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SELECTIVE CARBOMETALLATION OF α,β-UNSATURATED CARBONYL COMPOUNDS AND SUBSTITUTED OXACYCLOPROPANES WITH ZIRCONIUM-DIENE COMPLEXES

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Summary

The reactions of zirconium-diene complexes, $ZrCp_2$(s-*cis*-diene), with bifunctional electrophiles, i.e. α,β-unsaturated ketones, unsaturated esters and substituted oxacyclopropanes, were investigated. Reaction of $ZrCp_2$(s-*cis*-isoprene) with an equivalent of 3-buten-2-one or alkyl acrylates, selectively gives 1,2-addition products. C–C bond formation occurred at the C(1) atom of the isoprene moiety whereas 1,3-pentadiene-, 2-methyl-1,3-pentadiene- and 2,4-dimethyl-1,3-pentadiene complexes induced the regioselective 1,2-addition at the C(4) position of the diene moiety. Phenyloxacyclopropane and 2-methyl-3-phenyl-oxacyclopropane also react with $ZrCp_2$(isoprene) leading to C–C bond formation from the C(1) atom of isoprene to the oxirane carbon bearing the phenyl group. The corresponding reactions of 2-methyl-2-butene-1,4-diylmagnesium with α,β-unsaturated carbonyl compounds were also studied and found to give quite different products.

Introduction

An extended series of pure diene complexes containing Group 3–5 elements has built up during the past several years, owing to the advent of certain organometallic precursors [1]. Diene metal complexes can serve as a useful tool to reveal the characteristics of early transition metal complexes since these complexes display multilateral functions in reactions with variuos substrates, reflecting its bifunctionality and enhanced σ-bonding ability. The coordinated diene is reversibly converted during the reaction to s-*cis*- and s-*trans*-π^2-1,3-diene, bent σ^2,π-butene-1,4-diyl, planar σ^2-butene-1,4-diyl and 1,2-η^2-1,3-diene, depending upon reaction conditions, electronic nature of the participating groups and the steric bulk of the diene substituents [2]. This sensitivity makes it possible to detect the subtle interfacial difference between reagents and substrates. Such a fine structural interchange of diene complexes up to now has not been found in conventional late transition

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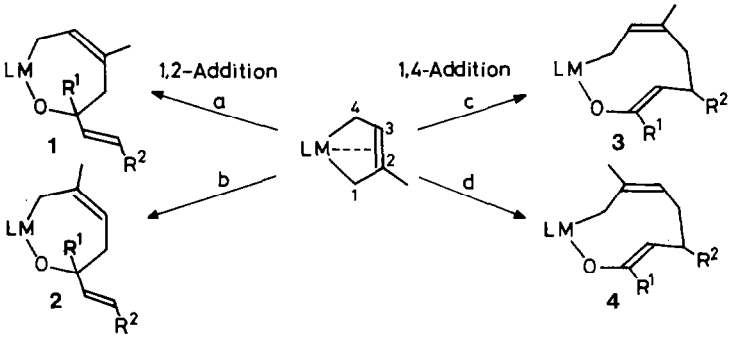
metal-diene complexes or for alkyl- or allyl compounds of Group 4–5 metals. Hence diene complexes will become very useful in organic synthesis if the above characteristics can be elucidated sufficiently. The fairly good thermal stability of these complexes is of practical importance and is advantageous in handling these complexes as reagent.

Previously a variety of highly selective additions of $ZrCp_2$(diene) complexes to simple electrophiles (ketones, aldehydes, esters, nitriles) [3] together with unsaturated hydrocarbons (alkenes, alkynes, dienes) [4] have been reported. To further extend the above studies, the carbometallations of oxygen-containing bifunctional electrophiles, i.e. α,β-unsaturated ketones, unsaturated esters and substituted oxiranes, were investigated with zirconium-diene complexes. This paper focuses on the synthetic utility of the zirconium-diene complexes in carbometallation. The structural details of the resultant organometallic compounds will be given separately.

Results and discussion

Selective addition of zirconium-diene complexes to unsaturated aldehydes and ketones

Four different types of configuration (**1–4**) are possible when mono-substituted diene-metal complexes are treated with α,β-unsaturated carbonyl compounds $R^2CH{=}CHC(O)R^1$; 1,2-addition of Zr-C(1) or Zr-C(4) into enones or unsaturated aldehydes leads to **1** or **2** and 1,4-addition leads to **3** or **4**. Although selective 1,4-addition to yield enones has already been realized with specially designed or-

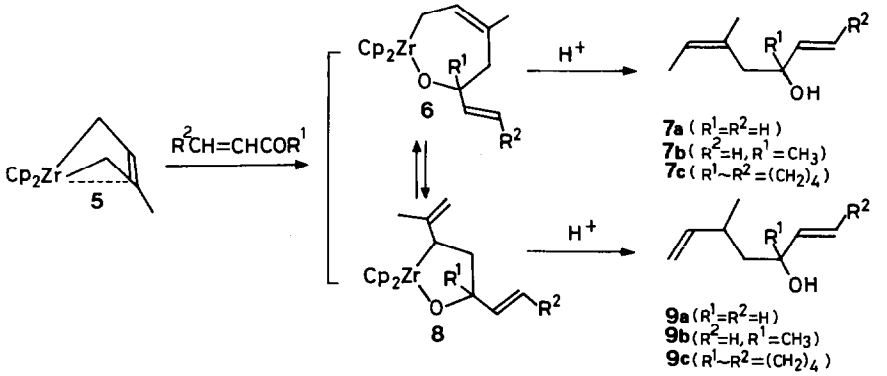


ganocopper compounds at low temperature [5], strict control of the reaction pathway, allowing general application, is difficult. The reaction of $ZrCp_2$(s-*cis*-isoprene) (**5**) with 3-buten-2-one and propenal was examined in an attempt to find a highly regioselective carbometallation. The addition reaction proceeds rapidly and cleanly under mild conditions (5 °C in benzene) to yield 1,2-addition product selectively (> 98%). The formation of the 1,4-addition products is negligible. The C–C bond formation occurred exclusively at the C(1) atom of the isoprene unit (eq. 1), this was assumed from the result of the reaction of the isoprene complexes **5** with simple ketones or aldehydes [3] (the diene complex is best described as having the bent zirconacyclo-3-pentene structure). Base-catalyzed cleavage of the product (**6**) with secondary amines (diethylamine, piperidine) gave the unsaturated alcohol **7** with good selectivity (> 86%), while acid-catalyzed cleavage with CH_3COOH or aq. HCl gave predominantly isomer **9** (Table 1).

TABLE 1

DISTRIBUTION OF 1,2-ADDITION PRODUCTS PREPARED FROM $ZrCp_2$(isoprene) AND α,β-UNSATURATED KETONES

Substrates	Protonolysis agent	Isomer (ratio) (%) [product]		Total yield (%)
		7	9	
Propenal	CH_3CO_2H	6 [7a]	94(64:36) [9a]	96
	Et_2NH	86 [7a]	14 [9a]	97
3-Buten-2-one	CH_3CO_2H	4 [7b]	96(77:23) [9b]	95
	Et_2NH	88 [7b]	12 [9b]	95
2-Cyclohexenone	CH_3CO_2H	4 [7c]	96 [9c]	94



(1)

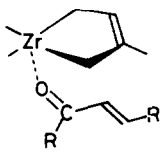
The geometry of the internal olefin in adduct **7** is *Z* which was confirmed by NOE measurement. This chemical behavior of **5** toward unsaturated ketones compares closely with the reaction of **5** with 2,4-dimethyl-3-pentanone which gives a seven-membered oxametallacycle with *Z* geometry as established from X-ray crystallographic analysis [3b]. In view of this, an oxametallacyclic structure is proposed for the unsaturated ketone adducts (**6**). Acid cleavage of the adduct proceeds through a transient five-membered oxazirconacycle (**8**) (a species which equilibrates with **6**) whereas base catalyzed cleavage occurs via **6** reflecting the enhanced polar M^+-C^- bonding character of Zr–C(4) resulting from the coordination of base to metal. Similarly, a disubstituted enone, 2-cyclohexenone, inserts into Zr–C(1) in a 1,2-fashion with high selectivity (96%). Thus, 1,2-addition is commonly observed in the reaction of enones with zirconium-diene complexes. The resulting highly regioselective 1,2-addition may be ascribed to the tetrahedral configuration of the organozirconiuim complexes together with the shape of the empty *d*-orbital which restricts access of substrate to the metal in a specific direction. It is well known that $[Cp_2M]^{2+}$ (M = Ti, Zr) species (16e, d^0 species) exhibit coplanar three non-bonding orbitals and thereby only one non-bonding orbital is available to bis(cyclopentadienyl)zirconacyclo-3-pentene [6]. The α,β-unsaturated ketone approaches that metal orbital at the oxygen atom (**10a**) because of the high oxophilicity of the zirconium metal toward the carbonyl group. The addition then proceeds through an intermediate **10b**. Alternative coordination in the form of **11** is impossible from the MO proposed above. Although $ZrCp_2ClR$ is inert to saturated or unsaturated ketones

TABLE 2

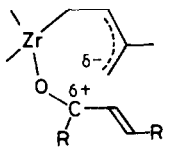
REGIOSELECTIVITY IN THE REACTION OF $ZrCp_2$(diene) WITH 3-BUTEN-2-ONE

Reagents	Isomer ratio (%) (C–C bonding position)		Total yield (%)
	C(1)	C(4)	
$ZrCp_2$(isoprene) (**5**)	96 [**16a'**]	4 [**16b'**]	95
$ZrCp_2$(2-methyl-1,3-pentadiene) (**12**)	3 [**17a'**]	97 [**17b'**]	96
$ZrCp_2$(2,4-dimethyl-1,3-pentadiene (**13**)	1 [**18a'**]	99 [**18b'**]	99
$ZrCp_2$(1,3-pentadiene) (**15**)	3 [**19a'**]	97 [**19b'**]	93
$ZrCp_2$(3-methyl-1,3-pentadiene) (**14**)	54 [**20a'**]	46 [**20b'**]	86
$Ti(OBu)_4/[MgC_5H_8]_n$	82 [**16a'**]	18 [**16b'**]	56
$TiCl_2(OiPr)_2/[MgC_5H_8]_n$	85 [**16a'**]	15 [**16b'**]	85
$Zr(OEt)_4/[MgC_5H_8]_n$	99 [**16a'**]	1 [**16b'**]	33

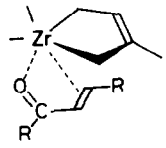
The products **16–20a'** and **16–20b'** were obtained by hydrolysis of **16–20**.



10a



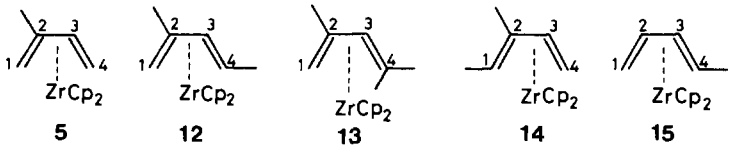
10b



11

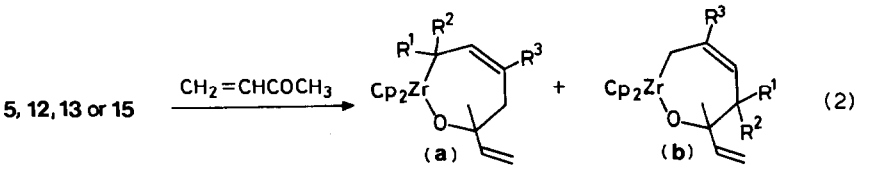
even at 60–80 °C and $Ti(CH_2Ph)_4$ adds (by 1,4-addition) only to some α,β-unsaturated ketones [7], L_2TiR_2(L = Cl, OR, NR_2) [8a] and RLnX(Ln = Yb, Eu) [8b] are known generally to prefer the 1,2-addition to α,β-unsaturated aldehydes or ketones. In contrast, more ionic organometallics like Grignard reagents favor 1,4-addition when their steric bulk is sufficiently large (e.g. t-BuMgBr) while less bulky methylmagnesium halides primarily perform the 1,2-addition which is well-documented for reactions with simple α,β-unsaturated carbonyl compounds [9]. Thus, preference of 1,2-addition is generally valid for Group 4 organometallic compounds as a consequence of the diminished ionicity (hardness) of the reagents together with the tetrahedral geometry of this class of organometallics.

To ensure the versatility of the present reaction sequence, the effet of alkyl substitution on the diene ligand was also examined with various zirconium-pentadiene complexes (Table 2). Although isoprene complex **5** undergoes 1,2-addition selectively at the sterically congested C(1) of the diene unit to give **16a**, the introduction of a methyl group into its C(4) position caused reversed regiochemistry

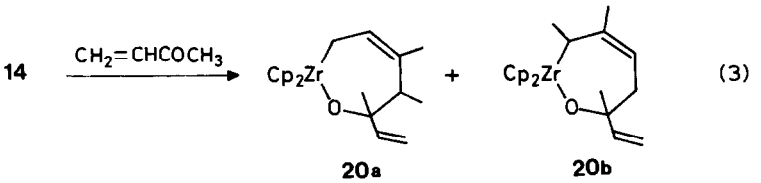


5 **12** **13** **14** **15**

(eq. 2). The 2-methyl-1,3-pentadiene complex (**12**) ultimately undergoes 1,2-addition at C(4), affording **17b** in place of **17a**. Similarly, 2,4-dimethyl-1,3-pentadiene complex (**13**) reacts with 3-buten-2-one at the C(4) position exclusively. The formation of 1,4-adducts is negligible in both cases. The drastic change observed may be ascribed to the inductive effect of the methyl group bringing about an increase in



16 (R^1=R^2=H, R^3=CH_3)
17 (R^1=H, R^2=R^3=CH_3)
18 (R^1=R^2=R^3=CH_3)
19 (R^1=CH_3, R^2=R^3=H)



20a **20b**

the negative charge on the C(4) carbon rather than on the C(1) atom. Actually, the 1,3-pentadiene complex bearing a methyl group at the C(4) position also permits 1,2-addition at the C(4) carbon selectively, whereas the complex comprises a mixture (42 : 58) of s-*cis* and s-*trans* isomers [1d]. The other complexes **5** and **12–14** consist only of the s-*cis* isomer. An exceptional reaction is shown by 3-methyl-1,3-pentadiene complex (**14**), which gives a mixture of **20a** and **20b** in 64 : 36 ratio (eq. 3). This is contrary to our expectation of it giving **20a** selectively, by the overlapping inductive effect of the two methyl groups. The unusual behavior of the 3-methyl-1,3-pentadiene complex is specific not only for enones but also for simple ketones. For example, 3-pentanone gave the corresponding isomers in 55 : 45 ratio indicating that the apparent reactivities of C(1) and C(4) of the diene moiety in complex **14**

TABLE 3

DISTRIBUTION OF THE 1,2-ADDITION PRODUCTS OBTAINED FROM ISOPRENE COMPLEXES AND UNSATURATED ESTERS

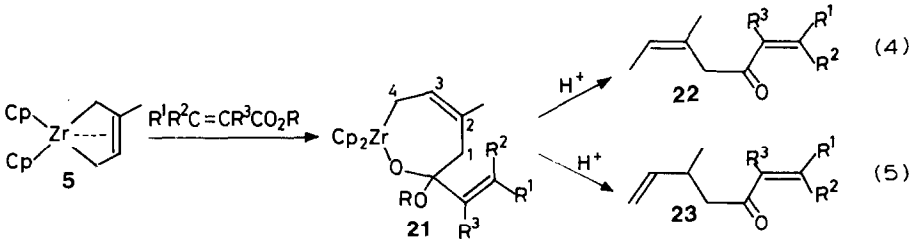
Reagents	Esters	Isomer ratio (%) product			Total yield (%)
		type **22**	type **23**	type **22′**	
$ZrCp_2$(isoprene)	CH_2=$CHCO_2CH_3$	99 [**22a**]	0	0	96
$ZrCp_2$(isoprene)	CH_3CH=$CHCO_2CH_3$	94 [**22b**]	5	1	92
$ZrCp_2$(isoprene)	CH_2=$C(CH_3)CO_2CH_3$	92 [**22c**]	7	1	85
$ZrCp_2$(isoprene)	$(CH_3)_2C$=$CHCO_2C_2H_5$	98 [**22d**]	0	2	91
$Ti(OEt)_4/[MgC_5H_8]_n$	CH_3CH=$CHCO_2CH_3$	83 [**22a**]	3	14	45
$Ti(OPr^i)_4/[MgC_5H_8]_n$	CH_3CH=$CHCO_2CH_3$	81 [**22a**]	4	15	62
$TiCl_2(OPr^i)_2/[MgC_5H_8]_n$	CH_3CH=$CHCO_2CH_3$	85 [**22a**]	2	13	78
$Zr(OEt)_4/[MgC_5H_8]_n$	CH_3CH=$CHCO_2CH_3$	99 [**22a**]	0	1	36
$Ti(OPr^i)_4/[MgC_5H_8]_n$	$(CH_3)_2C$=$CHCO_2C_2H_5$	82 [**22d**]	5	13	54
$TiCl_2(OPr^i)_2/[MgC_5H_8]_n$	$(CH_3)_2C$=$CHCO_2C_2H_5$	86 [**22d**]	3	11	77

Protonolysis was carried out with acetic acid. Base-catalyzed cleavage gave nearly the same result. Type **22′** product expresses the regioisomer of **22** binding isoprene unit with the ester at the C(4) carbon of the isoprene unit.

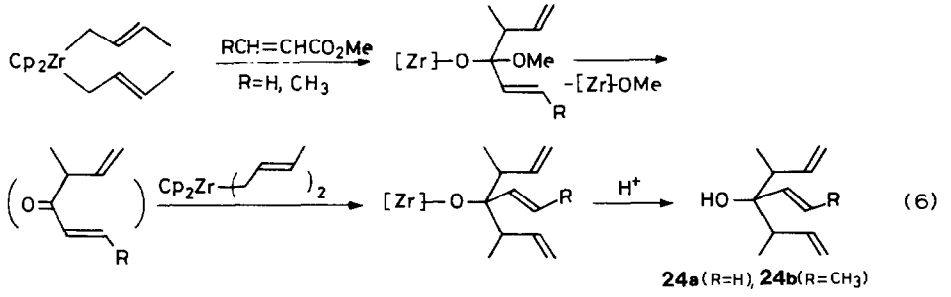
become comparable by the combined steric and electronic effects of the methyl groups.

Selective addition of zirconium-diene complexes to unsaturated esters

$ZrCp_2$(isoprene) reacts with simple aliphatic esters, acid amides, acetic anhydride and acyl halides to yield acylated 2-butene derivatives upon hydrolysis as reported briefly in a previous paper [10]. A series of α,β-unsaturated ester was found to react readily with $ZrCp_2$(isoprene) at C(1) of the isoprene moiety and gave the expected acyl compounds upon hydrolysis of adduct **21** (Table 3). The oxametallacyclic structure of simple ester adducts has previously been confirmed [10]. Whereas the acid catalyzed protonolysis of α,β-unsaturated ketone adducts occurs at C(2) of the isoprene unit to give external olefinic products (**9** in eq. 1), the present α,β-unsaturated ester adducts lead exclusively to compounds **22**, having an internal olefin, regardless of the acidity of the protonolyzing agents (eq. 4). This is probably as a consequence of the enhanced M^+–C^- bonding character of C(4) of complex **21** relative to C(2).

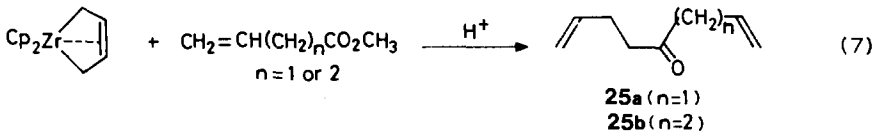


If the zirconium-diene complexes behave as an allylzirconium species, the addition should occur at the C(2) or C(3) atom [11]. Actually, $ZrCp_2$((E)-2-butenyl)$_2$, a typical isolable allylzirconium compound reacts with methyl crotonate or ethyl 3, 3-dimethylacrylate at the C(3) carbon of the allyl group leading to a tertiary alcohol (**24**) as in eq. 6. Thus, the chemical behavior of allylzironium compounds is entirely different from that of zirconacyclo-3-pentenes but resembles well the mode of reaction reported for well-documented Grignard reactions. The unique chemical behavior of the diene complex is therefore ascribed to the metallacyclic structure which inhibits the insertion through a conventional six-membered transition state.



The β,γ- and γ,δ-unsaturated esters also react with $ZrCp_2$(isoprene) or $ZrCp_2$(butadiene) to give acylated compounds. Though unsaturated hydrocarbons

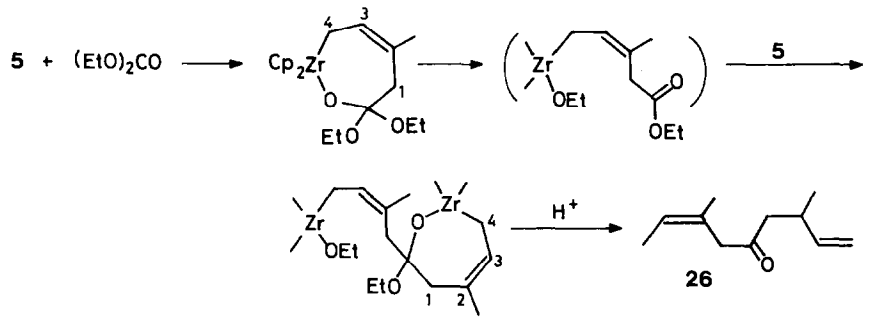
such as olefins, dienes and alkynes are known to be reactive towards these complexes at ambient temperature [4], no C–C bond formation occurred at the olefinic part in these cases. Thus, unsaturated esters react preferentially at the ester



(7)

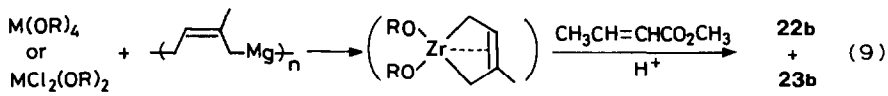
part irrespective of whether the conjugation system is present or not (eq. 7). To determine the chemoselectivity between ketone and ester groups, the stoichiometric reaction of methyl 4-oxopentanoate with complex **5** was examined, and it was found that the complex reacts exclusively with the ketone group (selectivity, 95%). The corresponding ketone/ester differentiation has already been recognized in the reactions of alkyltitanium compounds [12].

Since the alkoxy group of esters has been found to serve as a good leaving group in above-mentioned reactions, the reaction of diethyl carbonate with complex **5** was examined once more. As expected, its mode of reaction differs greatly from that of ester. The carbonate acts as a carbonylation agent to give di-(*Z*)-2-methyl-2-butenyl ketone in 92% selectivity (yield, 80%). The same product was recently obtained by reaction of **5** with carbon dioxide [13]. These results suggest the following reaction mechanism (eq. 8).



(8)

For the purpose of developing a more facile and economical method of preparation, the utility of commercially readily available titanium alkoxides, $Ti(OR)_4$ (R=C_2H_5, i-C_3H_7, n-C_4H_9) and readily obtainable $TiCl_2(O\text{-}i\text{-}C_3H_7)_2$ and $Zr(OEt)_4$ were tested in place of $ZrCp_2Cl_2$. Dialkoxytitanium(isoprene) complexes generated in situ by treating $Ti(OR)_4$ or $TiCl_2(OR)_2$ with an equivalent of magnesium-isoprene adduct in THF were found to induce similar addition in fairly good selectivity. The hydrolysis product comprises a mixture of **22** and its regioisomer **22′** (acylated product resulting from bonding with C(4) of the isoprene unit) in ca. 6 : 1 ratio regardless of the bulkiness of the alkoxy group in $Ti(OR)_4$ and $TiCl_2(OR)_2$ (eq. 9). Thus, these titanium alkoxides are convenient alternative precursors to

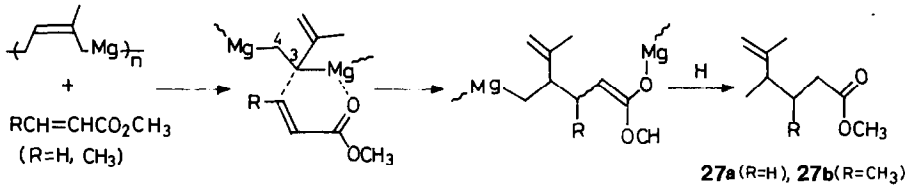


(9)

zirconocene dichloride for use in large scale organic synthesis. The method involving addition of excess $Ti(OR)_4$ (3–4 equiv.) to the magnesium-isoprene adduct, then

leaving the mixture to stand at ambient temperature for a prolonged period should not be attempted since it causes significant decreases in yields. The use of $Zr(OEt)_4$ is unsuited because of poor yield in spite of good regioselectivity (99%). All attempts to isolate the $M(OR)_2$(isoprene). (M = Ti, Zr) failed owing to great thermal instability of the compounds.

The chemical behavior of the starting magnesium-isoprene adduct for unsaturated esters differs markedly from that of the zirconium- or titanium-isoprene complex. The 1,4-addition occurs predominantly in all reactions attempted. Methyl acrylate and methyl crotonate probably undergo 1,4-addition through an intermediate shown in eq. 10 which upon hydrolysis yields unsaturated esters, **27a** or **27b** in ca 90% yield (selectivity 95%), while methyl 3,3-dimethylacrylate is converted to a cyclic unsaturated ketone 28 in 78% yield (selectivity, 78%) presumably following



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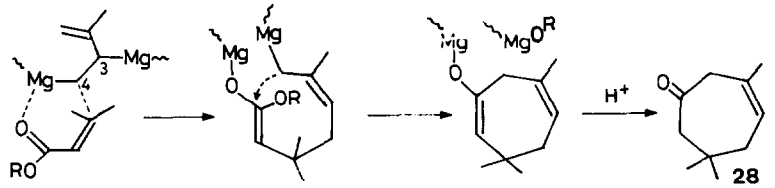
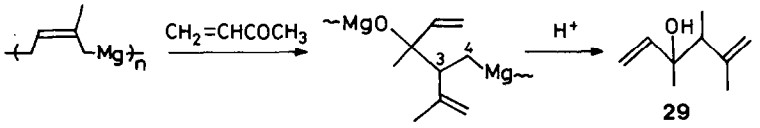


(11)

the reaction pathway shown in eq. 11. The cyclic structure of the product was confirmed by NMR, mass and IR spectroscopy. Unlike unsaturated esters, 3-buten-2-one undergoes 1,2-addition at the C(3) of the 2-butenyl group in 92% selectivity to give **29** in good yield (85%) (eq. 12).

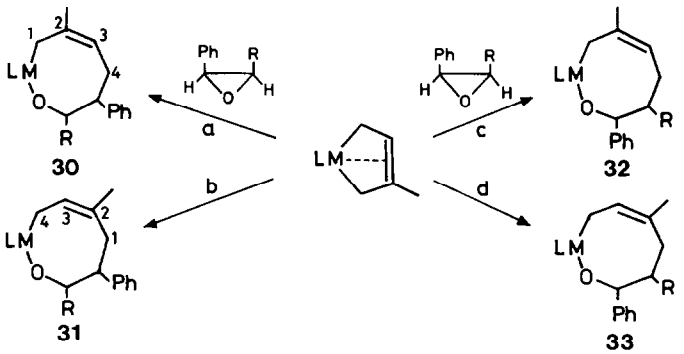


(12)

Selective additon of zirconium-diene complexes leading to substituted oxiranes

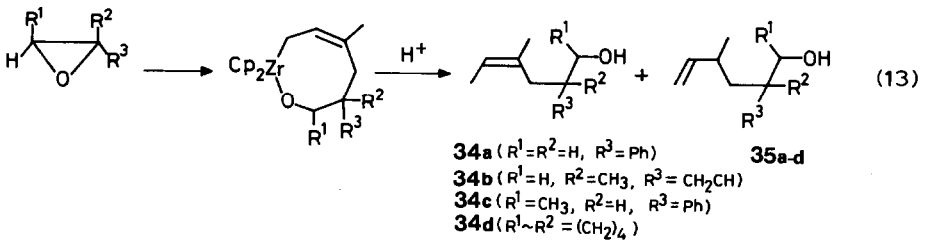
Simple oxacyclopropanes are less reactive toward zirconium-diene complexes compared with aliphatic ketones, aldehydes, nitriles and esters. Unactivated oxiranes, oxacyclopropane and methyloxacyclopropane, are inert to the isoprene complex **5** at ambient temperature and elevation of the reaction temperature to 100 °C only resulted in the polymerization of the oxiranes. In contrast, a strained oxacyclopropane, 7-oxabicyclo[4.1.0]heptane, as well as phenyl or vinyl substituted oxacyclopropanes such as 1-methyl-2-phenyloxacyclopropane and 1-methyl-1-vinyloxacyclopropane show a fairly good reactivity. A stoichiometric reaction occurred smoothly at 30–60 °C in these cases.

Four types of C–C bond formation are envisaged for the phenyl substituted oxirane. As a result, phenyloxacyclopropane rearranges, regioselectively (99%) for-



SCHEME 1

ming C–C bond between C(1) of isoprene and the oxirane carbon bearing the phenyl group as shown by reaction pathway a in Scheme 1. The oxazirconacyclic structure of **30** is confirmed by preliminary NMR studies. Any other products derived from the reaction pathways b–d in Scheme 1 were not detected in the reaction system. The insertion, however, is accompanied by a small amount of deoxygenation of oxacyclopropane generating an olefin, for example, styrene, in 5–18% yield. The correlation between the insertion and deoxygenation reactions is ambiguous at present. The acidic cleavage of the phenyloxacyclopropane adduct with acetic acid gave the isomers **34a** and **35a** in 75 : 13 ratio while



(13)

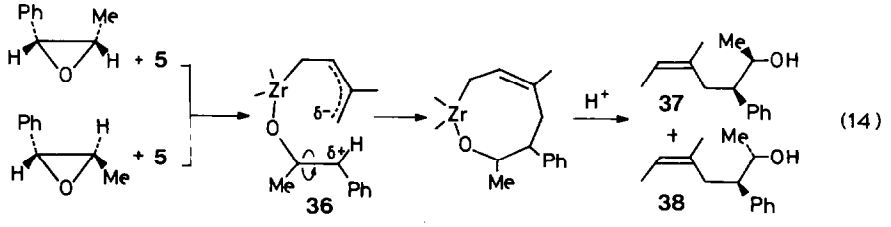
TABLE 4

PRODUCT DISTRIBUTION FOR THE REACTION OF COMPLEX 5 WITH OXACYCLOPROPANES

Oxiranes	Protonolysis agent	Distribution (%)			Total yield (%)
		34	35	olefin	
Phenyloxacyclopropane	CH_3CO_2H	75 [**34a**]	13 [**34b**]	12	89
	Et_2NH	41 [**35a**]	47 [**35b**]	12	90
2-Methyl-2-vinyloxacyclopropane	CH_3CO_2H	42 [**35a**]	40 [**35b**]	18	95
	Et_2NH	25	59	16	97
(E)-2-Methyl-3-phenyloxa-cyclopropane	CH_3CO_2H	68 [**36a**]	15 [**36b**]	17	78
	Et_2NH	53	31	16	90
(Z)-2-Methyl-3-phenyloxa-cyclopropane	CH_3CO_2H	76 [**36a**]	12 [**36b**]	12	80
	Et_2NH	49	38	13	83
7-Oxabicyclo[4.1.0]heptane	CH_3CO_2H	78 [**37a**]	17 [**37b**]	5	75
	Et_2NH	65	30	5	81

base-catalyzed protonolysis gave these isomers in 41 : 47 ratio (eq. 13). The exclusive generation of either **34** or **35** was unsuccessful. A disubstituted oxirane, 2-methyl-2-vinyloxacyclopropane, also induces selective insertion. The regioselectivities in binding with the isoprene C(1) (99%) and with the oxirane C(1) (99%) are excellent but selection with respect to the internal olefin (**34**) and the external olefin derivatives (**35**) is again insufficient (Table 4).

A 2,3-dialkyl substituted oxacyclopropane, 7-oxabicyclo[4.1.0]heptane, also performs a similar insertion into Zr–C(1) of complex **5** with good selectivity (98%) under the normal conditions. The driving force initiating the reaction may be the ring strain, since less hindered 2,3-dimethyloxacyclopropane is completely inert to complex **5** even under vigorous conditions. To gain further information on the stereochemistry involved in the ring opening of oxacyclopropanes, the stoichiometric reaction of (*Z*)- and (*E*)-2-methyl-3-phenyloxacyclopropane was examined. Highly regioselective C–C bond formation (99%) occurred between C(1) of the isoprene unit and the oxirane carbon attached to the aryl group. The hydrolysis



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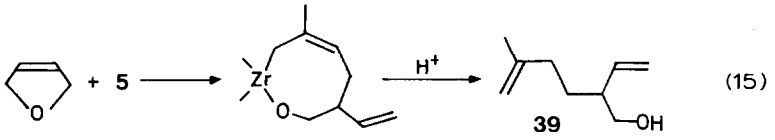
products again comprised the isomers **34** and **35** in 5 : 4–6 : 1 ratio. Especially noteworthy is that isomers **34c** and **35c** are each composed of two diastereoisomers in ca. 2 : 1 ratio regardless of the initial geometry of 2-methyl-3-phenyloxacycloacyclopropane (only the diastereoisomers of **34c** are given as **37** and **38** in eq. 14). This result indicates that the present insertion step involves an intermediate such as **36** which allows free rotation around the C(1)–C(2) bond prior to formation of the new C–C bond. In view of this, we propose reaction mechanism as shown in eq. 14. The mode of this reaction may also account for the C–C bond formation observed in the thermally induced addition reaction of $ZrCp_2$(isoprene) to carbonyl compounds, while a different process, via [2 + 2] oxidative coupling, seems to account for the photochemically induced insertion reaction of carbonyl compounds [14]. The 1-propenylbenzene generated as a minor product as a result of deoxygenation of the oxirane has the (*E*)-geometry irrespective of the geometry (*E* or *Z*) of the starting oxiranes. This result also suggests the presence of a common intermediate in the above-mentioned reactions (eq. 14).

Although tetrahydrofuran and dialkyl ethers are highly resistant to ring opening by complex **5**, 2,5-dihydrofuran was found to readily undergo ring opening to give an unsaturated alcohol **39** upon hydrolysis of the products (eq. 15). This mode of insertion is quite different from those described above. Further experimental work is required to account for the mechanism of this type of ring opening.



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Conclusion

The characteristic chemical nature of zirconium-diene complexes has been confirmed in the reaction of bifunctional substrates, unsaturated carbonyl compounds and substituted oxiranes. The mode of reaction is totally different from those of allylzirconium and allylmagnesium compounds. The highly regioselective C–C bond formation demonstrates further synthetic utility by appropriate combination of the reagents and substrates.

Experimental

General remarks. All manipulations were conducted with Schlenk glassware under argon. Solvents were dried over Na/K alloy and distilled before use. $ZrCp_2Cl_2$ and magnesium-diene adducts [15] were prepared by published procedures. α,β-Unsaturated ketones and esters (Aldrich Chem.) were dried over calcium hydride and purified by distillation. 2-Methyl-3-vinyloxacyclopropane, (*E*)- and (*Z*)-2-methyl-3-phenyloxacyclopropanes were synthesized by oxidation of isoprene and (*E*)- or (*Z*)-1-propenylbenzene, respectively, with MCPBA. $Ti(OR)_4$ (Aldrich Chem.) was distilled before use. Tetraethoxyzirconium was prepared by a standard method [16]. The characterization of products was deduced from NMR spectra recorded on a Varian XL-100 instrument, along with the mass spectra (EI) measured with a JEOL 01SG-2 spectrometer, and the IR spectra recorded on a Hitachi EPI-2 spectrometer.

Reaction of isoprene complex **5** *with* α,β*-unsaturated ketones*

To a solution of $ZrCp_2$(isoprene) (3 mmol, 0.87 g) in benzene (20 ml) was added dropwise 3-buten-2-one (3 mmol, 0.3 ml) with stirring at 5 °C. The red-brown solution turned to pale yellow when addition was complete. Stirring was continued for 1 h at 30 °C and acetic acid (1 ml) or diethylamine (1 ml) was added to decompose the adduct. The mixture was evaporated to dryness then ether (100 ml), and subsequently water (10 ml) were added to the residue. The ether fraction was distilled and isomeric products were separated on a gas chromatograph with a column packed with DEGS on Uniport-B.

*5-Methyl-1,5-heptadien-3-ol (**7a**).* Reaction of complex **5** with propenal followed by base-catalyzed cleavage of the product gave **7a** as an oil. ^{1}H NMR δ ($CDCl_3$) 1.62 (3H, d, *J* 7.0 Hz, CH_3), 1.74 ((4H, s, CH_3 and OH), 2.16 (1H, dd, *J* 6.0 and 14.1 Hz), CH_2CHO), 2.44 (1H, dd, *J* 8.1 and 14.1 Hz, CH_2CHO), 4.26 (1H, m, CHOH), 5.10, 5.25 (2H, m, CH_2=), 5.44 (1H, q, *J* 7.0 Hz, CH), 5.92 (1H, ddd, *J* 6.0, 6.0 and 10.2 Hz, CH=) ppm. IR (neat) 3370, 3080, 2970, 2920, 2865, 1642, 1443, 1378, 1013, 992, 920, 865 cm^{-1}. Mass *m/z* 126 (M^+). Found: C; 75.92, H; 11.18. $C_8H_{14}O$ calc: C; 76.14, H; 11.18%.

*5-Methyl-1,6-heptadien-3-ol (**9a**).* Reaction of complex **5** with propenal followed by acidic cleavage of the product gave **9a** as an oil. ^{1}H NMR δ ($CDCl_3$) 1.04 (3H, d, CH_3), 1.37–1.52 (3H, m, CH_2 and OH), 2.35 (1H, m, CH), 4.18 (1H, m, CHOH), 4.88–5.40 (4H, m, CH_2=), 5.60–6.10 (2H, m, CH=) ppm. IR (neat) 3350, 3080, 2965, 2875, 1642, 1455, 1420, 995, 917 cm^{-1}. Mass *m/z* 126 (M^+). Found: C; 75.91, H; 11.09. $C_8H_{14}O$ calc: C; 76.14, H; 11.18%.

*3,5-Dimethyl-1,5-heptadien-3-ol (**7b**).* Reaction of complex **5** with 3-buten-2-one followed by base-catalyzed cleavage of the product gave **7b** as an oil. ^{1}H NMR δ

($CDCl_3$) 1.31 (3H, s, CH_3), 1.61 (3H, d, J 6.5 Hz, $CHCH_3$), 1.69 (1H, s, OH), 1.76 (3H, s, CH_3), 2.22 (1H, d, J 13.5 Hz, CH_2COH), 2.45 (1H, d, J 13.5 Hz, CH_2COH), 5.05 (1H, dd, J 2.0 and 10.5 Hz, CH_2=), 5.23 (1H, dd, J 2.2 and 17.1 Hz, CH=), 5.47 (1H, q, J 7.0 Hz, CH_3CH=), 6.00 (1H, dd, J 10.5 and 17.0 Hz, CH_2=) ppm. IR (neat) 3460, 3090, 2975, 2860, 1640, 1454, 1413, 1115, 997, 920, 820 cm^{-1}. Mass m/z 140 (M^+). Found: C; 77.36, H; 11.55. $C_9H_{16}O$ calc: C; 77.09, H; 11.50%.

*3,5-Dimethyl-1,6-heptadiene-3-ol (**9b**).* Reaction of complex **5** with 3-buten-2-one followed by acidic cleavage of the product gave the diastereoisomers *A* and *B* of **9b** in 77 : 23 ratio.

Diastereoisomer **A**: ^1H NMR δ ($CDCl_3$) 1.04 (3H, d, J 7 Hz, $CHCH_3$), 1.30 (3H, s, CH_3), 1.50–1.70 (2H, m, CH_2COH), 1.80 (1H, s, OH), 2.43 (1H, m, $CHCH_3$), 4.80, 5.21 (4H, m, CH_2=), 5.85 (1H, m, CH=), 588 (1H, m, CH=) ppm. IR (neat) 3450, 3080, 2970, 1638, 1455, 1413, 1375, 997, 915 cm^{-1}. Mass m/z 139 ($M^+ - 1$). Found: C, 77.36, H; 11.5. $C_9H_{16}O$ calc: C; 77.09, H; 11.50%.

Diastereoisomer **B**: ^1H NMR δ ($CDCl_3$) 0.99 (3H, d, J 6.0 Hz, CH_3) 1.23 (3H, s, CH_3), 1.60 (2H, m, CH_2CO), 2.13 (1H, s, OH), 2.41 (1H, m, $CHCH_3$), 5.07 5.09 (4H, m, CH_2=), 5.85, 5.89 (2H, m, CH=) ppm. IR(neat) 3460, 3080, 2965, 1640, 1455, 1412, 997, 917 cm^{-1}. Mass m/z 139 ($M^+ - 1$).

*1-(2-Methyl-3-butenyl)cyclo-2-hexenol (**9c**).* Prepared from 2-cyclohexenone and complex **5**. ^1H NMR δ ($CDCl_3$) 1.05 (3H, d, CH_3), 1.45–1.78 (3H, d, CH_3 and CH_2), 1.75 (1H, s, OH), 2.25 (2H, m, CH_2), 2.41 (2H, m, CH_2), 4.95, 5.20 (2H, d, CH_2=), 5.75–5.92 (3H, m, CH=) ppm. IR(neat) 2940, 2875, 1643, 1538, 888 cm^{-1}. Mass m/z 166 (M^+), 148 ($M^+ - H_2O$).

Reaction of zirconium-pentadiene complexes with 3-buten-2-one

$ZrCp_2$(1,3-pentadiene) and its higher analogues were prepared from $ZrCp_2HCl$ and 2,4-pentadienyl-, 2-methyl-2,4-pentadienyl-, 3-methyl-2,4-pentadienyl- or 2,4-dimethyl-2,4-pentadienylpotassium as described previously [17]. The reactions of the resulting pentadiene complexes with 3-buten-2-one were carried out in the same manner as that described for the reaction of complex **5** with enones.

*3,4,6-Trimethyl-1,6-heptadien-3-ol (**17b'**).* Prepared from $ZrCp_2$(2-methyl-1,3-pentadiene). ^1H NMR δ ($CDCl_3$) 0.86 (3H, d, J 5.8 Hz, CH_3), 1.25 (3H, s, CH_3), 1.50 (2H, m, CH_2), 1.67 (3H, s, CH_3), 2.27 (1H, m, CH), 4.64, 4.71 (2H, bs, CH_2=), 5.06, 5.19 (2H, d, CH_2=), 5.79 (1H, dd, CH) ppm. IR (neat) 3460, 2980, 1643, 1451, 1118, 921, 887 cm^{-1}. Found: C, 77.87, H; 11.72. $C_{10}H_{18}O$ calc: C; 77.87, H; 11.76%.

*3,4,4,6-Tetramethyl-1,6-heptadien-3-ol (**18b'**).* Prepared from $ZrCp_2$(2,4-dimethyl-1,3-pentadiene). ^1H NMR δ ($CDCl_3$) 0.96 (6H, s, CH_3), 1.05 (3H, s, CH_3), 1.71 (3H, bs, CH_3), 1.57 (1H, s, OH), 2.20 (2H, m, CH_2), 4.74, 4.81 (2H, 4.96–5.20 (2H, m, CH_2=), 5.78 (1H, m, CH=) ppm. IR(neat) 3460, 2975, 2940, 1640, 1451, 921 cm^{-1}. Mass m/z 167 ($M^+ - 1$). Found: C; 78.34, H; 11.87. $C_{11}H_{20}O$ calc: C; 78.57, H; 11.90%.

*3,4-Dimethyl-1,6-heptadien-3-ol (**19b'**).* Obtained from $ZrCp_2$(1,3-pentadiene). ^1H NMR δ ($CDCl_3$) 0.91 (3H, d, CH_3), 1.23 and 1.25 (3H, s, CH_3), 2.34 (1H, m, $CHCH_3$), 1.85 (2H, m, CH_2), 1.48 (1H, s, OH), 4.91–5.17 (4H, dd, CH_2=), 5.70 (1H, m, CH=), 5.88 (1H, m, CH=) ppm. Mass m/z 140 (M^+), 122 ($M^+ - H_2O$). Found: C; 77.87, H; 11.22. $C_9H_{16}O$ calc: C; 77.09, H; 11.50%.

*3,4,5-Trimethyl-1,6-heptadien-3-ol (**20a'**).* Obtained upon hydrolysis of adduct **20a**. ^{1}H NMR δ ($CDCl_3$) 0.96 (3H, d, CH_3), 1.00 (3H, d, CH_3), 1.22 (3H, s, CH_3), 1.54 (1H, s, OH), 1.88 (1H, dq, CH), 2.70 (1H, m, CH), 5.01, 5.20 (2H, m, CH_2=), 4.91, 5.12 (2H, bs, CH_2=), 5.76 (1H, m, CH=), 5.92 (1H, dd, CH=) ppm. Mass *m/z* 154 (M^+). Found: C; 77.75, H; 11.79. $C_{10}H_{18}O$ calc: C, 77.87, H; 11.76%.

3,6-Dimethyl-1,5-octadiene-3-ol. The isomer **20b'** obtained from $ZrCp_2$(3-methyl-1,3-pentadiene). ^{1}H NMR δ ($CDCl_3$) 0.90 (3H, t, CH_3), 1.24 (2H, q, CH_2), 1.28 (3H, s, CH_3), 1.56 (3H, s, CH_3), 1.72 (2H, m, CH_2), 5.00, 5.18 (2H, dd, CH_2=), 5.75 (1H, m, CH), 5.85 (1H, q, CH=). Mass *m/z* 154 (M^+). Found: C; 77.72, H; 11.91. $C_{10}H_{18}O$ calc: C; 77.87, H; 11.76%.

Reaction of zirconium-diene complexes with unsaturated esters.

The reaction of complex **5** with an α,β-, β,γ- or γ,δ-unsaturated ketone was carried out in essentially the same way as described for the reaction with α,β-unsaturated ketones. A typical experiment for the reaction of a dialkoxyzirconium(diene) complex with an unsaturated ester is as follows. To a solution of $Ti(OR)_4$ (R = C_2H_5, i-C_3H_7, n-C_4H_9; 3.0 mmol) or $TiCl_2$(O-i-C_3H_7)$_2$ (3 mmol) in THF (20 ml) was added magnesium-isoprene adduct (3 mmol) in THF at $-78°C$. The mixture was stirred at $0°C$ for 5 min and again cooled to $-70°C$. After the addition of an unsaturated ester at that temperature, the solution was allowed to warm to ambient temperature, quenched with acetic acid (1 ml) or diethylamine (1 ml), and evaporated to dryness. The products were extracted with ether containing water, and isolated by distillation.

*5-Methyl-1,5-heptadien-3-one (**22a**).* Synthesized from methyl acrylate and complex **5**. ^{1}H NMR δ ($CDCl_3$) 1.63 (3H, d, *J* 7 Hz, CH_3), 1.71 (3H, s, CH_3), 3.30 (2H, s, CH_2), 5.49 (1H, q, *J* 7.0 Hz, $CHCH_3$), 5.79 (1H, dd, *J* 3.2 and 8.4 Hz, CH=), 6.24 (1H, dd, *J* 3.0 and 16.1 Hz, CH_2=), 6.47 (1H, dd, *J* 8.5 and 16.0 Hz, CH=) ppm. IR(neat) 3095, 3025, 2975, 2920, 2865, 1690, 1616, 1443, 1380, 1175, 1071, 990, 915, 850 cm^{-1}. Mass *m/z* 124 (M^+). Found: C; 76.99, H; 9.77. $C_8H_{12}O$ calc: C; 77.37, H; 9.74%.

*6-Methyl-2,6-octadien-4-one (**22b**).* Prepared from methyl crotonate and complex **5**. ^{1}H NMR δ ($CDCl_3$) 1.64 (3H, d, *J* 6.8 Hz, CH_3CH), 1.71 (3H, s, CH_3), 1.90 (3H, *J* 2.2 and 7.0 Hz, CH_3CH), 3.24 (2H, s, CH_2), 5.48 (1H, q, *J* 7.0 Hz, $CHCH_3$), 6.16 (1H, dq, *J* 14.1 and 2.2 Hz, CHCO), 6.92 (1H, dq, *J* 7.0 and 14.1 Hz, $CHCH_3$) ppm. IR(neat) 3035, 2965, 2915, 2860, 1693, 1673, 1630, 1445, 1378, 1317, 1293, 1086, 970 cm^{-1}. Mass *m/z* 138 (M^+). Found: C; 78.10, H; 10.22. $C_9H_{14}O$ calc: C; 78.22, H; 10.21%.

*2,5-Dimethyl-1,5-heptadien-3-one (**22c**).* Prepared from methyl methacrylate and complex **5**. ^{1}H NMR δ ($CDCl_3$) 1.61 (3H, d, *J* 7.0 Hz, CH_3), 1.70 (3H, s, CH_3), 1.89 (3H, s, CH_3), 3.44 (2H, s, CH_2), 5.45 (1H, q, $CHCH_3$), 5.78, 5.99 (2H, bs, CH_2=) ppm. IR(neat) 3100, 3035, 2975, 2865, 1675, 1632, 1454, 1378, 1173, 1110, 1067, 996, 932 cm^{-1}. Mass *m/z* 276 (M^+). Found: C, 76.99, H; 9.77. $C_8H_{12}O$ calc: C; 77.37, H; 9.74%.

*2,6-Dimethyl-2,6-octadien-4-one (**22d**).* Prepared from ethyl 3,3-dimethylacrylate. ^{1}H NMR δ ($CDCl_3$) 1.62 (3H, d, *J* 6.0 Hz, CH_3), 1.69 (3H, m,, CH_3), 1.89, 2.14 (6H, s, CH_3), 3.12 (2H, s, CH_2), 5.45 (1H, q, *J* 6.0 Hz, $CHCH_3$), 6.07 (1H, bs, CH, CH=) ppm. IR (neat) 3025, 2970, 2915, 2865, 1685, 1620, 1445, 1481, 1302, 1208, 1175, 1109, 1028. 814 cm^{-1}. Mass *m/z* 152(M^+). Found: C; 78.63, H; 10.66. $C_{10}H_{16}O$ calc: C; 78.90, H; 10.60%.

*1,6-Octadien-4-one (**25a**).* Prepared from methyl 3-butenoate and $ZrCp_2$-(butadiene). ^1H NMR δ ($CDCl_3$) 1.68 (3H, d, J 6.1 Hz, CH_3), 3.13 –3.15 (4H, m, CH_2), 5.00, 5.07 (2H, d, CH_2=), 5.45 (2H, m, CH=), 5.84 (1H, ddd, CH=) ppm. IR(neat) 3020, 2970, 2920, 1715, 1618, 1435, 965 cm^{-1}. Mass m/z 124 (M^+). Found: C; 77.28, H; 9.99. $C_8H_{12}O$ calc: C; 77.42, H; 9.68%.

*1,7-Nonadien-5-one (**25b**).* Prepared from methyl 4-pentenoate and $ZrCp_2$-(butadiene). ^1H NMR δ ($CDCl_3$) 1.70 (3H, d, J 5.8 Hz, CH_3), 1.92 (2H, m, CH_2), 2.35–2.48 (2H, m, CH_2), 3.12 (2H, m, CH_2), 4.81, 4.91 (2H, dd, CH_2=), 5.40 (2H, m, CH=), 5.65 (1H, m, CH=) ppm. IR(neat) 2860, 1718, 1640, 1601, 1441, 1403, 962 cm^{-1}. Mass m/z 138 (M^+). Found: C; 77.41, H; 9.72. $C_9H_{14}O$ calc: C; 79.41; H; 10.14%.

*3,7-Dimethyl-1,7-nonadien-5-one (**26**).* Prepared from diethyl carbonate and complex **5**. ^1H NMR δ ($CDCl_3$) 1.02 (3H, d, J 6.1 Hz, CH_3), 1.62 (3H, d, J 6.0 Hz, CH_3), 1.69 (3H, s, CH_3), 2.32 (1H, dd, J 7.0 and 16.0, CH_2), 2.52 (1H, dd, CH_2), 2.75 (1H, m, CH), 3.11 (2H, s, CH_2), 4.85–5.15 (2H, m, CH_2=), 5.47 (1H, q, J 6.1 Hz, CH=), 5.78 (1H, ddd, CH=) ppm. IR (neat) 1715 cm^{-1}. Mass m/z 166 (M^+).

Reaction of crotylzirconium complex with unsaturated esters.

Bis(cyclopentadienyl)bis((*E*)-2-butenyl)zirconium was isolated by a published method [11]. Methyl crotonate or ethyl 3,3-dimethylacrylate (3 mmol) was added to a stirred benzene solution (20 ml) of $ZrCp_2(C_4H_7)_2$ (2.0 mmol) at ambient temperature and the mixture was kept at 40 °C for 5 h and then quenched with 4 *N* aq. HCl. Neutralization with aq. Na_2CO_3 followed by distillation gave the 1,2-addition product as an oil.

*3,5-Dimethyl-4-(1-propenyl)-1,6-heptadien-4-ol (**24a**).* ^1H NMR δ ($CDCl_3$) 0.92 (6H, d, J 6.1 Hz, CH_3), 1.63 (1H, S, OH), 1.69 (3H, d, J 5.9 Hz, CH_3), 2.32 (2H, dq, J 9.0 Hz, CH), 4.94, 5.01 (4H, dd, CH_2=), 5.63 (2H, ddd, CH=) ppm. IR(neat) 3360, 1628, 908, 886 cm^{-1}. Mass m/z 179 ($M^+ - 1$). Found: C; 79.85, H; 11.50. $C_{12}H_{20}O$ calc: C; 80.00, H; 11.11%.

*3,5-dimethyl-4-(2-methyl-1-propenyl)-1,6-heptadiene-4-ol (**24b**).* Prepared from ethyl 3,3-dimethylacrylate. ^1H NMR δ ($CDCl_3$) 0.91 (6H, d, J 6.0 Hz, CH_3), 1.58 (1H, s, OH), 1.66 (3H, s, CH_3), 1.76 (3H, s, CH_3), 2.25 (2H, dq, CH), 4.98, 5.04 (4H, dd, CH_2=), 5.07 (1H, m, CH), 5.76 (2H, ddd, CH=) ppm. IR (neat) 3360, 922 cm^{-1}. Mass m/z 194 (M^+). Found: C, 80.57, H; 11.10. $C_{13}H_{22}O$ calc: C; 80.46, H; 11.34%.

Reaction of magnesium-isoprene adduct with unsaturated esters

To a stirred solution of 2-methyl-2-butene-1,4-diylmagnesium (3 mmol) in THF (25 ml) was added methyl crotonate or ethyl 3,3-dimethylacrylate (3 mmol) at −50 °C. The mixture was stirred at 25 °C for 30 min, quenched with 4 *N* aq. HCl and neutralized. After evaporation of the solvent, the products were extracted with ether and distilled.

*Methyl 3,4,5-trimethyl-5-hexenoate (**27b**).* Prepared starting from methyl crotonate. ^1H NMR δ ($CDCl_3$) 0.86 (3H, d, CH_3), 0.96 (3H, d, CH_3), 1.62 (3H, s, CH_3), 1.64 (1H, m, CH), 1.97 (1H, m, CH), 2.30 (2H, dd, CH_2), 3.61 (3H, s, CH_3O), 4.62, 4.69 (2H, s, CH_2) ppm. IR(neat) 1775, 1175 cm^{-1}. Mass m/z 170 (M^+). Found: C; 70.32, H; 10.89. $C_{10}H_{18}O_2$ calc: C; 70.59, H; 10.59%.

3,6,6-Trimethylcyclo-3-heptanone (28). Prepared from ethyl 3,3-dimethylacrylate. ^{1}H NMR δ ($CDCl_3$) 0.94 (6H, s, CH_3), 1.73 (2H, t, J 6.7 Hz, CH_2), 1.99, 2.06 (2H, s, CH_2), 2.33 (3H, s, CH_3), 2.84, 2.91 (2H, s, CH_2), 5.43 (1H, t, CH=) ppm. IR (neat) 1708 cm^{-1}. Mass m/z 152 (M^+). Found: C; 78.99, H; 10.44. $C_{10}H_{16}O$ calc: C; 78.95, H; 10.53%.

Reactions of complex 5 with substituted oxacyclopropanes

To a solution of $ZrCp_2$(isoprene) (3 mmol) in benzene (20 ml) was added a mono- or disubstituted oxacyclopropane (3 mmol). The mixture was stirred for 10 h at 30 °C or 60 °C and then evaporated to dryness. The product was dissolved in ether (100 ml), decomposed with water and distilled.

2-Phenyl-4-methyl-4-hexenol (34a). Obtained from phenyl oxacyclopropane and complex **5**. NMR δ ($CDCl_3$) 1.38 (1H, s, OH), 1.48 (3H, d, J 6.5 Hz, CH_3), 1.63 (3H, bs, CH_3), 2.26 (1H, dd, J 8.1 and 14.0 Hz, CH_2), 2.52 (1H, dd, J 7.0 and 14.0 Hz, CH_2), 3.00 (1H, ddt, J 7.1, 7.0 and 8.0 Hz, CHPh), 3.78 (2H, d, J 7 Hz, CH_2O), 5.24 (1H, q, J 6.5 Hz, CH=), 7.15–7.42 (5H, m, Ph) ppm. IR(neat) 3350 3060, 2910, 1600, 1493, 1055, 1030, 1910, 815 cm^{-1}. Mass m/z 190 (M^+). Found: C, 81.88, H; 9.60. $C_{13}H_{18}O$ calc: C; 82.06, H; 953%.

2-Phenyl-4-methyl-5-hexenol (35a). The isomer of **34a** obtained from phenyl oxacyclopropane (mixture of diastereoisomer). ^{1}H NMR δ ($CDCl_3$) 1.04 (3H, dd, CH_3), 1.64 (2H, m, CH_2), 1.39 (1H, s, OH), 2.04 (1H, m, CH), 2.89 (1H, m, CH), 3.85 (2H, m, CH_2O), 4.90, 5.00 (2H, m, CH_2=), 5.68 (1H, m, CH=), 7.20–7.41 (5H, m, Ph) ppm. IR(neat) 3330, 3045, 3010, 2940, 2840, 1635, 1600, 1490, 1445, 1035, 990, 907, 750 cm^{-1}. Mass m/z 190(M^+). Found: C; 82.11, H; 9.57. $C_{13}H_{18}O$ calc: C; 82.06, H; 9.53%.

2,4-Dimethyl-2-vinyl-4-hexenol (34b). Prepared by reaction of 2-methyl-2-vinyl-oxacyclopropane with complex **5**. ^{1}H NMR δ ($CDCl_3$) 1.04 (3H, s, CH_3), 1.58 (4H, d, J 7.1 Hz, CH_3 and OH), 1.70 (3H, bs, CH_3), 2.04, 2.22 (2H, d, J 14.0 Hz, CH_2), 3.40 (2H, s, CH_2O), 5.08 (1H, dd, J 2.0 and 11.0 Hz, CH_2=), 5.12 (1H, dd, J 2.2 and 17.0 Hz, CH_2=). 5.36 (1H, q, J 7.0 Hz, CH_3CH), 5.86 (1H, dd, J 11.3 and 17.0 Hz, CH=) ppm. IR(neat) 3380, 2970, 2945, 2870, 1640, 1460, 1415, 1380, 1040, 914, 820 cm^{-1}. Mass m/z 154(M^+). Found: C; 77.23, H; 11.76. $C_{10}H_{18}O$ calc: C, 77.87, H; 11.76%.

2,4-Dimethyl-2-vinyl-5-hexenol (35b). Obtained as an isomer of **34b** from 2-methyl-2-vinyl oxacyclopropane (mixture of diastereoisomer). ^{1}H NMR δ ($CDCl_3$) 1.00, 1.02 (3H, d, J 7.0, CH_3), 1.06 (3H, s, CH_3), 1.20–1.65 (2H, m, CH_2), 1.70 (1H, s, OH), 2.24 (1H, m, CH) 4.80–5.24 (4H, m, CH_2=), 5.54–6.00 (2H, m, CH=). IR (neat) 3380, 2970, 2930, 2880, 1640, 1455, 1415, 1378, 1040, 1000, 910 cm^{-1}. Mass m/z 154 (M^+). Found: C; 76.89, H; 11.69. $C_{10}H_{18}O$ calc: C; 77.87, H; 11.76%.

5-Methyl-3-phenyl-5-hepten-2-ol (34c). Obtained from 2-methyl-3-phenyl-oxacyclopropane. ^{1}H NMR δ ($CDCl_3$) 1.02 (3H, d, J 6.0 Hz, CH_3), 1.46 (3H, d, J 7.1 Hz, CH_3), 1.55 (3H, bs, CH_3), 2.02 (1H, s, OH), 2.24–2.96 (3H, m, CH_2 and CH), 3.80–4.16 (1H, m, CHO), 5.15 (1H, q, J 7.2 Hz, CHPh), 7.00–7.40 (5H, m, Ph) ppm. IR (neat) 3370, 3050, 2950, 2910, 1600, 1490, 1447, 1370, 1120, 1078, 922, 750, 695 cm^{-1}. Mass m/z 204(M^+). Found: C; 82.18, H; 9.88. $C_{14}H_{20}O$ calc: C; 82.30, H; 9.87%.

5-Methyl-3-phenyl-6-hepten-2-ol (35c). A mixture of diastereoisomers obtained

from (*E*)- or (*Z*)-2-methyl-3-phenyloxacyclopropane. ^{1}H NMR δ ($CDCl_3$) 0.90–1.10 (6H, m, CH_3), 1.40–2.00 (3H, m, CH_2 and OH), 2.50–2.90 (2H, m, CH), 3.70–4.10 (1H, m, CHO), 4.60–5.10 (2H, m, CH_2=), 5.60–5.90 (1H, m, CH=), 7.00–7.50 (5H, m, Ph) ppm. IR (neat) 3400, 3070, 3030, 2970, 2930, 1638, 1600, 1494, 1375, 1085, 996, 912, 757 cm^{-1}. Mass *m/z* 204(M^+). Found: C; 82.10, H; 9.86. $C_{14}H_{20}O$ calc: C; 82.38, H; 9.87%.

*2-(2-Methyl-2-butenyl)cyclohexanol (**34d**).* Obtained from 7-oxabicyclo[4.1.0]-heptane. ^{1}H NMR δ $CDCl_3$ 1.02–1.98 (15H, CH_3, CH_2 and CH), 2.08 (2H, d, J = 7.0 Hz, CH_2), 3.82 (1H, m, CHO), 5.18 (1H, q, J 6.0 Hz, $CHCH_3$). IR(neat) 3300, 2935, 2860, 1640, 1450, 1378, 1068, 978 cm^{-1}. Mass *m/z* 168 (M^+). Found: C; 78.45, H; 12.04. $C_{11}H_{20}O$ Calcd: C; 78.51, H; 11.98%.

*2-(2-Methyl-3-butenyl)cyclohexanol (**35d**).* A mixture of *cis* and *trans* isomers. ^{1}H NMR δ ($CDCl_3$) 1.00, 1.66 (3H, d, CH_3), 1.00–1.97 (10H, CH_2), 2.25 (1H, m, $CHCH_3$), 3.84, 4.10 (1H, m, CHO), 4.84–5.10 (2H, m, CH_2=), 5.64–5.90 (1H, m, CH=) ppm. IR(neat) 3390, 3070, 2930, 2860, 1640, 1448, 997, 973, 910, 890 cm^{-1}. Mass *m/z* 168 (M^+). Found: C; 78.43, H; 12.05. $C_{11}H_{20}O$ calc: C; 78.51, H; 11.98%.

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