (> 85% yield) having a cyclopropane ring and a vinyl group. ^{1}H NMR (500 MHz, C_6D_6, parameters are obtained by computer simulation): δ 5.25(dd, H^a, J_{ac} 10.4 Hz, J_{ab} −2.2 Hz), 5.34(dd, H^b, J_{bc} 17.3 Hz), 5.98(ddd, H^c, J_{cd} 9.4 Hz), 1.50(ddd, H^d, J_{df} 9.4 Hz, J_{de} 6.3 Hz), 0.98(dd, H^e, J_{ef} −4.9 Hz), 0.92(dd, H^f), 1.44(s, CH_3), 4.04(q, H^h, J_{hi} 6.8), 1.25(t, H^i). ^{13}C NMR (125 MHz, C_6D_6 at 30 °C, J(CH) in parentheses): 111.9(t, C^1, 151), 140.0(d, C^2, 154), 31.21(d, C^3, 150), 23.60(t, C^4, 157), 68.50(s), 26.89(q, C^6, 125), 68.78(t, C^7, 141), 20.00(q, C^8, 125).



Preparation of the 1/1 adduct of diene complexes with acid amides

The reaction of an acid amide with **3**, **6**, **1** or **2** and the isolation of the product was carried out in the same way as that described for the adduct of **3** with 2,4-dimethyl-3-pentanone.

$ZrCp_2(C_4H_6)/C_6H_5CONH_2$ (22a), m.p. 80 °C. EIMS (rel. intensity): m/z 399(M^+; ^{94}Zr, 1.1), 397(M^+; ^{92}Zr, 1.7), 396(M^+; ^{91}Zr, 1.8), 395(M^+, ^{90}Zr, 3.7), 220 (Cp_2Zr, ^{90}Zr, 100), 171(CpZrO, ^{90}Zr, 29.3). Anal. Found: C, 62.10; H, 5.77; N, 3.40. $C_{21}H_{23}NOZr$ calcd.: C, 63.59; H, 5.85; N, 3.53%.

$ZrCp_2(C_4H_6)/HCONHPh$, m.p. 145 °C. EIMS m/z 399(M^+; ^{94}Zr, 3.7), 397(M^+; ^{92}Zr, 5.0), 396(M^+; ^{91}Zr, 5.3), 395(M^+; ^{90}Zr, 11.2), 220(Cp_2Zr; ^{90}Zr, 100), 171 (CpZrO; ^{90}Zr, 33.5). Anal. Found: C, 62.70; H, 5.88; N, 3.42. $C_{22}H_{25}NOZr$ calcd.: C, 64.59; H, 5.85; N, 3.53%.

$ZrCp_2(C_5H_8)/C_6H_5CONH_2$ (22b), m.p. 85 °C. EIMS m/z 413(M^+; ^{94}Zr, 2.7), 411 (M^+; ^{92}Zr, 3.4), 410(M^+; ^{91}Zr, 3.6), 409(M^+; ^{90}Zr, 7.9), 220(CP_2Zr; ^{90}Zr, 100), 171(CpZrO; ^{90}Zr, 35.1). Anal. Found: C, 63.11; H, 5.97; N, 3.30. $C_{31}H_{43}NOZr$ calcd.: C, 69.35; H, 8.07; N, 2.61%.

$ZrCp^{\star}_2(C_4H_6)/OHCNH(C_6H_5)$ (22c), m.p. 157 °C. EIMS: m/z 539(M^+; ^{94}Zr, 1.7), 537(M^+; ^{92}Zr, 2.3), 536(M^+; ^{91}Zr, 2.3), 535(M^+; ^{90}Zr, 5.2), 360($Cp^{\star}_2Zr$; ^{90}Zr, 100), 241($Cp^{\star}$ZrO; ^{90}Zr, 21.8). Anal. Found: C, 68.11; H. 7.94; N, 2.50. $C_{27}H_{43}NOZr$ calcd.: C, 69.35; H, 8.07; N, 2.61%.

$ZrCp^{\star}_2(C_4H_6)/OHCN(CH_3)_2$ (22d), m.p. 125 °C. EIMS: m/z 491(M^+; ^{94}Zr, 1.2), 489(M^+; ^{92}Zr, 1.7), 488(M^+; ^{91}Zr, 1.8), 487(M^+; ^{90}Zr, 3.1), 360($Cp^{\star}_2Zr$; ^{90}Zr, 100), 241($Cp^{\star}$ZrO; ^{90}Zr, 18.7). Anal. Found: C, 64.91; H, 8.76; N, 2.80. $C_{27}H_{43}NOZr$ calcd.: C, 66.34; H, 8.87; N, 2.87%.

Double insertion of carbonyl compounds into $ZrCp_2(C_4H_6)$ (3)

To a hexane solution of $ZrCp_2(C_4H_6)$ (3) (2.0 mmol) was added acetone (4.2 mmol) by syringe at −70 °C. The mixture was allowed to warm to room temperature and stirred at 30 °C for 2 h. Concentration of the solution followed by cooling to −20 °C gave the 1/2 adduct as colorless crystals in 65% yield. M.p. 192 °C. EIMS (rel. intensity): m/z 394(M^+; ^{94}Zr, 3.1), 392(M^+; ^{92}Zr, 3.8), 391(M^+; ^{91}Zr), 390(M^+; ^{90}Zr, 8.9), 325($M^+ -$ Cp; ^{90}Zr, 8.9), 278($M^+ - C_7H_{12}O$; ^{90}Zr, 54.9), 220(Cp_2Zr; ^{90}Zr, 100), 171(CpZrO; ^{90}Zr, 87.8). ^{1}H NMR (C_6D_6 at 60 °C) data determined by the computer simulation with respect to the $CH^3H^{3'}CH^4{=}CH^5CH^6H^{6'}$ unit: δ 1.18(s, 12H, CH_3). 1.88, 2.14(m, 4H, $J_{3,3'}$ −8.0 Hz, $J_{3,4} = J_{5,6} = 7.0$ Hz, $J_{3',4} = J_{5,6'} = 7.3$ Hz, 3- and 6-CH_2), 5.37(m, 2H, $J_{4,5}$ 15.0 Hz, $J_{3,5} = J_{3',5} = J_{4,6} = J_{4,6'} = -1.5$ Hz, CH=CH), 6.04(s, 10H, Cp); ^{13}C NMR (C_6D_6, J(CH)): δ 48.20(t, 128, CH_2), 130.90(d, 151, CH=), 79.32(s, tertiary C), 32.33, 29.29(q, CH_3), 111.37(d, Cp). Anal. Found: C, 61.25; H, 7.08. $C_{30}H_{28}O_2Zr$ calcd.: C, 61.33; H, 7.21%. Hydrolysis of $ZrCp_2(C_4H_6)/2(CH_3)_2CO$ adduct followed by vacuum distillation gave (E)-2,7-dimethyl-4-octen-2,7-diol as an oil in 87% yield. ^{1}H NMR ($CDCl_3$) data were assigned with the help of computer simulation: δ 1.20(s, 12H, CH_3), 1.65(s, 2H, OH), 2.10(m, 4H, $J_{3,3'}$ −10.0Hz, $J_{3,4} = J_{3',4} = J_{5,6} = J_{5,6'} = 7.3$ Hz, 3- and 6-CH_2), 5.45(m, 2H, $J_{4,5}$ 15.0 Hz, $J_{3,5} = J_{3',5} = J_{4,6} = J_{4,6'} = -1.5$Hz, $J_{3,6}$ 0.5 Hz, CH=CH).

In a similar manner, the 1/2 adducts of **3** with 2-methylpropanal or 3-pentanone were obtained in ca. 90% yields. NMR data for their hydrolyzates are shown below:

(E)-2,9-Dimethyl-5-decen-3,8-diol (product from 3/2(i-C_3H_7CHO)). ^{1}H NMR ($CDCl_3$): δ 0.95(d, 12H, CH_3), 1.66(m, 2H, 2- and 9-CH), 1.65(s, 2H, OH), 3.24 (m, 2H, 3- and 8-CH), 2.18, 2.20(m, 4H, CH_2), 5.56(m, 2H, J 15.1 Hz, CH=CH).

(E)-3,8-Diethyl-5-decen-3,8-diol (product from 3/2($C_2H_5)_2$CO). ^{1}H NMR ($CDCl_3$): δ 0.90(t, 12H, J 7.0 Hz, CH_3), 1.48(q, 8H, CH_2), 2.19(d, 4H, 4- and 7-CH_2), 5.56(m, 2H, J 15.0 Hz, CH=CH).

Double insertion of 2-methylpropanal into $ZrCp_2$(pentadiene)

To a hexane solution (6 ml) of the pentadiene complexes **4** or **9–12** (3.0 mmol) was added 2-methylpropanal (6.0 mmol) at $-70\,^{\circ}C$. The mixture was stirred at $30\,^{\circ}C$ for 5 h, quenched with acetic acid and then distilled in vacuo (10^{-2} mmHg) to give unsaturated alcohols in ca. 60% yield.

2,4,7,9-Tetramethyl-5-decen-3,8-diol (product from **4**/2(i-C_3H_7CHO)). ^{1}H NMR ($CDCl_3$): δ 0.90(d, 12H, CH_3), 1.03(d, 6H, 4- and 7-CH_3), 1.72(m, 2H, 2- and 9-CH), 1.75(s, 2H, OH), 2.34(m, 2H, 4- and 7-CH), 3.14(m, 2H, 3- and 8-CH), 5.49 (m, 2H, J 15.5 Hz, CH=CH); EIMS m/z 228(M^+).

2,4,9-Trimethyl-5-decen-3,8-diol (product from **9**/2(i-C_3H_7CHO)). ^{1}H NMR ($CDCl_3$): δ 0.90, 0.94(d, 12H, CH_3), 0.98(d, 3H, 4-CH_3), 1.68, 1.69(m, 2H, 2- and 9-CH), 1.68(s, 2H, OH), 2.18(m, 2H, 7-CH_2), 2.32(m, 1H, 4-CH), 3.05, 3.33(m, 2H, 3- and 8-CH), 5.45, 5,49(m, 2H, CH=CH); EIMS m/z 214(M^+).

2,4,6,9-Tetramethyl-5-decen-3,8-diol (product from **11**/2(i-C_3H_7CHO)). ^{1}H NMR ($CDCl_3$): δ 0.96, 0.98(d, 12H, CH_3), 0.98(d, 3H, 4-CH_3), 1.62, 1.64(m, 2H, 2- and 9-CH), 1.66(s, 3H, 6-CH_3), 1.82(s, 2H, OH), 2.06, 2.11(dd, 2H, J 9.8 and 4.8 Hz, 7-CH_2), 3.12, 3.44(m, 2H, 3- and 8-CH), 5.20(t, J 8.7 Hz, CH=); EIMS m/z 228(M^+).

2,4,4,6,9-Pentamethyl-5-decen-3,8-diol (product from **12**/2(i-C_3H_7CHO)): ^{1}H NMR ($CDCl_3$): δ 0.93, 0.95(d, 12H, CH_3), 1.02(s, 6H, 4-CH_3), 1.70, 1.72(m, 2H, 2- and 9-CH), 1.76(s, 3H, CH_3), 1.85(s, 2H, OH), 2.12, 2.22(dd, 2H; J 11.5 and 4.9 Hz, 7-CH_2), 5.22(s, 1H, CH=); EIMS m/z 242(M^+).

Sequential insertion of ester and aldehyde into 3

To a toluene solution (6 ml) of the $ZrCp_2(C_4H_6)/CH_3CO_2C_2H_5$ adduct (0.7 g, 2.0 mmol) was added 2-methylpropanal (0.2 ml, 2.5 mmol). The mixture was heated to $60\,^{\circ}C$ for 10 h and then evaporated to dryness to give the adduct as an oil in 68% yield. The product was extracted into ether and hydrolyzed to give a ketone-alcohol:

8-Methyl-4-nonen-7-ol-2-one. ^{1}H NMR ($CDCl_3$, computer-simualted): δ 0.92(d, 6H, CH_3), 1.64(m, 1H, 8-CH), 1.67(s, 1H, OH), 2.13(s, 3H, 1-CH_3), 2.25(m, 2H, $J_{6,7}$ 5.8 Hz, $J_{6,6'}$ -9.8 Hz, $J_{5,6}=J_{5,6'}=7.3$ Hz, $J_{4,5}$ 15.5 Hz, 6-CH_2), 3.12(m, 2H, $J_{3,3'}=-10.0$Hz, $J_{3,4}=J_{3',4}=7.2$ Hz, 3-CH_2), 3.38(m, 1H, 7-CH), 5.50(m, 1H, 4-CH), 5.55 (m, 1H, 5-CH); EIMS m/z 170(M^+).

Sequential insertion of ketone and aldehyde to 3

To a toluene solution (6 ml) of the $ZrCp_2(C_4H_6)$/3-pentanone adduct (0.7 g, 2.0 mmol) was added 2-methylpropanal (0.2 ml, 2.5 mmol) at ambient temperature. The mixture was heated to $60\,^{\circ}C$ for 5 h and then hydrolyzed. Vacuum distillation of the hydrolyzate gave a diol in 65% isolated yield.

3-Ethyl-9-methyl-5-decen-3,8-diol. ^{1}H NMR ($CDCl_3$) δ 0.84(t, 6H, J 7.8 Hz, CH_3), 0.88(d, 6H, J 5.7 Hz, CH_3), 1.61(m, 1H, CH), 1.68–1.69(bs, 2H, OH), 2.14(m, 2H, 4-CH_2), 2.16(m, 2H, 7-CH_2), 3.33(m, 1H, CH), 5.50, 5.51(m, 2H, J 13.5 Hz, CH=). EIMS m/z 214, 213, 212.

Double insertion of acid amides into 3

The reactions of $ZrCp_2$(butadiene)(**3**) (2.0 mmol) with N,N-dimethylformamide (4.1 mmol) or acetamide (4.0 mmol) were carried out at $45\,^{\circ}C$ in benzene in essentally the same way as described for the reaction of **3** with acetone.

$ZrCp_2(C_4H_6)/2(N,N$-dimethylformamide). M.p. 135 °C. EIMS(rel. intensity) m/z 424(M^+, ^{94}Zr), 422(M^+ ^{92}Zr), 421(M^+, ^{91}Zr), 420(M^+, ^{90}Zr), 220($ZrCp_2$, 100), 171(CpZrO, 29.8). ^{1}N NMR (C_6D_6): δ 2.28(bs, 12H, NCH_3), 2.34, 2.38(m, 4H, CH_2), 4.26(dd, 2H, CH), 5.12(m, 2H, J 13.2 Hz, CH), 5.97(s, 10H, Cp). Hydrolysis gave the following diketone in 73% isolated yield.

(E)-4-Octen-2,7-dione. ^{1}H NMR ($CDCl_3$): δ 2.16(s, 6H, CH_3), 3.20(d, 4H, CH_2), 5.46(dt, 2H, J 14.5 Hz, CH). IR(neat): 1640 cm^{-1} (ν(CO), 960(ν(C=C)). Anal. Found: C, 68.45; H, 8.63. $C_8H_{12}O_2$ calcd.: C, 68.57; H, 8.57%.

$ZrCp_2(C_4H_6)/2$(acetamide). M.p. 125 °C. EIMS (rel. intensity): m/z 396(M^+, ^{94}Zr, 1.1), 394(M^+, ^{92}Zr, 3.0), 393(M^+, ^{91}Zr, 3.3), 392(M^+, ^{90}Zr, 6.3), 220(Cp_2Zr, 100), 171(CpZrO, 21.1). Characterization of the hydrolyzate is unsuccessful because of its instability in air (polymerization occurs).

Sequential addition of isobutene and carbonyl compound to **6**

The precursor $Cp_2Zr[CH_2C(CH_3)_2CH_2CHC(CH_3)CH_2]$ (**26**) was obtained from the reaction of **6** with isobutene by the procedure reported previously [17]. To a hexane solution (6 ml) of **26** (2.0 mmol) was added acetone (2.0 mmol) at room temperature. The mixture was stirred at 60 °C for 6 h, then concentrated, and cooled to −20 °C to give colorless crystals of the adduct $ZrCp_2$(isoprene/isobutene/acetone) in 80% yield. M.p. 152 °C. EIMS (rel. intensity): m/z 406(M^+; ^{94}Zr, 8.5), 404(M^+; ^{92}Zr, 9.3), 403(M^+; ^{91}Zr, 9.7), 402(M^+; ^{90}Zr, 18.8). ^{1}H NMR (C_6D_6): δ 1.01(s, 2H, $ZrCH_2$), 1.03(s, 6H, 2-CH_3), 2.06(d, 2H, 3-CH_2), 5.40(t, J 8.5 Hz, CH=), 1.73(s, 3H, 5-CH_3), 1.91(s, 2H, 6-CH_2), 1.28(s, 6H, $OC(CH_3)_2$), 5.80(s, 10H, Cp). The (E)-geometry was confirmed by the NOE effect(8%) on CH_2 signals which appeared upon irradiation. Anal. Found: C, 64.98; H, 7.91. $C_{22}H_{32}OZr$ calcd.: C, 65.45; H, 7.99%. Similarly, the adducts of **26** with acetaldehyde, ethyl acetate and pivalonitrile were obtained. ^{1}H NMR spectral data for the hydrolysis products are given below:

2,4,7,7-Tetramethyl-4-octen-2-ol (product from **6**/isobutene/acetone). δ 0.91(s, 9H, t-C_4H_9), 1.21(s, 6H, CH_3), 1.73(s, 3H, CH_3), 1.85(s, 1H, OH), 1.94(d, 2H, J 8.5 Hz, 6-CH_2), 2.21, 2.24(d, 2H, 3-CH_2), 5.30(t, 1H, CH=); EIMS m/z 184(M^+).

4,7,7-Trimethyl-4-octen-2-ol (product from **6**/isobutene/acetaldehyde). δ 0.90(s, 9H, t-C_4H_9), 1.19(d, 3H, CH_3), 1.62(s, 3H, CH_3), 1.80(s, 1H, OH), 1.88, 1.96(dd, 2H, J 8.7 Hz, 6-CH_2), 2.08, 2.12(dd, 2H, J 4.2 and 8.0 Hz, 3-CH_2), 5.33(t, 1H, CH=). EIMS m/z 170(M^+).

4,7,7-Trimethyl-4-octen-2-one (product from **6**/isobutene/$CH_3CO_2C_2H_5$). δ 0.92(s, 9H, t-C_4H_9), 1.64(s, 3H, CH_3), 1.96(d, 2H, J 8.2 Hz, 6-CH_2), 2.15 (s, 3H, CH_3CO), 3.12(S, 2H, 3-CH_2), 5.41(t, 1H, CH=); IR(KBr) 1660 cm^{-1}. EIMS m/z 168(M^+).

2,2,5,8,8-Pentamethyl-5-nonen-3-one (product from **6**/isobutene/t-BuCN). δ 0.90(s, 9H, t-C_4H_9), 1.14(s, 9H, t-C_4H_9), 1.64(s, 3H, CH_3), 1.96(d, 2H, 7-CH_2), 3.12(bs 2H, 4-CH_2), 5.41(t, 1H, CH=); IR(KBr) 1670 cm^{-1}. EIMS m/z 210(M^+).

Sequential addition of 1-butene and carbonyl compounds to **6**.

The 1-butene adducts of **6** were isolated by the procedure described earlier. A mixture of $ZrCp_2$(isoprene)/1-butene (2.0 mmol) with acetaldehyde, acetone or acetonitrile (2.2 mmol) was stirred at 60 °C for 5 h in hexane and then hydrolyzed with acetic acid. Distillation of the product under vacuum (10^{-3} Torr) gave the three-component adducts in 60–70% yield.

4,7-Dimethyl-4-nonen-2-ol (product from **6**/1-butene/CH_3CHO): δ 0.89(d, 3H, J 6.2 Hz, 7-CH_3), 0.91(t, 3H, J 6.5 Hz, 9-CH_3), 1.17(d, 3H, J 6.3 Hz, 1-CH_3), 1.36(m, 2H, 8-CH_2), 1.62(s, 3H, 4-CH_3), 1.70(m, 1H, 7-CH), 1.78(s, 1H, OH), 1.95, 2.00(dd, J 5.6 and 6.7 Hz, 6-CH_2), 2.12, 2.14(dd, J 4.3 and 8.5 Hz, 3-CH_2), 3.88(m, 1H, 2-CH), 5.26(dd, 1H, J 7.8 Hz, 5-CH); EIMS 170(M^+).

2,4,7-Trimethyl-4-nonen-2-ol (product from **6**/1-butene/acetone): δ 0.88 (d, 3H, 7-CH_3), 0.90(t, 3H, 9-CH_3), 1.25(s, 6H, CH_3), 1.37(m, 2H, 8-CH_2), 1.71(s, 3H, 4-CH_3), 1.68(m, 1H, 7-CH), 1.82(s, 1H, OH), 1.92, 1.94(dd, 2H, 6-CH_2), 2.12(s, 2H, 3-CH_2), 5.22(t, 1H, CH=); EIMS 184(M^+).

4,7-Dimethyl-4-nonen-2-one (product from **6**/1-butene/CH_3CN): δ 0.88(d, 3H, 7-CH_3), 0.91(t, 3H, 9-CH_3), 1.39(m, 2H, 8-CH_2), 1.63(s, 3H, 4-CH_3), 1.72(m, 1H, 7-CH), 1.93, 2.02(dd, 2H, 6-CH_2), 3.06(s, 2H, 3-CH_2), 5.32(t, 1H, J 7.3 Hz, CH); EIMS 168(M^+).

Sequential addition of 2-butyne and carbonyl compounds to **6**

To a hexane solution (6 ml) of the $ZrCp_2$(isoprene)/2-butyne adduct (0.7 g, 2.0 mmol) was added acetaldehyde or acetone (2.5 mmol). The mixture was stirred at 60 °C for 5 h and then concentrated. Cooling of the solution to −20 °C gave the adduct as colorless crystals in 45–55% yield.

$ZrCp_2$(isoprene)/2-butyne/CH_3CHO (1/1/1 adduct). M.p. 45 °C. EIMS (rel. intensity): m/z 390(M^+; ^{94}Zr, 8.2), 388(M^+; ^{92}Zr, 9.5), 387(M^+; ^{91}Zr, 7.8), 386(M^+; ^{90}Zr, 42.2), 220(Cp_2Zr; ^{90}Zr, 100), 171(CpZrO; ^{90}Zr, 95.2); ^{1}H NMR (C_6D_6): δ 1.10(d, 3H, CH_3CO), 1.65(s, 3H, ZrC(CH_3)), 1.75(s, 3H, CH_3), 1.95(s, 3H, CH_3), 2.45, 2.57(dd, 2H, J 7.5 Hz, $OCCH_2$), 3.25, 3.65(dd, 2H, J 8.3 and 8.8 Hz, =CCH_2C=), 3.95(q, 1H, OCH), 5.48(dd, 1H, CH=), 5.80, 5.88(s, 10H, Cp). Acid cleavage followed by vacuum distillation gave 4,7-dimethyl-4,7-nonadien-2-ol in 56% yield (gas chromatographic yield 95%). ^{1}H NMR ($CDCl_3$): δ 1.19(d, 3H, J 6.3 Hz, 1-CH_3), 1.58(d, 3H, 8-CH_3), 1.59(s, 3H, 7-CH_3), 1.64(s, 3H, 4-CH_3), 1.82 (s, 1H, OH), 2.15(d, 2H, J 8.2 Hz, 3-CH_2), 2.71(d, 2H, J 7.0 Hz, 6-CH_2), 3.89(m, 1H, 2-CH), 5.23(t, 1H, 5-CH).

$ZrCp_2$(isoprene)/2-butyne/$(CH_3)_2CO$ (1/1/1 adduct). M.p. 109 °C. EIMS (rel. intensity): m/z 404(M^+; ^{94}Zr,11.2), 402(M^+; ^{92}Zr,12.5), 401(M^+; ^{91}Zr, 8.8), 400(M^+; ^{90}Zr,45.2),220(Cp_2Zr; ^{90}Zr, 100), 171(CpZrO; ^{90}Zr,115.3); ^{1}H NMR (C_6D_6): δ 0.99(s, 6H, CH_3), 1.65(s, 3H, ZrC(CH_3)), 1.75(s, 3H, CH_3), 1.98(s, 3H, CH_3), 1.79, 1.92(d, 2H, CH_2), 2.91(d, 2H, J 8.0 Hz, =CCH_2C=) 5.08(t,, 1H, Ch=), 5.85, 5.87(s, 10H, Cp). Acid cleavage followed by vacuum distillation gave 2,4,7-trimethyl-4,7-nonadien-2-ol in 70% yield. ^{1}H NMR($CDCl_3$): δ 1.22(s, 6H, CH_3), 1.60(s, 3H, 4-CH_3), 1.65(d, 3H, 9-CH_3), 1.68(s, 1H, OH), 1.75(s, 3H, 7-CH_3), 1.93, 2.01(dd, 2H, 6-CH_2), 2.21, 2.25(d, 2H, 3-CH_2), 5.24(bt, 1H, CH); EIMS (rel. intensity): 404(M^+; ^{94}Zr, 7.5), 402(M^+; ^{92}Zr, 8.0), 401(M^+; ^{91}Zr, 7.9), 400(M^+; ^{90}Zr, 45.3), 220($ZrCp_2$; ^{90}Zr, 100).

Acknowledgment

The authors are indebted to Grant-in-Aid for Special Project Research (No. 61225015) from the Ministry of Education, Science and Culture, Japan.

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